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Antimony(III) complexes with N-phenylthiourea derivative ligands: Design, Synthesis, Characterization and Computational studies

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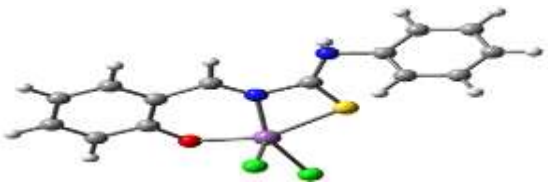
Abstract: The reactions of antimony(III)chloride with N-phenylthiourea derivative ligands gives antimony(III) complexes of type, $[SbCl_2L]$. The reaction was performed in 1:1 molar ratio. The newly synthesized complexes were characterized by melting point, elemental analysis, FT-IR, UV–Vis, ^{1}H and ^{13}C NMR spectroscopy and Mass spectrometry. The computational calculations using density functional theory (DFT) of ligands and complexes were also performed to obtained optimized molecular geometry, the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and other parameter. The spectroscopic data and computational studies suggest five coordination around antimony atom.
Keywords: Antimony(III) complex, N-phenylthiourea, DFT, HOMO-LUMO energy.
Graphical Abstract. The ground state optimized geometry of antimony(III) complex



1. Introduction

The role of antimony based drugs has growing importance in therapeutics and diagnostics. The bioactivities of coordination metal complexes governed by the ligand attached to it. On coordination to metals, biologically potent ligands may improve their biological properties while in some case inactive ligands may acquire pharmacological properties[1]. The binding properties of metal complexes to DNA gains significant importance because of their potential applications as diagnostic agents for medical applications and cleavage agents for probing nucleic acid structure. In addition, metal coordination is one of the most efficient strategies in the design of repository, slow release or long-acting drugs[2-3].

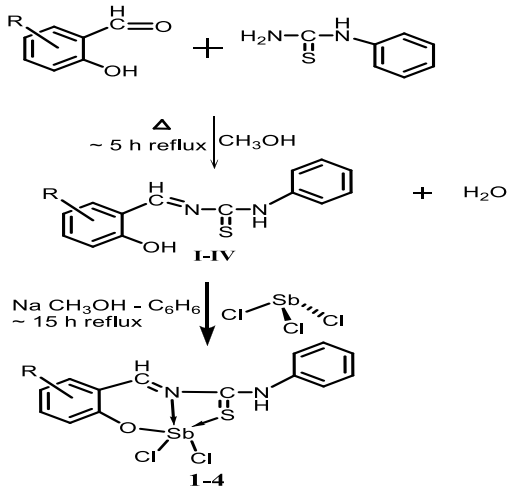
Antimony compounds are used in treatment for leishmaniasis[4]. However, the role of some antimony compounds as the antitumor agents got recognition earlier[5-6]. Moreover, antimony(III) compounds are now being proposed as a novel therapy for acute promyelocytic leukemia (APL). On the other hand, antimony complexes have various potential usage in the field of pharmacy such as anthelminthic, antitrypanosomal, anticancer, antileishmanial and antimicrobial agents[7-13].

Sulfur containing ligands are generally considered as bioactive ligands and their metal complexes gain significant attraction due to their structural characteristics as well as applicability in various fields. The presence of N and S as donor sites in thiourea act in ambidentate manner and susceptible for coordination to relevant binding sites in living organisms[14-16]. This interesting chemistry helps in activation of biological activities of thiourea and its derivative. Thiourea and its derivatives have several potential applications in the pharmacological development. Thiourea and its derivatives act as antifungal, antiviral, and antibacterial agents[17-20]. The coordination chemistry of thiourea derivatives with p-block elements are unexplored than that of the transition metal elements and so this is still a matter of research interest. Therefore in this article synthesis and characterization of antimony(III) complexes with thiourea derivative Schiff base ligands have been discussed.

