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Quantochemical study of the thiosemicarbazone coordination and its methylated derivatives

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Abstract
Thiosemicarbazone is a molecule containing the R1R2C=N-NR^3-C (=S)-NR^{4}R^5 group. The sulfur and nitrogen atoms has some free electron pairs. Some thiosemicarbazone are known to have many medicinal properties. 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 investigation is a quantum study of the thiosemicarbazone complexation and its methylated derivatives. This study's aim is to determine the most favorable coordination site of each of these ligands. On the basis of values of some coordination indicators (CI) it appears that the sulphur atom is the most favorable coordination site of the studied thiosemicarbazone. Complexes of these ligands with the Zn (II) were modeled. The calculations were made by the DFT / B3LYP method.

Keywords: coordination compounds, thiosemicarbazones, physiological properties

1. Introduction
The study at molecular level of the interaction between metals and bio ligands (proteins, nucleic acids, their fragments, and other substances contained in the organism) is topical [1-4].
The bioinorganic chemistry which is currently in full swing is concerned, inter alias, 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.
Yes, the coordination of bio ligands profoundly modifies the physiological properties of metals and those of ligands with an overall improvement in the activity of the pure ligand and of the complexing metal salt [5-13].
The semicarbazones (SCZ) and thiosemicarbazone (TSCZ) are molecules having a group R^{1}R^{2}C=N-NR^3-C (=O)-NR^{4}R^5 or a group R^{1}R^{2}C=N-NR^3-C(=S)-NR^{4}R^5 ; thus, these molecules have donor atoms (N and O or S) capable of forming bonds with complexing metals.
Certain semicarbazones and thiosemicarbazone are known for their antiviral, antibacterial, antitrypanosomal (antiparasitic), anticonvulsive, anti-tumor, anti-cancer, etc. activities, generally mediated by a binding with copper or iron [14- 16].
To explain the competitive nature of the coordination of the sulfur and nitrogen atoms of the different thiosemicarbazone, experimental methods (infrared spectroscopy, for example) and quantum methods are used successfully.
The present work concerns a quantum study of the complexation of thiosemicarbazone and its methylated derivatives. The purpose of this study is to determine the most favorable coordination site for each of these ligands and to shed some light on the geometry of the complex without which metabolism issues cannot be addressed. The coordination indicators (CI) used in the study are interatomic bond lengths, atomic charges, electrostatic potentials, boundary orbitals structures, and atomic electrophilic superdelocalizabilty indexes.

2. Material and Methods
The present work, which is a theoretical study of the coordination of thiosemicarbazone and its methylated derivatives, was carried out by quanto chemical calculations 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 Gaussian in versions 03 and 09 [17] on a Samsung intel® core i32.4 GHz computer. The different representations were made by Gauss view software and by Chem Draw ultra 8.

After studying the coordination possibility of different ligands with respect to criteria such as geometrical parameters, atomic charges, electrostatic potentials (ESPs), the HOMO components and atomic electrophilic superde localization indexes, we modeled the formation of their respective complexes with zinc (II) chloride.

We have attempted to elucidate the type of hybridization of Zn (II) and therefore the shape of the complex.

The ligands that were the subject of the present study are thiosemicarbazones and some of its methylated derivatives. The studies were conducted at 25 ° C and 1atm.

3. Results and discussion

3.1-Study about the ligands

This study allowed us to predict the ligand coordination site through the analysis of certain parameters of the system, recognized as coordination indicators (CI). These factors correspond to the geometry of the species, atomic charges, boundary orbitals, energetic data and atomic electrophilic superdelocalizabilty indexes needed to explain donor-acceptor bond formation. Figure 1 brings together the structures of the molecules studied in this work.

