

Theoretical Study of the Coordination of Semicarbazone and Its Methylated Derivatives

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Abstract

Semicarbazone is a molecule with a group $R^1R^2C=N-NR^3-C(=O)-NR^4R^5$.

The oxygen atom has two free electron pairs; each nitrogen atom has one free electron pair. These free electron pairs are potential sites of coordination. The simplest molecule in this series is the semicarbazone which the formula is $H_2C=N-NH-C(=O)NH_2$. By replacing the oxygen atom by a sulfur atom is obtained a thiosemicarbazone. Some semicarbazones, such as nitrofurazone, and some thiosemicarbazones are known to have many properties: antiviral, antibacterial, antitrypanosomal, anticonvulsant, antitumor, anticancer. They are usually mediated by an association with copper or iron.

Indeed transition metal complexes with given chemical structures are useful alternatives in the treatment of certain diseases since coordination of active ingredients deeply modifies both the physiological properties of metals and ligands in the meaning of overall improvement of these properties.

The present work focuses on quantum study of the complexation of semicarbazone and its methylated derivatives. The purpose of this study is to determine the most favorable coordination site of each of these ligands. It was found that the oxygen atom appears more favorable to the coordination of semicarbazones.

Complexes of these ligands with the Zn (II) were modeled. The calculations were made by the method DFT / B3LYP with the orbital basis 6-31G (d, p).

Keywords: coordination compounds, semicarbazones, DFT/ B3LYP, 6-31G (d,p) basis set

1. Introduction

The study at the molecular level of the interaction between metals and bioligands (proteins, nucleic acids, their fragments, and other substances contained in the organism) is topical (Knouniats, 1990) (Williams, 1975) (Yatsimirskii, 1976) (Kembal, 1975). The bioinorganic chemistry which is currently in full swing is concerned, inter alia, with the coordination of trace elements with organic ligands. The results of these studies find their applications in various fields of science and technology such as medicine, agriculture, environmental protection, catalysis.

In fact, the coordination of bioligands profoundly modifies both the physiological properties of metals and those of ligands with an overall improvement in the activity of the pure ligand or of the complexing metal salt (Azizov, 1969) (Büchel, Moretto et al. 2000) (Bäuerlein, Arias et al. 2007) (Bäuerlein, Kawasaki et al., 2007) (Bäuerlein, Frankel et al.2007) (Andersen, 1999) (Wong & Giandomenico, 1999) (Shaw 1999), (Caravan & Ellison, 1999).

Semicarbazones (SCZ) are molecules having a group $R^1R^2C=N-NR^3-C(=O)-NR^4R^5$, thus having donor atoms (N and O) capable of forming bonds with complexing metals. They are of particular interest as ligands. Semicarbazones are derivatives of aldehydes or ketones. They are formed by condensation of these compounds with a semicarbazide as shown by the reaction: $H_2NNHC(=O)NH_2 + RC(=O)R^2 \rightarrow RR^2C=NNHC(=O)NH_2 + H_2O$

where R^2 is a hydrogen atom (if it is an aldehyde) or an alkyl group (if it is a ketone). The simplest molecule of this series is the semicarbazone of formula $H_2C=N-NH-C(=O)NH_2$. Certain semicarbazones, such as nitrofurazone, and certain thiosemicarbazones are known for their antiviral, antibacterial, antitrypanosomal (antiparasitic), anticonvulsive, anti-tumor, anti-cancer, etc. activities, generally mediated by a binding with copper or iron (Picot, 2008) (Sakirigui et al., 2011) (Kenneth, 1999).

The present work deals with a quantum study of the complexation of semicarbazone and its methylated derivatives. The aim of this study is to determine the most favorable coordination site for each of these ligands and to provide some insights into the complex geometry without which metabolic issues cannot be addressed. The coordination indicators (ICs) used in the studies are: interatomic bond lengths, atomic charges, boundary orbital structures and indexes of electrophilic superdelocalisability.

2. Materials and Methods

The present work, which is a theoretical study of the complexation of semicarbazone and its methylated derivatives, was carried out by quantum chemical calculations. These calculations were carried out using the density functional theory (DFT) method with the functional B3LYP. The calculation basis set was 6-31g (d, p). The software used to perform the calculations is the Gaussian 03 and 09 (Frisch et al. 1998). The used computer was a Samsung intel® core i32.4 GHz; the indexes of electrophilic superdelocalisability of the atoms were determined by the D-Cent-QSAR program (Gómez-Jeria, 2014). The different figures were made by the software Gauss view and by Chem Draw ultra 8. After studying the possibility of complexation of the different ligands with respect to criteria such as geometric parameters, atomic charges, HOMO components and the indexes of electrophilic superdelocalisability (IESD) of the atoms, we have modeled the formation of their respective complexes with zinc chloride (II).