2. Experimental

Four antimony(III) complexes have been synthesized by reacting the N-phenylthiourea derivative ligand with antimony(III) chloride in methanol solutions. (Scheme 1) The reactions of antimony(III)chloride with N-

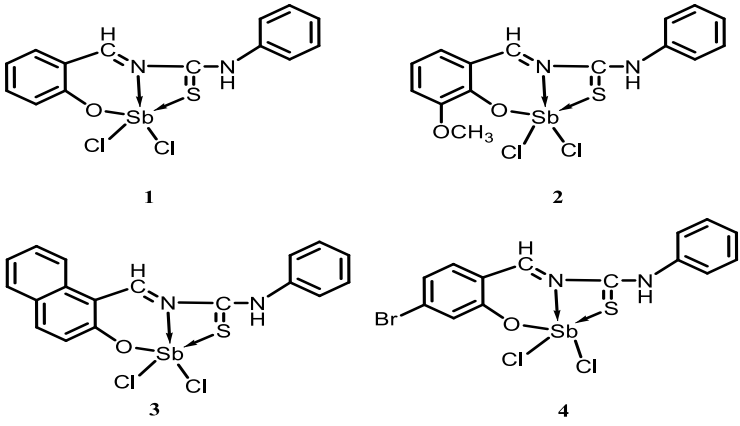
phenylthiourea derivatives were performed in 1:1 metal to ligand molar ratio. The ligands are coordinated to Sb(III) through tridentate mode in NOS atom. The structural representation of complexes is shown in Scheme 5.2.



where, R = H (**I, 1**); C_4H_4(**II, 2**); OCH_3 (**III, 3**); Br(**IV, 4**)

L= Schiff base sptuH= salicylidene-N-phenylthiourea I; vptuH= vanillidene-N-phenylthiourea II; nptuH= naphthalidene-N-phenylthiourea III; bsptuH= 4-bromo-salicylidene-N-phenylthiourea IV.

Scheme 1. Synthetic route for preparation of antimony(III) complexes 1-4



Scheme 2. Structural representation of antimony(III) complexes 1-4

3. Result and Discussion

The synthesized ligands and complexes were color solid and soluble in organic solvent. All the antimony(III) complexes were solid color compounds. All compounds are soluble in organic solvents. The general physical properties of complexes were summarized in Table 1.

Table 1 Some physical properties of ligands I-IV and antimony(III) complexes 1-4

S. No.	Complex		Mol. Wt.	Color State
1.	Sptu	I	Dark red solid	256.32
2.	Vptu	II	Dark orange solid	286.35
3.	Nptu	III	Brown solid	290.38
4.	Bsptu	IV	Brown solid	335.22
5.	$[SbCl_2(sptu)]$	1	Gray Solid	447.98
6.	$[SbCl_2(vptu)]$	2	Brown solid	478.01
7.	$[SbCl_2(nptu)]$	3	Dark brown solid	498.04
8.	$[SbCl_2(bsptu)]$	4	Gray Solid	526.88

3.1 Infrared spectroscopy: The characteristic IR bands of ligands and complexes (Figure 1) are collected in Table 2. The band due to phenolic OH in ligands was found in the region of 3520-3489 cm^{-1}. The broadening or disappearance of this band in complexes indicates deprotonation of phenolic hydrogen which results in formation of bond between oxygen with antimony. This coordination O-Sb was further supported by the band appear in the region 570-561 cm^{-1}. The azomethine band C=N which indicate the formation of ligands was found in the region 1620-1610 cm^{-1}. This band shows significant shift in complexes which indicate participation of azomethine nitrogen in coordination with antimony. These coordination modes were further supported by the band appeared in the region 436-430 cm^{-1}. The characteristic band of thio- group C=S found in the region 784-775 cm^{-1} shows downward shift in complexes and appeared at 767-748 cm^{-1}. This observation indicates participation of sulphur atom in coordination with antimony. This S-Sb coordination mode was further supported by the appearance of bands in the region 564-548 cm^{-1}.