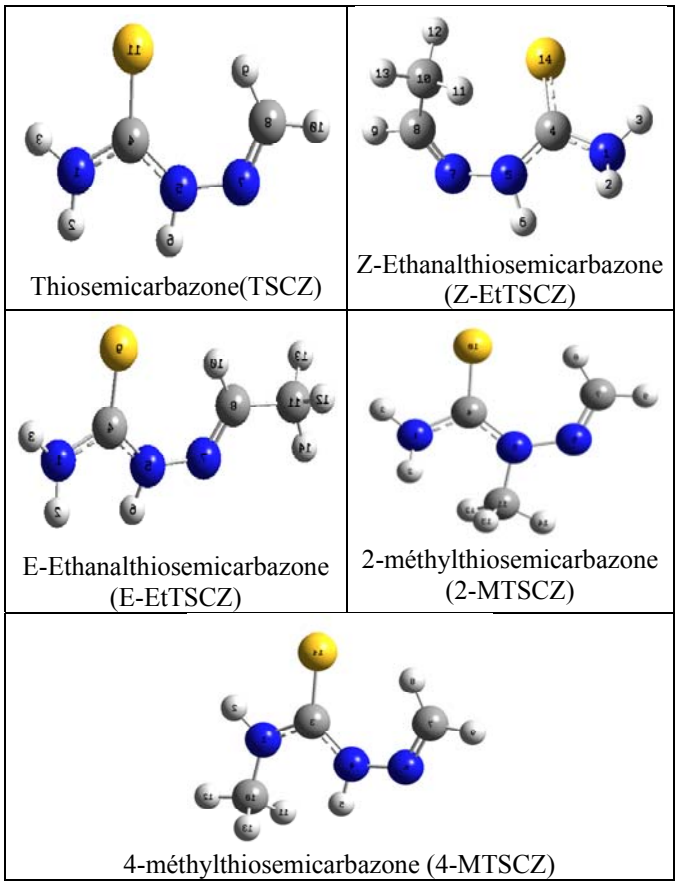


Fig 1: Structure of studied thiosemicarbazone calculated on DFT/B3LYP level at 25°C

3.1.1 Geometric analysis

In Table 1 are listed geometric data of the studied ligands.

By analyzing the TSCZ molecules, it is found that the length of the N^1C^4 bond and that of the N^5C^4 bond are approximately 1.38Å. This value is intermediate between 1.47 Å (C-N) and 1.27 Å (C = N) [18-20]. The lengths of the C^4S^5 bonds range from 1.67 to 1.73 Å, intermediate values between 1.57 Å (C-S) and 1.83 Å (C = S). This observation suggests that the C = S double bond interacts with the free electron pairs π of the N^1 and N^5 atoms.

The N^5N^7 bond lenght of which is about 1.39 Å is a single bond while the N^7C^8 bond with length 1.28 Å is double [18-20].

The sum of the bonding angles around the C^4 atom is equal to 360 ° and the dihedron angle $N^1C^4SN^5$ is about 180 °, which shows that the three bonds around C^4 are in the same plane. This confirms that the clouds of the free electrons pairs of N^1 and N^5 are delocalized to give conjugation bonds with the π pair of the C = S bond. The delocalization of the free doublets is not favorable for the coordination by the N^1 and N^5 atoms.

The bond length as a coordination index (CI) is therefore not favorable for the coordination with a metal ion by N^1 and N^5; on the other side, this index is favorable for coordination via S and N^7 whose free pairs are not delocalized [21].

Table 1: Geometric parameters of the studied thiosemicarbazones Exp: experimental values

Parameters	TSCZ	Z-Et TSCZ	E-Et TSCZ	2-MT SCZ	4-MT SCZ	Exp.* [18-20]
Lengths (Å)						
N^1C^4	1.366	1.374	1.374	1.374	1.365	C-N→ 1.47 C=N→1.27
C^4N^5	1.375	1.381	1.370	1.377	1.372	C-N→ 1.47 C=N→ 1.27
N^5N^7	1.394	1.413	1.385	1.386	1.378	N-N→ 1.40 N=N→ 1.23
N^7C^8	1.291	1.280	1.282	1.27	1.280	C-N→ 1,47 C=N→ 1.27
C^4S	1.73	1.670	1.678	1.68	1.685	C-S→ 1.83 C=S→ 1.57
C^8C	-	1.495	1.496	-	1.451 C^1C^{11}	
N^5C	-	-	-	1.468	-	
Angles (°)						
N^1C^4S	119.64	121,680	120,33	118,31	119,28	
$N^1C^4N^5$	113.23	111, 68	111,82	113,83	113,43	
SC^4N^5	127.12	126,51	127,81	127,8	127,3	
$C^4N^5N^7$	134.21	123,80	133,64	130,04	134,48	
$N^5N^7C^8$	123.53	116,67	121,36	124,42	122,63	
N^7C^8C	-	130,38	118,24	-	-	
C^4N^5C	-	-	-	119,86	127,60 C^4N^1C	
Dihedrals(°)						
$N^1C^4SN^5$	-180.	118,06	177,54	177,00	180.	
$N^1C^4N^5N^7$	180.	-162,61	-173,47	171,71	-180.	
$SC^4N^5N^7$	0.00	15,62	4,25	-11,18	0,01	
$C^4N^5N^7C^8$	0,00	-74,83	-22,74	4,06	-0,04	
$N^5N^7C^8C$	-	-2,70	-179,31	1,88	0,01	