We have tried to elucidate the type of hybridization of Zn (II) and consequently the shape of the complex. The ligands which have been the subject of the present study are semicarbazone and its methylated derivatives. Studies were performed at 25°C and 1 atm.

3. Results and Discussion

3.1 Study about the Ligands

This study allowed predicts the coordinatating sites of ligands by analysis of some system parameters known as coordinating indexes (CI). These IC was the geometric data, the atomic charges, the frontier orbitals, the energetic data, the atomic indexes of superdelolalisability. These data allow to explain the bond formation between donor and acceptor atoms. Figure 1 shows the molecules of the studied in this work semicarbazones (SCZs).

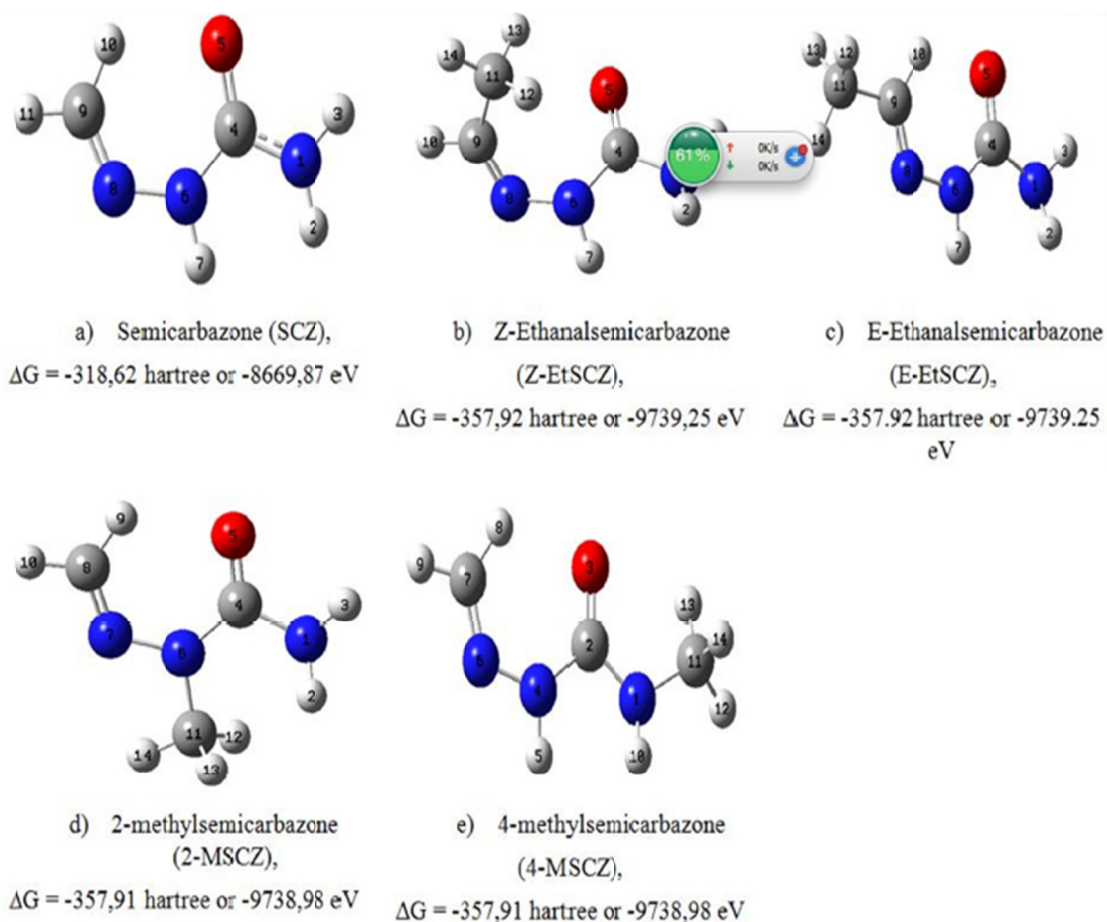


Figure 1. Calculated, on DFT/B3LYP level, geometries of the studied semicarbazones at 25°C and their energies

It is important to note that the more complete values of ΔG are -357.919752 hartree for the Z-Ethanalsemicarbazone and -357.924990 hartree for E-Ethanalsemicarbazone. The value -357.92 hartree which appears under these two isomers is written in the authors' concern to stop at two digits after the decimal point. So there is no question of thinking that the two isomers have the same stability.

3.1.1 Geometric Analysis

The table 1 contains some geometric data of the studied ligands. Analysing SCZs molecules we notice that bond lengths N^1C^4 and N^6C^4 are equal to about 1.39Å. This value is intermediate between 1.47 Å (C-N length) and 1.27 Å (C=N length) (Mason, 1961) (Potapov & Tatarintchik, 2008) (Sakurai, Yoshikawa, Yasui, 2008). In other hand we found that C^4O^5 bonds are about 1.22 Å long, it correspond to a double C=O bond. These observations suggest that the double C=O bond interacts with the free π electronic pairs of N^1 and N^6 nitrogen atoms while a part of electronic pairs clouds off O atom compenses the electronic defect, which issued from this conjugation, at the level of C=O double bond. That's why its length has not varied.