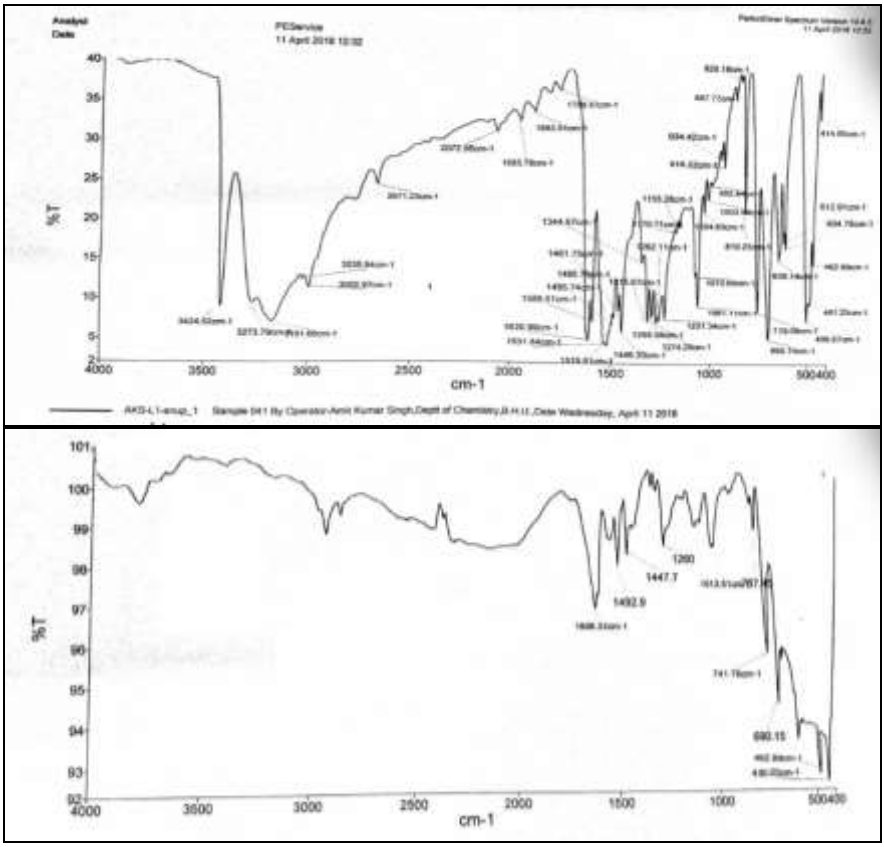


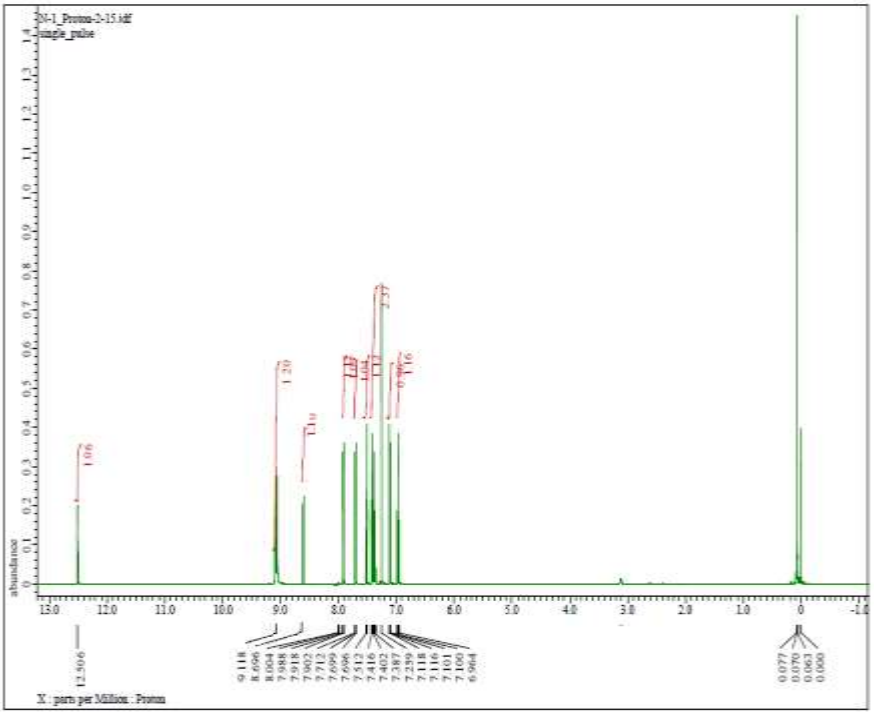
Figure 1. IR spectrum of ligand, sptuH antimony(III) complex, $[SbCl_2(sptu)]$ 1

