

Microwave Synthesis, Spectral, Thermal, and Pharmacological Evaluation of Some Metal Complexes Containing Benzene Sulfonyl Thiourea Moiety

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Abstract

Synthesis and characterization of organic ligand N-(2-chloro phenyl)-N' benzenesulfonyl thiourea (H_2L^1) was described. The formed ligand incorporated several potential donor sites, making it a versatile complexing agent with metal ions due to the presence of the sulfonyl and thiourea groups, each solely may act as a key constituent of many biologically active species. In this work, we present the synthesis of Pt (II), Pd (II) and Au (III) metal complexes and their coordination behavior towards the unsymmetrical organic ligand (H_2L^1) using microwave-assisted irradiation. The microwave approach provides clean, shorter reaction times and enhancements in yields. The prepared metal complexes have been characterized by elemental analysis, FT-IR, ¹HNMR, UV-Vis, thermal analysis and magnetic susceptibility. They were tested for their antibacterial activity against Gram positive, Gram-negative bacteria as well as fungi. Also anti-cancer assay was applied against two cell lines; breast cancer cells (MCF-7) and liver cancer cells (HepG-2). The IR spectral data indicate that the ligand H_2L^1 coordinates to metal ions through sulfonyl and thionyl groups in a tetradentate square planer manner for Pd^{II} and Pt^{II} ions while in case of Au^{III} it takes an octahedral shape. Based on spectrophotometric investigations, it is suggested that Pd(II), Pt(II) and Au (III) form 1:1 complexes. The molecular compositions of the complexes were proposed on the basis of chemical analyses and spectrophotometric evidences.

Keywords: Thermal analysis • FT-IR • ¹HNMR

Introduction

Metal complexes are being nowadays widely used as analytical and antimicrobial reagents owing to their versatile activities. Also, metal complexes have been found to possess important biological and catalytic activity [1]. The uprising need to understand bio-coordination chemistry helps in improving the design of metal complexes and interpreting their kinetics and thermodynamic actions under biologically relevant conditions [2]. Metal complexes have become of great influence in the medical practice [3]. In some cases, they were used as antibacterial [4], antifungal [4], antioxidant [5], anti-inflammatory [6], and anticancer [7] agents.

Sulfonamides are synthetic antibiotics that inhibit bacterial multiplication. They occupy a unique position in the drug industry and exhibit a wide spectrum of biological activities. A sulfonyl group plays an important role as a key constituent of number of biologically active molecules. Several drugs containing sulfonamide functionality are in clinical uses which include antibacterial and antifungal drug, carbonic anhydrase inhibitors and anti-inflammatory agents [8]. They are also found to have extensive applications in cancer chemotherapy. A general method for the synthesis of sulfonamides involves the coupling of sulfonyl chloride with primary or secondary amine or

a substituted amine [9]. The presence of several potential donor sites, e.g. the sulfonamidic nitrogen, one amino nitrogen, and two sulfonyl oxygen atoms make them versatile complexing agents with metal ions.

Thiourea derivatives (TUD) are important class of molecules having chemical and biological applications. They are of marked significance industrially and physiologically. They, also, have been incorporated in various therapeutics as anti-inflammatory [10], antioxidant [11], antibacterial [12], antifungal [13] and anticancer [14] agents. Based on the just mentioned properties of both sulfonyl and thiourea groups, we are taking the advantage of incorporating both in the synthesis and characterization of organic ligand (H_2L^1) N-(2-chloro phenyl)-N' benzenesulfonyl thiourea and its incorporation in metal complex formation to be tested for its biological activity.

In the background of green chemistry, microwave-assisted synthesis provide a clean, fast, low cost, eco-friendly, solvent free and higher yield rather than conventional heating processes, aiming to introduce energy into the system [15]. In this work, we present the synthesis of Pt (II), Pd (II) and Au (III) metal complexes and their coordination behavior towards the unsymmetrical organic ligand N-(2-chloro phenyl)-N' benzenesulfonyl thiourea using microwave-assisted technique. The prepared metal complexes have been characterized by elemental analysis, FT-IR, NMR, UV-Vis, thermal analysis and magnetic susceptibility. They were tested for their

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antibacterial activity against Gram positive, Gram-negative bacteria as well as fungi. Also anti-cancer assay was applied against two cell lines; breast cancer cells (MCF-7) and liver cancer cells (HepG-2). The molecular compositions of the complexes were proposed on the basis of chemical analyses and spectrophotometric evidences. The metal complexes obtained can be used as precursors for the formulation of new compounds with significant biological activities.