3.1.2- Atomic charge analysis

Table 2 corresponds to the atomic charges of the ligands studied in the present work. In the TSCZ molecules, the charges of the N^1, N^5 nitrogen atoms and of S are about -0.8; -0.7 and -0.6 ua respectively; the N^7 atoms carry instead positive charges (0.108, 0.015, 0.042 and 0.077 respectively for TSCZ, E-EtTSCZ, 2-MTSCZ and 4-TMSCZ); only at the level of Z-EtTSCZ, N^7 has a negative charge but it is considerably weaker than the charge of the S atom. It is deduced that the charge as CI is not favorable to coordination by N^7. Although the N^1 and N^5 atoms are negative but the coordination through them is disadvantaged by their rather positive environment; in fact, H^2, H^3, H^6, $C^{10}$and C^{11} carry significant positive charges (approximately 0.2 ua for the hydrogen atoms, 0.4 ua for C^{10} and 0.3 ua for C^{11}) capable of

repelling the coordination cation. These reasons assume that the charge is favorable for the coordination of semicarbazones via the sulfur atom.

Table 2: Atomic charges

	TSCZ	Z-EtTSCZ	E-EtTSCZ	2MTSCZ	4MtSCZ
N^1	-0,842	-0,755	-0,773	-0,723	-0,796
N^5	-0,719	-0,619	-0,689	-0,707	-0,654
N^7	0,108	-0,199	0,015	0,042	0,077
S	-0,546	-0,555	-0,571	-0,585	-0,611
C^4	1,128	1,146	1,147	1,079	1,134
C^8	0,022	0,338	0,197	0,043	0,051
H^2	0,240	0,199	0,201	0,205	0,377(C^{10})
H^3	0,269	0,282	0,233	0,231	0,192(H^2)
H^6	0,200	0,190	0,175	0,317(C^{11})	0,187(H^5)

3.1.3 Analysis Electrostatic potentials (ESP)

Table 3: Electrostatic potentials

	TSCZ	Z-EtTSCZ	E-EtTSCZ	2MTSCZ	4MTSCZ
N^1	-18,29	-18,31	-18,31	-18,31	-18,3
N^5	-18,26	-18,28	-18,26	-18,25	-18,26
N^7	-18,31	-18,33	-18,32	-18,32	-18,31
S	-59,24	-59,25	-59,24	-59,24	-59,25
C^4	-14,60	-14,62	-14,61	-14,61	-14,61
C^8	-14,71	-14.69	-14,70	-14,71	-14,71
H^2	-0,99	-1,00	-1,00	-1,00	-14,67(C^{10})
H^3	-1,	-1,01	-1,01	-1,01	-1,01(H^2)

Reading table 3, which shows the ESP of some atoms of the ligands, it can be seen that in the TSCZ, the sulfur atom (59.2 ua) is clearly the most favorable site for coordination since it is followed only by the nitrogen atoms ESP of which equal to 18.3 ua.

3.1.4 Frontier orbitals analysis

Table 4: Energetic values of TSCZs

Energies (eV)	TSCZ, dominant atomic orbital	Z-EtTSCZ, dominant atomic orbital	E-EtTSCZ, dominant atomic orbital	2MTSCZ, dominant atomic orbital	4MTSCZ, dominant atomic orbital
HOMO-1	-6,15 ; S px(1,18)	-6,00 ; S pz(0,94)	-6,12 ; S pz(1,11)	-6,07 ; S pz(1,1)	-5,96 ; S pz(1,18)
HOMO	-5,79 ; S px(1,3)	-5,66 ; S px(1,18)	-5,69 ; S px(1,28)	-5,69 ; S py(0,94)	-5,65 ; S px(1,16)
LUMO	-1,07	-0,48	-0,83	-0,93	-0,83
LUMO+1	0,62	-0,1	0,84	0,73	0,93
ΔG,hartree	-641,47	-680,87	-680,88	-680,86	-680,86
ΔG, eV	-17454,85	-18526,95	-18527,22	-18526,68	-18526,68

The table 4 gathers energy values of the thiosemicarbazones studied. It is noted that the energies of the HOMO and HOMO-1 are respectively of the order of -5.7 eV and -6.1 eV; these molecular orbitals are dominated by the atomic orbital p_x of the sulfur atom in the molecule of TSCZ, by p_x (HOMO) and p_z (HOMO-1) of S in the case of Z-EtTSCZ and E-EtTSCZ, by p_y (HOMO) and p_z (HOMO-1) of S in 2-MTSCZ and by p_x (HOMO) and p_z (HOMO-1) of sulfur in 4MTSCZ. Thus the analysis of the frontier orbitals indicates that the most favorable site for the coordination of TSCZ is the sulfur atom.

3.1.5 Atomic indexes of electrophilic superdelocalisability (IESD)

The main indexes of electrophilic superdelocalizability are shown in Table 5.