Table 1. Geometric parameters of investigated SCZs, *Exp.= experimental values

Parameters	SCZ	Z-EtSCZ	E-EtSCZ	2-MSCZ	4-MSCZ	xp (Mason, 1961) (Potapov & Tatarintchik, 008) (Sakurai, Yoshikawa & Yasui, 2008)*
Lengths (Å)						
N^1C^4	1.39	1.39	1.39	1.39	1.38	C-N→1.47 ; C=N→1.27
C^4N^6	1.39	1.40	1.39	1.39	1.40	C-N→1.47 ; C=N→1.27
N^6N^8	1.37	1.41	1.38	1.38	1.37	N-N→1.40; N=N→1.23
N^8C^9	1.28	1.28	1.28	1.28	1.28	C-N→1.47 ; C=N→1.27
C^4O^5	1.22	1.22	1.22	1.22	1.22	C-O→1.43 ; C=O→1.21
C^9C^{11}	-	1.50	1.50	-	1.45	C^1C^{11}
N^6C^{11}	-	-	-	1.46	-	
Angles (°)						
$N^1C^4O^5$	122.78	123.21	122.52	121.35	123.3	
$N^1C^4N^6$	112.49	112.03	112.47	114.41	112.53	
$O^5C^4N^6$	124.72	124.75	125.00	124.18	124.17	
$C^4N^6N^8$	129.23	120.89	128.91	125.88	129.13	
$N^6N^8C^9$	121.15	117.04	120.77	122.97	121.33	
$N^8C^9C^{11}$	-	129.92	118.30	-	-	
$N^4C^6C^{11}$	-	-	-	121.54	119.51	$N^4C^1C^{11}$
Dihedrals(°)						
$N^1C^4O^5N^6$	178.14	178.69	178.51	177.13	178.93	
$N^1C^4N^6N^8$	-174.70	-162.11	-170.99	175.19	-173.96	
$O^5C^4N^6N^8$	3.60	16.71	7.64	-7.52	5.07	
$C^4N^6N^8C^9$	-10.77	-64.71	-17.11	2.99	-12.00	
$N^6N^8C^9C^{11}$	-	-3.25	-179.17	1.02	-171.92	$N^6C^4N^1C^{11}$

The N^6N^8 , bond length of which about 1.37, is a single bond while the N^8C^9 bond (1.28 Å) is a double one (Mason, 1961) (Potapov & Tatarintchik, 2008) (Sakurai, Yoshikawa & Yasui, 2008).

The sum of the bond angles around C^4 atom equals 360° and the dihedral $N^1C^4O^5N^6$ is about 180° ; this means that the three bonds (and the three atoms) which are around C^4 are in the same plane. Consequently the clouds of the π free electronic pairs of N^1 et N^6 and that of π C=O have a same orientation, so it is a confirmation that they forms conjugation bonds N^1C^4 , N^6C^4 and C^4O . This electronic pairs delocalization is not favorable to a coordination trough the N^1 and N^6 nitrogen atoms. Thus we can tell that the bond lengths as CI are not favorable to coordination with a metal ion trough the N^1 and N^6 ; contrarily that indice is favorable to coordination trough O and N^8 because their free electronic pairs are quasi no delocalized (Douglas & Anthony, 1993).

3.1.2 Atomic Charges Analysis

The table 2 corresponds to the atomic charges of the investigated ligands. In these ligands one notice that the atomic charges of N^1 , N^6 et O^5 are about -0,7 a.u.; the N^8 atoms carry rather positive charges (0.086 ; 0.035 ; 0.077 et 0.105 a.u. respectively for SCZ, Z-EtSCZ, E-EtSCZ, 2-MSCZ and 4-MSCZ). Thus the charge as CI is not favorable to a coordination trough N^8 . Although the N^1 and N^6 atoms are negatively charged, the coordination through them is disadvantaged by their rather positive environment; in fact H^2 , H^3 , H^7 et C^{11} carry high positive charges (about 0.2 a.u. for hydrogen atoms and 0.3 a.u. for C^{11}) capable of repelling the coordination cation. These reasons assume that the charge is favorable for the coordination of the semicarbazones via the oxygen atom.

Table 2. Atomic charges (a.u.)