Experimental Procedure

Chemicals and instrumentation

All chemicals used in the present work were of analytical AR grade. All the reagents were obtained from Sigma Aldrich. Metals were purchased from Loba Chemie. The solid reflectance spectra of the ligand and their metal complexes were recorded in the solid state on a Shimadzu 3101 PC spectrophotometer in the UV/Vis range of 200-800 nm. The TG/DTG were recorded from ambient to 1000°C with a heating rate of 10°C min⁻¹ under a nitrogen atmosphere (20 mL min⁻¹) using Shimadzu TG-50H and DTA-60H thermal analyzer. Elemental analysis of the constituting elements was carried out on Perkin Elmer 2400 model. The metal cations were determined using Atomic absorption instrument Perkin Elmer (AAS) for the quantitative determination of chemical elements using the absorption of optical radiation (light) by free atoms in gaseous state. The IR spectra were recorded using KBr pellets in the region 4000-400 cm⁻¹ on FT-IR spectrophotometer Shimadzu 8201. The ¹H-NMR spectra were recorded on a varian F.T-300

MHz spectrometer using TMS as internal standard and DMSO d₆ as solvent. The molar conductivities were performed in DMF solution (1 × 10⁻³ M), by using Jenway 4010 conductivity meter. The Magnetic susceptibility of the metal complexes in the solid state was recorded at room temperature on a Sherwood magnetic susceptibility balance. Mass spectra of the solid ligand and its metal complexes were measured at 70 eV on a JEOL JMS-AX 500 spectrometer.

Ligand and their metal complexes were subjected to be tested for in-vitro antibacterial activity against two species of Gram positive bacteria and two species of Gram negative bacteria as well as two species of fungi. Also anti-cancer assay was tested against two cell lines; breast cancer cells (MCF-7) and liver cancer cells (HepG-2).

Ligand (H₂L¹) synthesis

The ligand under study involves a two- step process for its preparation. The first step includes 1 h refluxing of equimolar amounts of benzenesulfonyl chlorine (0.01 mol) and ammonium thiocyanate (0.01 mol) dissolved in acetone (50 mL) to form benzene sulfonyl isocyanate. Secondly, 4 h refluxing of equimolar amounts of benzenesulfonyl isothiocyanate (0.01 mol) with 2-chloro aniline (0.01 mol) in (50 mL) acetone. The proposed chemical formula of the formed H₂L¹ is C₁₃H₁₁N₂O₂S₂Cl (H₂L¹) and the chemical structure is as shown in Figure 1.

The obtained solid was filtered, recrystallized using ethanol and dried over anhydrous CaCl₂ in a dessicator.

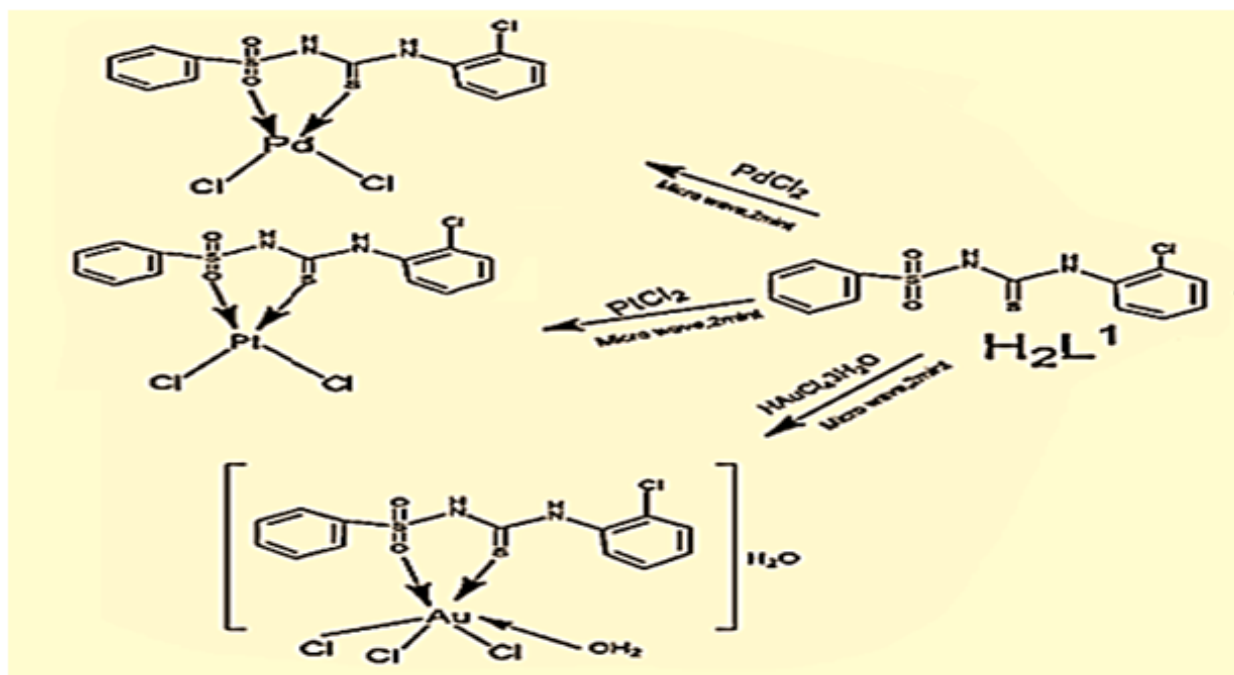


Figure 1. The proposed structures of the prepared ligand H₂L¹ and its metal complexes.