IESD is a magnitude which appreciates the ability of a site to attract to either an electrophilic center [22].

Table 5: IESD values of TSCZs

Atomes	IESD, eV				
	TSCZ	Z-EtTSCZ	E-EtTSCZ	2MTSCZ	4MTSCZ
N^1	-0.424	-0.437	-0.435	-0.433	-0.425
N^5	-0.394	-0.414	-0.399	-0.393	-0.398
N^7	-0.449	-0.464	-0.462	-0.452	-0.452
S	-0.834	-0.835	-0.820	-0.827	-0.836
C^4	-0.283	-0.290	-0.284	-0.285	-0.283
C^8	-0.343	-0,326	-0.311	-0.346	-0.347
H^2	-0.046	-0,050	-0.050	-0,049	-0.048
H^3	-0,045	-0,049	-0.047	-0,048	-
H^6	-0,047	-0.049	-0.048	-	-0.047

The coordination is thought to be more likely at the level of the atom with the most negative IESD [22]. We note that all IESDs calculated are negative. It follows from reading Table 5 that the most negative ESDI in each ligand studied in this work is that of the sulfur atom (-0.83 eV approximately). A summary analysis will allow us to identify the most likely coordination site.

3.1.6 Summary analysis

In Table 6 it can be seen, at the intersection of each ligand with each coordination indicator (CI), the atom through which coordination can occur during a coordinating process.

Table 6: Summary analysis of TSCZs

Molecules CI	TSCZ	Z-EtTSCZ	E-EtTSCZ	2MTSCZ	4MTSCZ
Bond legth	S, N^7	S, N^7	S, N^7	S, N^7	S, N^7
Atomic charges	S	S	S	S	S
ESP	S	S	S	S	S
HOMO	S	S	S	S	S
IESD	S	S	S	S	S

It emerges from the study of this table that all the considered ICs are favorable for the coordination of the studied thiosemicarbazone via the sulfur atom. Coordination through N^7 is unlikely. No IC gives N^1 or N^5 favorable to the coordination of these thiosemicarbazone.

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 $1s22s^22p^63s^23p^6$ $4s^03d^{10}4p^0$. Zinc (II) generally gives tetrahedral complexes close to the T_d 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 sp^3 hybridization. The sp^3 hybrid orbitals point to the vertices of a tetrahedron. The p orbital of atoms recognized, in tis investigation, as favorable for the coordination of the studied ligands are capable to overlap with these sp^3 orbitals.

3.2 Modeling of coordination compounds

3.2.1 Modeling

Complexes of thiosemicarbazone ($ZnCl_2$.TSCZ, $ZnCl_2$.Z-EtTSCZ, $ZnCl_2$.E-EtTSCZ, $ZnCl_2$.2MTSCZ and $ZnCl_2$.4MTSCZ on the one hand, $ZnCl_2$.2TSCZ, $ZnCl_2$.2 (Z-EtTSCZ), $ZnCl_2$.2 (E - EtTSCZ), $ZnCl_2$.2 (2MTSCZ) and $ZnCl_2$.2 (4MTSCZ) on the other hand) were mdeled.

These complexes have tetrahedral structure. Their structures are shown respectively on figures 2 and 3. On table 7 and 8, one can read some geometric parameters of the complexes. The interatomic distances of ZnS have values between 2, 41 and 2, 51 Å. This interval is consistent with the literature data [14] (between 2, 26 and 2, 44 Å for experimental data; between 2, 23 and 2, 56 Å for calculated DFT/B3LYP data). It is deduced that the molecules of thiosemicarbazones, objects of the present work, entered into coordination via the sulfur atom. The complexes of the $ZnCl_2$.ligand type are chelates: the coordination carried out by the both sulfur atom and the N^7 nitrogen atom; in fact the ZnN^7 distances in these compounds are approximately 2.15 Å.

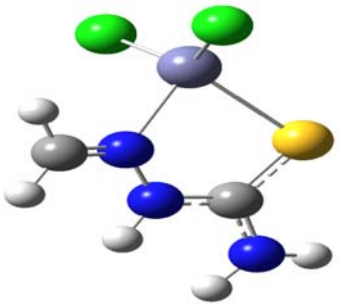
From all the foregoing it emerges that the combination of the analysis of interatomic distances, atomic charges, electrostatic potentials, frontier orbitals and atomic indexes of electrophilic super delocalization of ligands constitutes a fairly effective means of studying the coordination of thiosemicarbazones.