	SCZ	Z-EtSCZ	E-EtSCZ	2MSCZ	4MSCZ
N ¹	-0.734	-0.723	-0.75	-0.705	-0.773
N ⁶	-0.659	-0.591	-0.689	-0.699	-0.658
N ⁸	0.086	-0.138	0.035	0.077	0.105
O ⁵	-0.724	-0.717	-0.732	-0.752	-0.778
C ⁴	1.279	1.261	1.298	1.243	1.3
C ⁹	0.045	0.285	0.188	0.025	0.035
H ² ou	0.205	0.205	0.203	0.202	0.373
C ¹¹					
H ³	0.217	0.215	0.214	0.217	0.181
H ⁷ ou	0.21	0.185	0.182	0.328	0.19
C ^N					

3.1.3 Frontier Orbitals Analysis

The table 3 shows some energetic values of studied SCZs. One notice that the HOMO et HOMO-1 are respectively of -6,5 eV et -7 eV; these molecular orbitals are dominated respectively by the p_z atomic orbital of N⁶ and the p_x atomic orbital of O. According to this analysis, the frontier orbitals indicate that the coordinating favorable sites of studied SCZs in this investigation work are N⁶ nitrogen atom and O.

Table 3. Energetic values of the investigated SCZs

Orbitals	SCZ		Z-EtSCZ		E-EtSCZ	
	Energies (eV)	dominant atomic orbitals	Energies (eV)	dominant atomic orbitals	Energies (eV)	dominant atomic orbitals
HOMO-1	-6,85	O	-7,08	O px(0,74)	-6,73	O
HOMO	-6,66	px (0.72) N ⁶ pz (0.78)	-6,29	N ⁶ pz(0,74)	-6,35	px(0,72) N ⁶ pz(0.76)
Sites favorables	O and N ⁶		O and N ⁶		O and N ⁶	
Orbitals	2MSCZ,		4MSCZ		ZnCl ₂ ,	
	Energies (eV)	dominant atomic orbitals	Energies (eV)	dominant atomic orbitals	Energies (eV)	dominant atomic orbitals
HOMO-1	-6,72	O p (0,71)	-6,69	O px (0,67)	-	-
HOMO	-6,35	N ⁶ pz (0.82)	-6,52	N ⁶ pz (0.77)	-	-
LUMO	-	-	-	-	-2,18	Zn s(2,01)
LUMO+1	-	-	-	-	-0,82	Zn py(1,5)
Sites favorables	O and N ⁶		O and N ⁶		-	

3.1.4 Atomic Indexes of Electrophilic Superdelocalisability (IESD) Analysis

The main IESDs are shown in the table 4. We can notice that all these indexes are negatives.

Table 4. IESD values of studied SCZs atoms

Atoms	IESD, eV				
	SCZ	Z-EtSCZ	E-EtSCZ	2MSCZ	4MSCZ
N ¹	-0.449	-0.453	-0.454	-0.452	-0.450
N ⁶	-0.418	-0.436	-0.426	-0.418	-0.424
N ⁸	-0.459	-0.479	-0.476	-0.464	-0.463
O ⁵	-0.603	-0.611	-0.611	-0.616	-0.612
C ⁴	-0.234	-0.241	-0.237	-0.237	-0.234
C ⁹	-0.354	-0.326	-0.338	-0.359	-0.358
H ²	0.049	-0.050	-0.050	-0.049	-
H ³	-0.048	-0.049	-0.049	-0.049	-0.234
H ⁷	-0.048	-0.050	-0.049	-	-0.049

The atomic index of electrophilic superdelocalizability is a magnitude which shows the capacity of given specie to attract a electrophile system. The coordination is thought to be more likely at the level of the atom with the most negative IESD (Gómez-Jeria, 2014). Thus the table 5 reveals that oxygen atom. (-0,6eV) is the more favorable coordination site for all studied ligands. It is followed by the trigonal nitrogen atom N⁸ (about 0,46eV).

3.1.5 Recapitulative Analysis

In the table 5 you can read, at the intersection of each ligand with each CI, the atom through which coordination can occur during a complexation process.

Table 5. Recapitulative analysis, * BL= Bond lengths, ** AC= Atomic charges

molecules	SCZ	E-EtSCZ	E-EtSCZ	2MSCZ	4MSCZ
CI					
BL*	O, N ⁸	O, N ⁸	O, N ⁸	O, N ⁸	O, N ⁸
AC**	O	O	O	O	O
HOMO	O, N ⁶	O, N ⁶	O, N ⁶	O, N ⁶	O, N ⁶
ISDE	O	O	O	O	O

It can be seen that all the CIs considered are favorable for the coordination of the studied semicarbazones via the oxygen atom. Coordination through N⁸ or N⁶ is less likely. No CI is favorable for coordination of semicarbazones, object of the present study, by N¹.

These results should be confirmed by modeling the complexes of these molecules.