Table 2 Characteristic IR frequencies (cm^{-1}) of ligands I-IV and antimony(III) complexes 1-4

S. N	Complex		ν_{O-H}	$\nu_{C=N}$	$\nu_{C=S}$	ν_{Sb-O}	ν_{Sb-N}	ν_{Sb-S}
1.	sptuH	I	3424	1620	779	-	-	-
2.	vptuH	II	3490	1622	787	-	-	-
3.	nptuH	III	3510	1617	792	-	-	-
4.	bsptuH	IV	3495	1619	788	-	-	-
5.	$[SbCl_2(sptu)]$	1	-	1606	770	570	430	462
6.	$[SbCl_2(vptu)]$	2	-	1606	777	565	436	458
7.	$[SbCl_2(nptu)]$	3	-	1605	782	561	428	456
8.	$[SbCl_2(bsptu)]$	4	-	1608	771	562	434	462

3.2 ^{1}H NMR Spectroscopy: The ^{1}H NMR data of ligands and complexes (Figure 2) are summarized in Table 3. The comparison of ^{1}H NMR spectra of ligands and compounds gives some important information about coordination mode of ligands to metal complexes. The characteristic signal

due to phenolic –OH appears in the region of 12.91-12.50 ppm in free ligand was found absent in complexes indicate metallation through phenolic oxygen. The N-H signal of thiourea derived ligands in the region 9.12-9.08 ppm became less intense with down field shifting upon coordination in metal complexes and found in the region 9.22-9.17 ppm. This N-H signal deshielding shows coordination of sulfur atom of thion group through metal. The azometheine hydrogen in free ligands shows signals in the region 8.89-8.67 ppm. This signal shows a shift in the region 8.42 - 8.34 ppm indicative of participation of azomethine nitrogen. The signals due to aromatic hydrogen appear in the region 8.00-6.42ppm for free ligands shows slight shift in the complexes.