Table 7: Some interatomic distances of modeled complexes $ZnCl_2$.Ligand

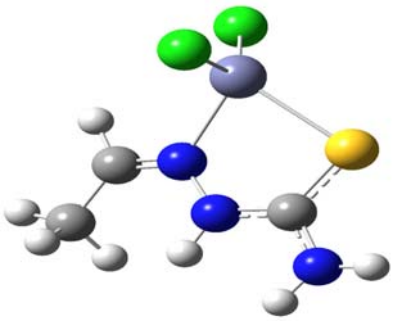
	$ZnCl_2$.TSCZ	$ZnCl_2$.E-EtTSCZ	$ZnCl_2$.Z-EtTSCZ	$ZnCl_2$.2MTSCZ	$ZnCl_2$.4MTSCZ
Distances (Å)					
Zn-S	2,51	2,51	2,48	2,47	2,50
Zn-N^7	2,16	2,14	2,16	2,15	2,16
Zn-N^1	4,47	4.45	4,46	4.43	4,48
Zn-N^5	3,02	2,14	3,01	3,02	3.02
Zn-Cl^{12}	2,20	2.20	2,21	2,19	2,20
Zn-Cl^{13}	2,19	2,20	2,20	2,20	2,20
Dihedrals (°)					
$SC^4N^5N^7$	0,61	-2,30	-0,02	6,15	-0,03
$N^1C^4N^5N^7$	178,93	179,86	179,92	-173.62	179,19
$C^4N^5N^7C^8$	-170,00	168,61	-179,01	162.87	-171,32
$N^5N^7C^8C^{10}$	-	-	-179,00	-	6,68
$N^5N^7C^8C^{11}$	-	-0,04	-	10.70	-
$ZnSC^4N^1$	169,95	-166,69	172.52	-166.01	171,07
$ZnSC^4N^5$	-11,84	15,61	-7,54	14.21	-9,76

Table 8: Some interatomic distances of modeled complexes $ZnCl_2$.2Ligand

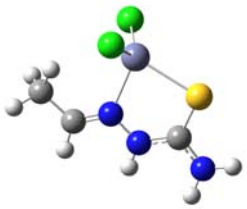
	$ZnCl_2$.2TSCZ	$ZnCl_2$.2E-EtTSCZ	$ZnCl_2$.2Z-TSCZ	$ZnCl_2$. 2(2-MTSCZ)	$ZnCl_2$.2 (4-MTSCZ)
Distances (Å)					
Zn-S^5	2,45	2,42	2,42	2,41	2,43
Zn-S^{19}	2,43	2,42	2,44	2,42	2,42
Zn-N^1	3,37	3,39	3,47	3,30	3,31
Zn-N^{15}	3,45	3,36	3,33	3,33	3,27
Zn-N^5	4,21	4,57	4,72	4,16	4,62
Zn-N^{20}	4,73	4,16	4,39	4,62	4,44
Zn-N^8	4,90	5,35	5,42	4,76	5,49
Zn-N^{22}	5,62	4,84	5,17	5,33	5,24
Zn-Cl^{13}	2,22	2,25	2,22	2,25	2,22
Zn-Cl^{14}	2,32	2,33	2,33	2,33	2,36
Dihedrals (°)					
$S^5C^4N^6N^8$	-2,09	6,54	21,21	-9,20	-12,78
$N^1C^4N^6N^8$	-177,99	-170,85	-159,16	176,55	167,77
$C^4N^6N^8C^9$	-55,38	-61,85	-82,09	-56,69	25,47
$N^6N^8C^9C^{11}$	-	178,40	-1,50	-35,36	-4,38
$ZnSC^4N^1$	-58,85	-30,80	1,65	-59,07	-21,18
$ZnSC^4N^6$	125,49	151,00	-138,70	126,84	159,41



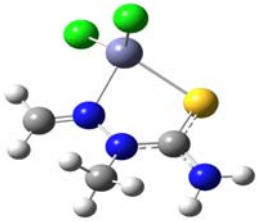
$ZnCl_2$.TSCZ
Dichlorothiosemicarbazonezinc(II)