The choice in the present study is focused on zinc (II), a trace element that is very present in the treatment of various pathologies. Its electronic structure is 1s²2s²2p⁶3s²3p⁶ 4s⁰3d¹⁰4p⁰. Zinc (II) generally gives tetrahedral complexes close to the Td point group. This is understandable when one observes its electronic structure: the orbital s, p_x, p_y and p_z are vacant and are capable of sp³ hybridization. The sp³ hybrid orbitals point to the tops of a tetrahedron. The orbital p of atoms recognized as favorable for the coordination of the ligands studied are capable to overlap with these sp³ orbitals.

3.2 Modeling of Coordination Compounds

3.2.1 Modeling

Semicarbazone complexes ZnCl₂.Ligand were modeled. They are ZnCl₂.SCZ, ZnCl₂.Z-EtSCZ, ZnCl₂.E-EtSCZ, ZnCl₂.2MSCZ and ZnCl₂.4MSCZ. Their structures and geometric parameters are shown respectively in the figure 2a and the table 7a. They are some chelates having tetrahedral structure. The coordination with the complexing atom took place via the oxygen atom (the length of Zn-O equals about 2 Å) and the trigonal nitrogen atom of the ligand (length of Zn-N⁸ equals about 2 Å) forming a pentagonal ring, which is known to be more stable than if the coordination was established by N⁶ instead of N⁸ since the cycle tension would be, in this case, higher. These results are consistent with the literature data (Douglas, West & Anthony, 1993) (Alomar, 2012).

Semicarbazone complexes ZnCl₂.2Ligand (ZnCl₂.2SCZ, ZnCl₂.2 (Z-EtSCZ), ZnCl₂.2(E-EtSCZ), ZnCl₂.2(2MSCZ) et ZnCl₂.2(4MSCZ)) were modeled too. These complexes have tetrahedral structure too. Their structures are shown in figure 2b and, in the table 6b, are recorded some of their geometric data. It is found that the interatomic distances ZnO are of the order 2 Å, length of the Zn-O bond according to the data of the literature (Kuevi, 1992); there is no ZnN link. It can be deduced that the molecules of the semicarbazones that are the subject of the present works, in the proportion Zn / ligand = 1/2, have entered into coordination via the oxygen atom.

From all the foregoing it emerges that the combination of the analysis of interatomic distances, atomic charges, electrostatic potentials, atomic indices of superdelocalizability and the frontier orbitals of the ligands constitute a fairly effective means of studying the coordination of semicarbazones. An energetic study of the complexation processes made it possible to assess the stability of the coordination compounds of these ligands with Zn (II).

Table 6a. Some geometric data of the modelised complexes ZnCl₂.Ligand

	ZnCl ₂ .SCZ	ZnCl ₂ .E-EtSCZ	ZnCl ₂ .Z-EtSCZ	ZnCl ₂ .2MSCZ	ZnCl ₂ .4MSCZ
Distances (Å)					
Zn-O ⁵	2,09	2,09	2,09	2,07	2,08
Zn-N ¹	4,17	4,17	4,17	4,15	4,16
Zn-N ⁶	2,94	2,93	2,94	2,97	2,94
Zn-N ⁸	2,19	2,17	2,17	2,17	2,19
Zn-Cl ¹³	2,19	2,19	2,19	2,19	2,19
Zn-Cl ¹⁴	2,19	2,19	2,19	2,19	2,19
Dihedrals (°)					
O ⁵ C ⁴ N ⁶ N ⁸	-0,57	-2,77	-2,74	8,34	-2,79
N ¹ C ⁴ N ⁶ N ⁸	178,23	176,42	176,44	-177,65	176,79
C ⁴ N ⁶ N ⁸ C ⁹	-175,08	-174,72	-174,75	-179,33	-176,23
N ⁶ N ⁸ C ⁹ C ¹¹	-	0,12	0,12	3,07	-
ZnOC ⁴ N ¹	177,54	-179,35	-179,37	169,91	-176,99
ZnOC ⁴ N ⁶	-3,73	-0,22	-0,24	-12,17	2,55