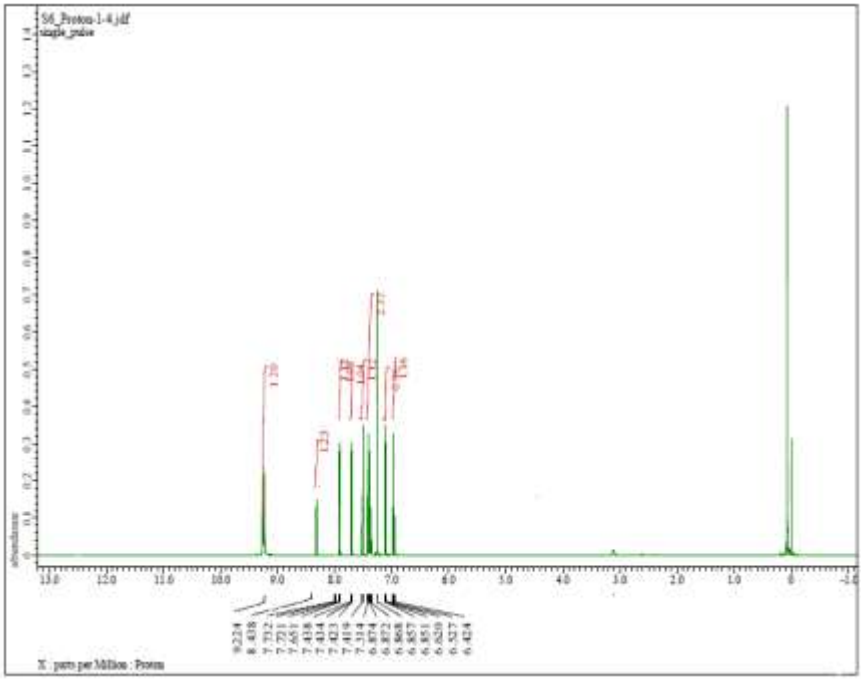


Figure 2. ^{1}H NMR spectrum of ligand, sptuH I and antimony(III) complex, [$SbCl_2$(sptu)] 1

Table 3. ^{1}H NMR data (ppm) for ligands ligands I-IV and antimony(III) complexes 1-4

S.No.	Complex		O-H	N-H	CH=N	Ar-H	-OCH_3
1.	sptuH	I	12.50	9.11	8.69	8.00 - 6.96	-
2.	vptuH	II	12.56	9.08	8.60	7.40 - 6.75	3.86
3.	nptuH	III	12.91	9.09	8.62	7.59 - 6.42	-
4.	bsptuH	IV	12.75	9.12	8.65	7.61 – 6.62	-
5.	[$SbCl_2$(sptu)]	1	-	9.22	8.34	7.21 - 6.65	-
6.	[$SbCl_2$(vptu)]	2	-	9.17	8.36	7.34 - 6.71	3.85
7.	[$SbCl_2$(nptu)]	3	-	9.19	8.42	7.39 - 6.62	-
8.	[$SbCl_2$(bsptu)]	4	-	9.20	8.37	7.41 – 6.61	-

3.3 ^{13}C NMR Spectroscopy: The ^{13}C NMR data of ligands and complexes (Figure 3) are summarized in Table 4. The comparison of ^{13}C NMR spectra of ligands and compounds gives some important information about coordination mode of ligands to metal complexes. The ^{13}C NMR spectra of ligands show signals in the region 182.8-184.5 ppm were assigned to C=S

bond. This signal shows a significant shift in the complexes and appeared in the region 171.4 – 173.5 ppm indication coordination of thion group through S atom. Another important signals appeared in the region 159.8 – 162.0 ppm were attributed to C=N. This signal also undergo shift in complexes and appeared at 157.5 – 159.8 ppm. The signals for aromatic carbon in ligands and complexes were observed in the region 148.0 – 114.5 ppm.