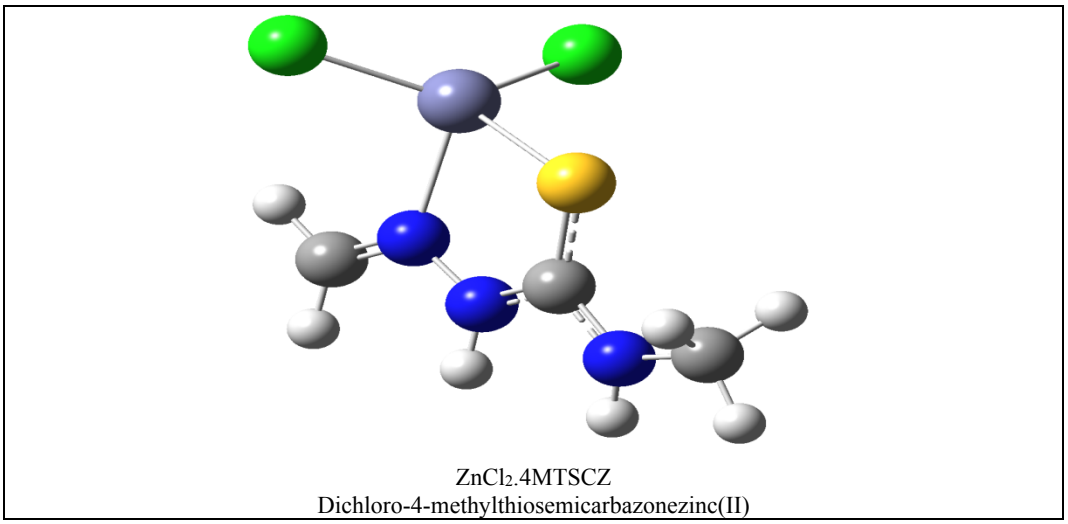
$ZnCl_2$.E-EtTSCZ
Diloro-E-ethanal thiosemicarbazone zinc (II)



$ZnCl_2$.Z-EtTSCZ
Dichloro-Z-ethanalthiosemicarbazonezinc(II)

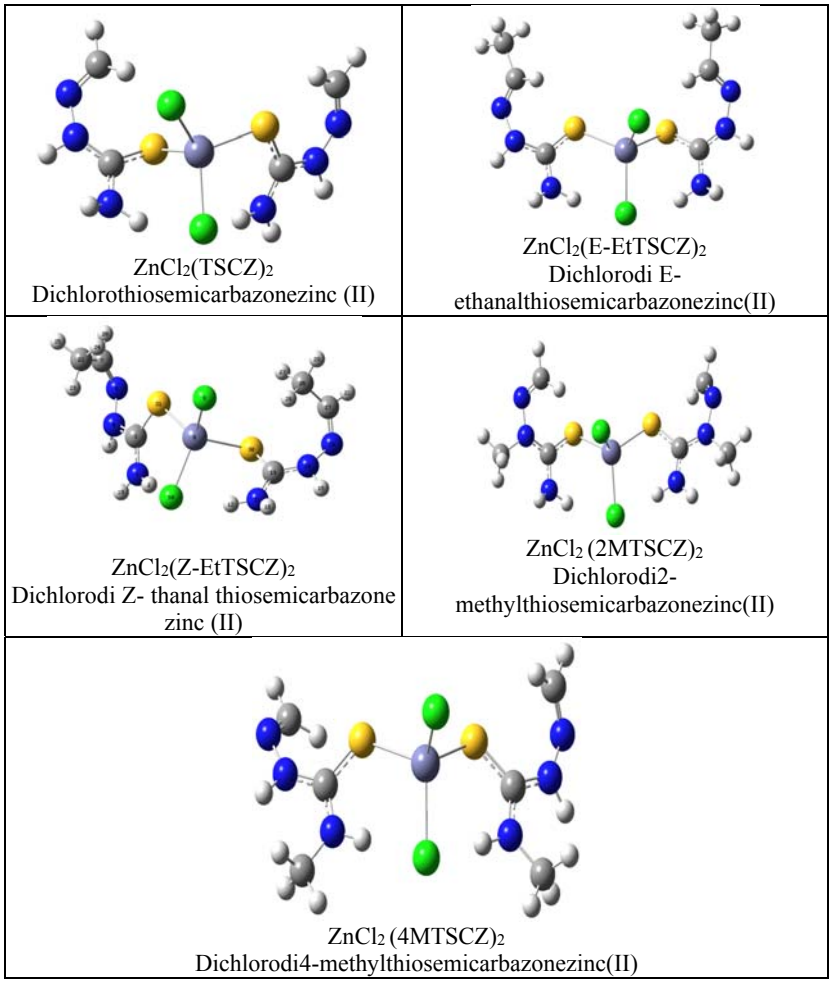


$ZnCl_2$.2MTSCZ
Chloro-2-methylthiosemicarbazonezinc(II)



$ZnCl_2$.4MTSCZ
Dichloro-4-methylthiosemicarbazonezinc(II)

Fig 2: Structure of complexes $ZnCl_2$.ligand



$ZnCl_2(TSCZ)_2$
Dichlorothiosemicarbazonezinc (II)

$ZnCl_2(E\text{-}EtTSCZ)_2$
Dichlorodi E-ethanalthiosemicarbazonezinc(II)

$ZnCl_2(Z\text{-}EtTSCZ)_2$
Dichlorodi Z- thanal thiosemicarbazone zinc (II)

$ZnCl_2\,(2MTSCZ)_2$
Dichlorodi2-methylthiosemicarbazonezinc(II)

$ZnCl_2\,(4MTSCZ)_2$
Dichlorodi4-methylthiosemicarbazonezinc(II)

Fig 3: Structure of the complexes $ZnCl_2$.2Ligand

3.2.2 Energetic study

The study of the energy of coordination the ligands with zinc (II) chloride allowed to assess the stability of the coordination bond.