Table 6b. Some geometric data of the modelised complexes ZnCl₂.2Ligand

	ZnCl ₂ .2SCZ	ZnCl ₂ .2E-EtSCZ	ZnCl ₂ .2Z-EtSCZ	ZnCl ₂ .2(2MSCZ)	ZnCl ₂ .2(4MSCZ)
Distances (Å)					
Zn-O ⁵	2.00	1.99	1.99	2.00	2.00
Zn-O ¹⁹	2.00	1.99	1.99	2.00	2.00
Zn-N ¹	3.40	3.40	3.42	3.40	3.36
Zn-N ¹⁵	3.40	3.40	3.42	3.40	3.36
Zn-N ⁶	4.21	4.14	4.22	4.21	4.22
Zn-N ²⁰	4.21	4.14	4.22	4.21	4.22
Zn-N ⁸	4.84	4.71	4.72	4.84	4.86
Zn-N ²²	4.84	4.71	4.72	4.84	4.86
Zn-Cl ¹³	2.20	2.22	2.21	2.20	2.20
Zn-Cl ¹⁴	2.31	2.30	2.31	2.31	2.33
Diedrals (°)					
O ⁵ C ⁴ N ⁶ N ⁸	0.51	9.24	16.5	0.51	-0.13
N ¹ C ⁴ N ⁶ N ⁸	-177.32	-169.08	-162.74	-177.32	-179.31
C ⁴ N ⁶ N ⁸ C ⁹	-19.61	-45.39	-70.01	-19.61	-14.82
N ⁶ N ⁸ C ⁹ C ¹¹	-	179.82	-2.8	-5.76	-4.27
ZnOC ⁴ N ¹	-25.36	-38.20	-20.57	-25.36	-19.56
ZnOC ⁴ N ⁶	156.97	143.59	160.24	156.97	161.31

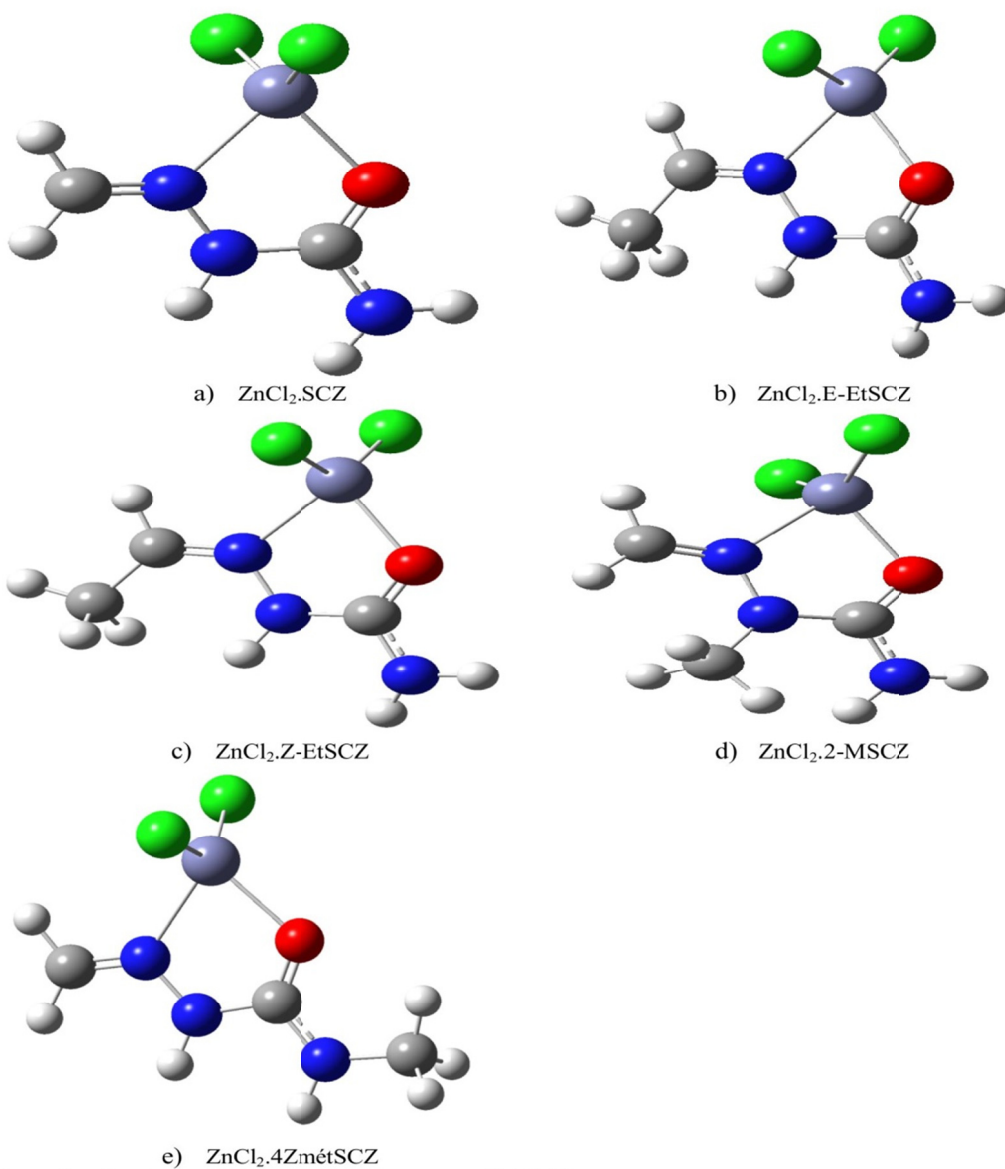
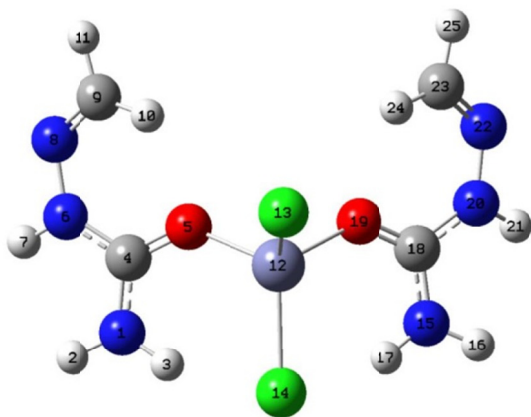
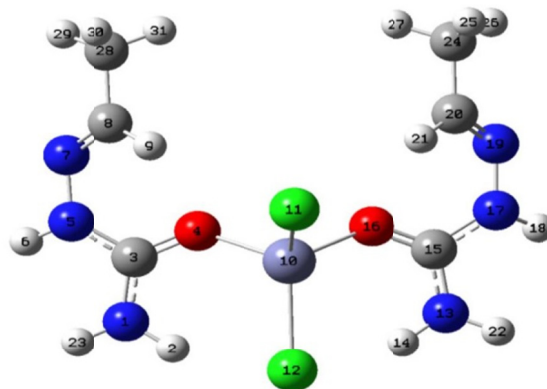