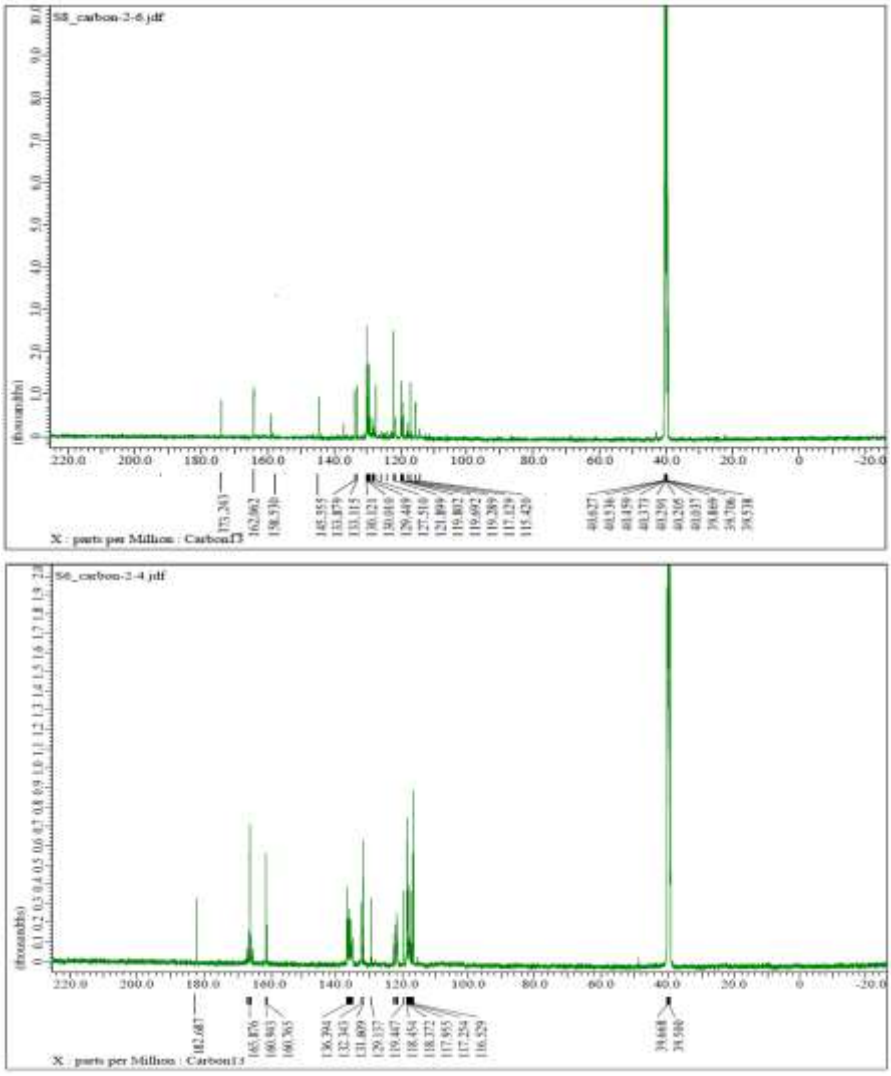


Figure 3. ^{13}C NMR spectrum of ligand, sptuH I and antimony(III) complex, $[SbCl_2(sptu)]$ 1.

Table 4 ^{13}C NMR data (ppm) for ligands I-IV and antimony(III) complexes 1-4

S. No.	Complex		^{13}C NMR			
			C=S	HC=N	Ar-C	OCH_3
1.	sptuH	I	182.6	161.5	147.5 - 115.3	-
2.	vptuH	II	184.5	162.0	146.1 - 116.9	56.4
3.	nptuH	III	182.8	159.8	148.0 - 114.8	-
4.	bsptuH	IV	184.1	161.8	148.5 – 115.5	-
5.	$[SbCl_2(sptu)]$	1	173.2	158.5	145.2 - 114.5	-
6.	$[SbCl_2(vptu)]$	2	171.4	159.8	146.6 – 116.7	56.5
7.	$[SbCl_2(nptu)]$	3	172.6	157.5	145.1 – 115.3	-
8.	$[SbCl_2(bsptu)]$	4	172.5	158.3	146.1 – 114.5	-

3.4 Mass Spectrometry: The mass spectra of ligands (I-IV) and complexes (1-4) exhibits molecular ion peaks (m/z) which is correspond to the molecular composition of ligand. In the mass spectra of ligands I, II, III and IV molecular ion peak observed at m/z 256.84, 286.75, 290.75 and 335.22 respectively. Some other peaks were also observed in the spectra of ligands which is correspond to small ions and radicals formed. In the spectra of complex 1, 2, 3 and 4 molecular ion peak observed at *m/z* 447.64 [($C_{14}H_{12}Cl_2NO_2SSb$); calculated mass = 447.98], 478.26 [($C_{15}H_{14}Cl_2N_2O_2SSb$); calculated mass = 478.01]; 497.69 [($C_{18}H_{14}Cl_2N_2OSSb$); calculated mass = 498.04] and 526.56 [($C_{14}H_{11}Cl_2BrNO_2SSb$); calculated mas = 526.88] respectively, which correspond to the monomeric molecular composition of the corresponding complexes. Some other peaks were also observed in the spectra of complexes which is correspond to small ions and radicals formed due to fragmentation.