Tables 9 and 10 show some energy values.

Table 9: Some energies about the complexes of $ZnCl_2$. ligand type

	ΔH, eV	ΔH_{coord}, eV	ΔG, eV	ΔG_{coord}, eV	Type of process
$ZnCl_2$	-73458,28	-	-73459,09	-	-
TSCZ	-17456,75	-	-17457,84		-
E-EtTSCZ	-18526,13	-	-18527,22	-	-
Z-EtTSCZ	-18525,86	-	-18526,94	-	-
2MTSCZ	-18525,59	-	-18526,68	-	-
4MTSCZ	-18525,59	-	-18526,68	-	-

$ZnCl_2$.TSCZ	-91985,21	-1070,18	-91986,82	-1069,7	Exothermic and Spontaneous
$ZnCl_2$.E-EtTSCZ	-91985,64	-1,23	-91987,25	-0,94	Exothermic and Spontaneous
$ZnCl_2$.Z-EtTSCZ	-91985,72	-1,58	-91987,33	-1,30	Exothermic and Spontaneous
$ZnCl_2$.2MTSCZ	-91985,17	-1,30	-91986,71	-0,94	Exothermic and Spontaneous
$ZnCl_2$.4MTSCZ	-91985,21	-1,34	-91986,82	-1,05	Exothermic and Spontaneous

ΔG= Free enthalpy of the species
ΔG_{coord}= Free enthalpy of coordination
$\Delta G_{coord}=\Delta G_{complexe} - (\Delta G_{ligand} + \Delta G_{ZnCl2})$
ΔH= Enthalpy of the species
ΔH_{coord}= Enthalpy of coordination
$\Delta H_{coord}=\Delta H_{complexe} - (\Delta H_{ligand} + \Delta H_{ZnCl}$

Table 10: Some energies about the complexes of $ZnCl_2$. 2ligand type

	ΔH, eV	**ΔH_{coord}, eV**	**ΔG, eV**	**ΔG_{coord}, eV**	**Type of the process**
$ZnCl_2$	-73458,28	-	-73459,09	-	-
TSCZ	-17456,75	-	-17457,84	-	-
E-EtTSCZ	-18526,13	-	-18527,22	-	-
Z-EtTSCZ	-18525,86	-	-18526,94	-	-
2MTSCZ	-18525,59	-	-18526,68	-	-
4MTSCZ	-18525,59	-	-18526,68	-	-
$ZnCl_2$.2TSCZ	-108373,42	-1,64	-108375,59	-0,82	Exothermic and Spontaneous
$ZnCl_2$.2(E-EtTSCZ)	-110512,18	-1,64	-110514,35	-5,06	Exothermic and Spontaneous
$ZnCl_2$.2 (Z-EtTSCZ)	-110511,90	-1,90	-110514,08	-1,11	Exothermic and Spontaneous
$ZnCl_2$.2 (2MTSCZ)	-110511,09	-1,63	-110513,26	-0,29	Exothermic and Spontaneous
$ZnCl_2$.2 (4MTSCZ)	-110511,09	-1,63	-110513,54	-1,09	Exothermic and Spontaneous

ΔG= Free enthalpy of the species
ΔG_{coord}= Free enthalpy of coordination
$\Delta G_{coord}=\Delta G_{complexe} - (2\Delta G_{ligand} + \Delta G_{ZnCl2})$
ΔH = Enthalpy of the species
ΔG_{coord}= Enthalpy of coordination
$\Delta H_{coord}=\Delta H_{complexe} - (2\Delta H_{ligand} + \Delta H_{ZnCl2})$