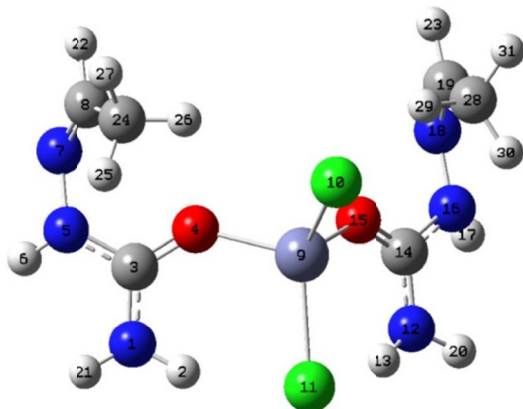
Figure 2a. Structures of the modelised complexes $ZnCl_2 \cdot \text{Ligand}$



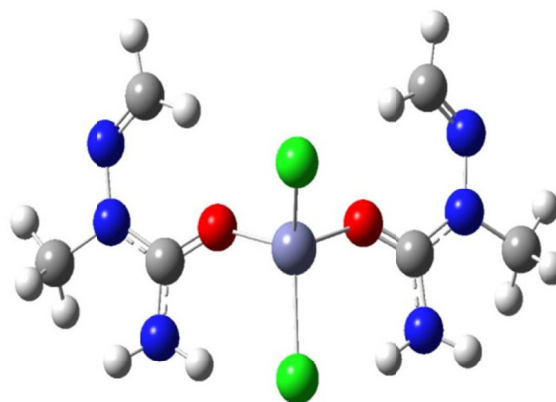
$ZnCl_2(SCZ)_2$
Dichlorodisemicarbazonezinc(II)



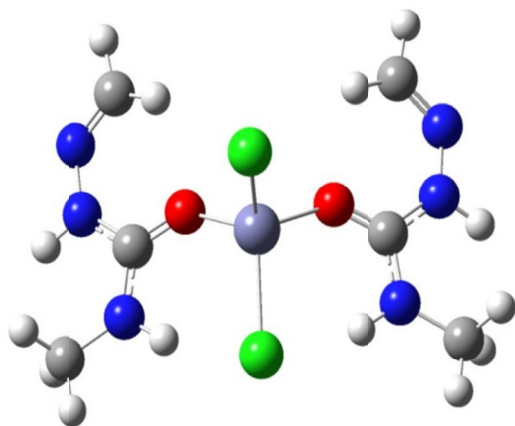
$ZnCl_2(E-EtSCZ)_2$
DichlorodiE-ethanalsemicarbazonezinc(II)



$ZnCl_2(Z-EtSCZ)_2$
DichlorodiZ-ethanalsemicarbazonezinc(II)



$ZnCl_2(2MSCZ)_2$
Dichlorodi2-methylsemicarbazonezinc(II)



$ZnCl_2(4MSCZ)_2$
Dichlorodi4-methylsemicarbazonezinc(II)

Figure 2b. Structures of the modelised complexes $ZnCl_2 \cdot 2Ligand$

3.2.2 Energy Study

The study of the energy of coordination between ligands and zinc (II) chloride was used to assess the stability of the coordination bond. Le table 8 present shows energy values.