3.5 Computational Studies: Computation studies of ligands and complexes were performed for further validation of spectroscopic interpretation. The computation studies were performed through density functional theory (DFT). The geometries of lignads and antimony(III) complexes were optimized using B3LYP/LANL2DZ method (Figure 4). The energy of frontier molecular orbital was calculated. The determination of energy gap between HOMO-LUMO is very helpful in knowing the stability of ligand and corresponding complexes (Figure 5). The important bond length and bond angle were also calculated and found in order with the reported value in literature.

4. Conclusion

In this article, synthesis of four NOS donor Schiff base donor ligand (I-IV) and their corresponding antimony(III) complexes has been discussed.

These ligands and complexes have been characterized by elemental analysis and spectroscopic techniques such as FTIR, NMR as well as mass spectrometry. The computational studies of the ligands and complexes were also performed using DFT program. On the basis of spectroscopic observations, tridentate coordination mode of ligand through metal has been proposed tentatively which results in five coordinated antimony(III) complexes.

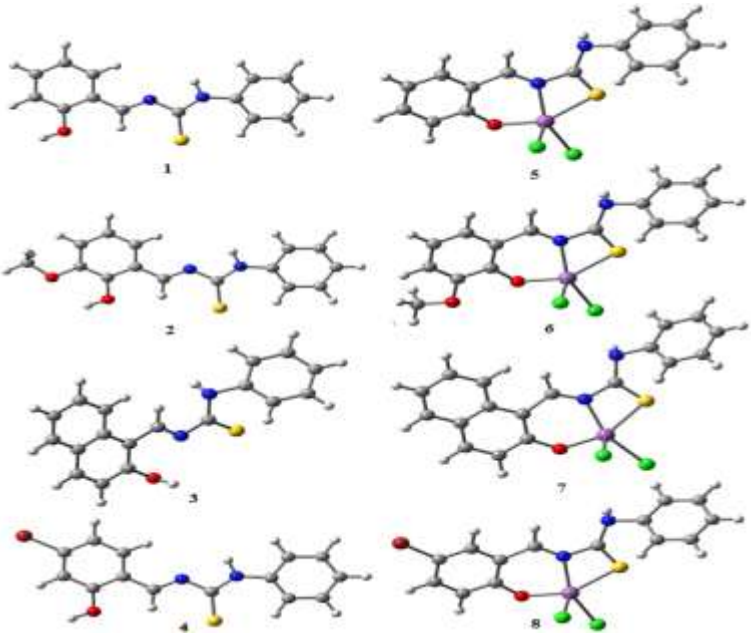


Figure 4. The ground state optimized geometry for ligand I-IV and complex 1-4 at B3LYP/LANL2DZ level.

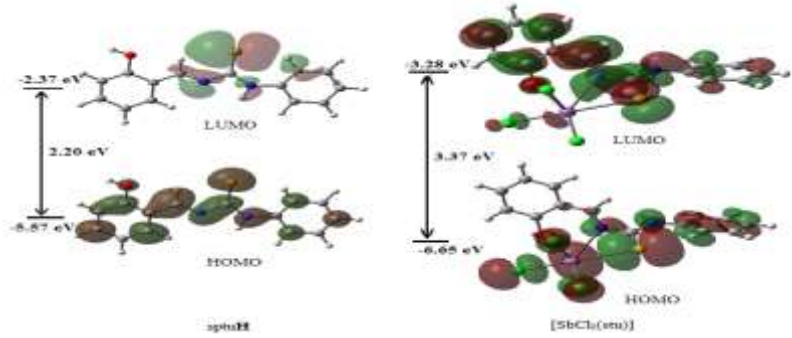


Figure 5. Energy diagram of Frontier molecular orbitals HOMO and LUMO of ligand, sptuH I and complex, $[SbCl_2(sptu)]$ 1 derived from DFT calculations using B3LYP/LANL2DZ level

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