The negative values of the coordination free enthalpies show that the coordination of the thiosemicarbazones studied is a spontaneous process. Enthalpies also are negative so the process is exothermic for all ligands.
It should be noted that the introduction of the methyl group in thiosemicarbazone 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 thiosemicarbazones. These were thiosemicarbazone, E-ethanalthiosemicarbazone, Z-ethanalthiosemicarbazone, 2-methylthiosemicarbazone and 4-methylthiosemicarbazone. This has been made possible by the analysis of coordination indicators such as bond lengths, atomic charges, atomic electrostatic potentials, boundary orbitals and atomic indexes of electrophilic superdelocalizabilty.
The results from our calculations showed that these molecules are able to form complexes with metal ions. Zinc (II) is one of these ions. The most favorable coordination site has been found to be the sulfur atom; it is followed by the N^7 atom, trigonal nitrogen, as evidenced by the formation of chelates.
The introduction of the methyl group did not significantly influence the properties of thiosemicarbazone. 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. The vertices of the tetrahedra are occupied by two chlorine atoms and two sulfur atoms in the 1/2 structures; in the 1/1 structures, the vertices of the tetrahedra are occupied by two chlorine atoms, the sulfur atom and the N^7 atom. All complexation processes were spontaneous and exothermic under the study conditions, namely 25 ° C. and one atmosphere.

5. References

1. Knouniats IL, Himitcheskaya Entsiklopédiya, Ed. Soviets kaya entsiklopédiya, Moscou, 1990; 212:213.
2. Williams D, Mettalli Jizni, ed. Mir, Moscou, 1975.
3. Yatsimirskiï KV, Vvedenie v bio neorganicheskoi you himiou, ed. Naoukova Doumka, Kiev, 1976.
4. Kembal J. Sovrémiénaya obchaya himia, ed. Mir, Moscou, 1975.
5. Azizov MA, O Komplexnih soédineniah nekotorih microélémentov s bioactivnimi vechestvami, ed. Médétsina, Tachkent, 1969.
6. Büchel KH, Moretto HH. Industrial inorganic chemistry, Weinheim, Wiley-VCH,2 ;2000 **:**667. (ISBN 9783527298495 et 9783527613328, DOI 10.1002/9783527613328
7. Bäuerlein E, Arias JL Handbook of biomineralization: biological aspects and structure formation, Biological aspects and structure formation, Weinheim, Germany, Wiley-VCH, 2007; 1:309-327. (ISBN 9783527316410, DOI 10.1002/9783527619443.ch18
8. Bäuerlein E, Kawasaki K. Handbook of biomineralization: biological aspects and structure formation, Biological aspects and structure formation, Weinheim, Germany, Wiley-VCH, (ISBN 9783527316410, DOI 10.1002/9783527619443.ch19, présentation ligne), chap. 2007; 19:331-347.
9. Bäuerlein E, FrankelR B, Handbook of biomineralization: biological aspects and structure formation, vol. 1: Biological aspects and structure formation, Weinheim, Germany, Wiley-VCH, (ISBN 9783527316410, DOI 10.1002/9783527619443.ch8, chap. 2007; 8:127-144.
10. Andersen O. Principles and recent developments in chelation treatment of metal intoxication », Chem. Rev.,

1999; 99:9:2683-2710. (ISSN 0009-2665, DOI 10.1021/cr980453a).
11. Wong E, Giandomenico CM. Current status of platinum-based antitumor drugs », Chem. Rev. 1999; 99(9):2451-2466 (ISSN 0009-2665, DOI 10.1021/cr980420v).
12. Shaw CF. Gold-based therapeutic agents », Chem. Rev. 1999; 99(9):2589–2600. (ISSN 0009-2665, DOI 10.1021/cr980431o).
13. Caravan P. Ellison JJ. *et al*. Gadolinium(III) chelates as MRI contrast agents: structure, dynamics, and applications », Chem. Rev. 1999; 99(9):2293–2352. (ISSN 0009-2665, DOI 10.1021/cr980440x)
14. Delphine Picot, Modelisation de la reaction d'alkylation du motif zinc-thiolate, Thèse de doctorat, 2008.
15. Sakirigui A. J. Soc. Ouest-Afr. Chim. 2011; 031:11-20.
16. Kenneth L. Williamson, Macroscale and Microscale Organic Experiments, 3rd ed., Boston, Houghton-Mifflin, 1999. 3e éd. (ISBN 978-0-395-90220-2, LCCN 98072094), p. 426–7
17. Frisch MJ, all. Gaussian 98W, Gaussian Inc., Pittsbourgh PA, 1998.
18. R. Mason Acta crystallogr. 1961; 14:720.
19. Potapov VP, Tatarintchik S, Chimie organique, Ed. Mir, Moscou, 1988; 34(37):65-66-74.
20. Sakurai H, Yoshikawa Y, Yasui H. Chem Soc Rev. 2008; 37(11):2383-92. doi: 10.1039/b710347f. Epub 2008 Sep 26.
21. Douglas, X West, Anthony E. Liberta, Coordination Chemistry Reviews. 1993; 123:49-71.
22. Gómez-Jeria JS. D-Cent-QSAR, v. 1.0. Santiago, Chile, 2014.