ΔG = Free enthalpy of the species

ΔG_{coord} = Free enthalpy of coordination

$\Delta G_{\text{coord}} = \Delta G_{\text{complexe}} - (\Delta G_{\text{ligand}} + \Delta G_{\text{ZnCl}_2})$ ou $\Delta G_{\text{coord}} = \Delta G_{\text{complexe}} - (2\Delta G_{\text{ligand}} + \Delta G_{\text{ZnCl}_2})$

ΔH = Enthalpy of the species

ΔH_{coord} = Enthalpy of coordination

$\Delta H_{\text{coord}} = \Delta H_{\text{complexe}} - (\Delta H_{\text{ligand}} + \Delta H_{\text{ZnCl}_2})$ ou $\Delta H_{\text{coord}} = \Delta H_{\text{complexe}} - (2\Delta H_{\text{ligand}} + \Delta H_{\text{ZnCl}_2})$

Table 7. Some energies of the studied systems

	ΔH , eV	ΔH_{coord} , eV	ΔG , eV	ΔG_{coord} , eV	Type de processus
ZnCl ₂	-73458,28	-	-73459,09	-	-
SCZ	-8669,06	-	-8669,87	-	-
E-EtSCZ	-9738,17	-	-9739,25	-	-
Z-EtSCZ	-9738,17	-	-9739,25	-	-
2MSCZ	-9737,89	-	-9738,98	-	-
4MSCZ	-9737,89	-	-9738,98	-	-
Complexes ZnCl ₂ .Ligand					
ZnCl ₂ .SCZ	-82128,70	-1,35	-82130,33	-1,37	Exothermic and Spontaneous
ZnCl ₂ .E-EtSCZ	-83197,80	-1,35	-83199,71	-1,37	Exothermic and Spontaneous
ZnCl ₂ .Z-EtSCZ	-83198,07	-1,62	-83199,71	-1,37	Exothermic and Spontaneous
ZnCl ₂ .2MSCZ	-83197,53	-1,36	-83199,16	-1,09	Exothermic and Spontaneous
ZnCl ₂ .4MSCZ	-83197,53	-1,36	83199,16	-1,09	Exothermic and Spontaneous
Complexes ZnCl ₂ .2Ligand					
ZnCl ₂ .2SCZ	-90798,57	-2,17	-90800,47	-1,64	Exothermic and Spontaneous
ZnCl ₂ .2(E-EtSCZ)	-92937,06	-2,44	-92939,23	-1,64	Exothermic and Spontaneous
ZnCl ₂ .2(Z-EtSCZ)	-92937,33	-2,71	-92939,23	-1,64	Exothermic and Spontaneous
ZnCl ₂ .2(2MSCZ)	-92936,24	-2,18	-92938,42	-1,37	Exothermic and Spontaneous
ZnCl ₂ .2(4MSCZ)	-92936,24	-2,18	-92938,42	-1,37	Exothermic and Spontaneous

The negative values of the free enthalpies of coordination show that the coordination of the studied semicarbazones is spontaneous process. The enthalpies are negative, so the process concerning the ligands is exothermic.

From the both conformers of ethanalsemicarbazone one obtains the same chelate; instead the Z-ETSCZ was transformed, during the complexation, into the E- form to avoid congstion with the ZnCl₂ system. The value -1.62 eV obtained in the column of the enthalpies of coordination for the complex Z-ETSCZ would be the sum of the coordination enthalpy of this complex and the reorganization energy of the Z-ETSCZ molecule to E-ETSCZ one.

It should be noted that the introduction of the methyl group in semicarbazone did not involve any significant modification of the properties.

4. Conclusion

The present works constitute a theoretical study of the coordination of the molecules of some semicarbazones. These were semicarbazone, E-ethanalsemicarbazone, Z-ethanalsemicarbazone, 2-methylsemicarbazone, 4-methylsemicarbazone. This has been possible through the analysis of coordination indicators such as bond lengths, atomic charges, electrostatic atom potentials, boundary orbitals, and atomic electrophilic superdelocalizability indexes.

The results from our calculations showed that these molecules are able to form complexes with metal ions. Zn²⁺ is one of those ions. It has been found that the most favorable coordination site is the oxygen atom for these semicarbazones followed by the trigonal nitrogen atom. The methyl group in semicarbazone did not involve any significant modification of the properties.

The complexes obtained with Zinc (II) provided by the zinc (II) chloride are of the proportion Zn / ligand equal to 1/1 and 1/2. The central element, Zn (II), has a tetrahedral structure in all the complexes obtained. The vertices of the tetrahedra are occupied by two chlorine atoms and two oxygen atoms for the 1/2 structures; in the 1/1 structures, the vertices of the tetrahedron are occupied by the two Cl atoms, the O atom and the trigonal N atom of the ligand. The complexes of the proportion Zn / ligand equal to 1/1 are chelates resulting from the coordination of the ligands via the O and Ntrigonal atoms thus forming a five-membered ring.

All complexation processes were spontaneous and exothermic under the study conditions of 25 ° C and one atmosphere.

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