Preparation of Pd (II), Pt (II) and Au (III) complexes using microwave-assisted irradiation

The IN-(2-chloro phenyl)-N' benzenesulfonyl thiourea ligand and the metal salts (Au (III) chloride trihydrate, Pt (II) chloride anhydrous and Pd (II) chloride anhydrous) were mixed in equimolar ratio (1:1) (metal: ligand) in a grinder.

Then the reaction mixture of each was irradiated in 1-3 mL of dry ethanol. The reaction was completed in a short time (3-10 min) with a high % yield.

The obtained product was washed several times with ethanol and ether and finally dried in a desiccator under reduced pressure over anhydrous CaCl₂. The progress of the reaction and purity of the product was monitored by TLC using silica gel G (yield: 89-90%). The results are tabulated in the

Table 1 and Table 2 and from the results we can conclude that the future scope of the investigated compound.

Table 1. Analytical and physical data of the ligand H_2L^1 and its related complexes.

Compounds	M.P Color	Theoretical (found) (%)						Molar conductance ($\Omega^{-1}\text{mol}^{-1}\text{cm}^2$)
		C	H	N	S	Cl	M	
H_2L^1	128, Brown	47.75 (48.04)	3.39 (3.69)	8.57 (9.01)	19.62 (19.23)	10.85 (11.02)		—
[Pd(H_2L^1)Cl ₂]	>300, Brown	30.97 (30.54)	2.20 (2.51)	5.56 (5.43)	12.72 (12.61)	21.10 (21.18)	21.11 (20.95)	27.62
[Pt(H_2L^1)Cl ₂]	>300, Black	26.33 (27.15)	1.87 (2.13)	4.73 (5.26)	10.82 (11.31)	17.94 (18.34)	32.90 (31.54)	19.30
[Au(H_2L^1)Cl ₃ .H ₂ O]	>300, Black	23.43 (25.21)	2.88 (2.49)	4.20 (4.90)	9.63 (11.08)	21.28 (19.26)	29.57 (30.32)	17.58

Table 2. Significant IR, UV and NMR data of H_2L^1 and its metal complexes.

Compounds	IR bands ν (cm^{-1})					NMR chemical shift (d, ppm)	λ max, nm (assignments)	Structure
	ν N-H	ν S=O	ν C=S	ν M-O	ν M-S			
H_2L^1	3322	1380	1260	—	—	11.15 (s, 1H, N-H), 6.52 (ring, m, 11H)	244 ($\pi \rightarrow \pi^*$), 375 ($n \rightarrow \pi^*$)	
[Pd(H_2L^1)Cl ₂]	3240	1345	1240	582	421		470 ($^1A_{1g} \rightarrow ^3A_{2g}$) 380 ($^1A_{1g} \rightarrow ^1A_{2g}$) 360 ($^1A_{1g} \rightarrow ^1B_{1g}$)	Square planer
[Pt(H_2L^1)Cl ₂]	3236	1340	1232	580	428		777 ($^1A_g \rightarrow ^3T_{1g}$) 579 ($A_{1g} \rightarrow 3T_{2g}$) 530 ($^1A_{1g} \rightarrow ^1T_{1g}$)	Square planer
[Au(H_2L^1)Cl ₃ .H ₂ O]	3244	1350	1215	563	420		778 ($^1H_{1g} \rightarrow E_g$) 445 ($^1A_{1g} \rightarrow ^3B_{1g}$)	Octahedral

Pharmacological activity

The obtained metal complexes were screened for their activities as antibacterial, against Gram-positive of *Streptococcus pneumonia* (RCMB 010010) and *Bacillus subtilis* (RCMB 010067); Gram-negative species of *Pseudomonas aeruginosa* (RCMB 010043) and *Escherichia coli* (RCMB 010052) as well as anti-fungal of *Aspergillus fumigatus* (RCMB 02568) and *Candida albicans* (RCMB 05036). Antimicrobial activity was tested by the disc diffusion method [16]. The Amphotericin B, Ampicillin and Gentamicin were used as standard references for Gram-positive, Gram-negative bacteria and fungi, respectively, serving as positive controls. Nutrient agar was prepared then autoclaved at 121°C for 15 min, cooled and finally poured in Petri dishes. Water/methanol (99:1 v/v) was used as solvent. The filter paper discs were soaked in different dilutions of the ligand and its metal complexes (50 to 1000 ppm) to find out the minimum concentration required for inhibition of microbial growth. The discs were then dried and placed in Petri dishes previously spotted with the just mentioned antibacterial and antifungal species. After 24 h incubation at 37°C, the inhibition zone around each disc

was measured in mm by the help of a Zone Reader. The average value was determined in triplicate readings for each zone of inhibition in millimeter. The highest antibacterial action was for H_2L^1 complex against species. It is obvious that the incorporation of the ligand in metal complexes exhibited higher biological activity. This may be attributed to the donated coordination bonds to the central metal ions in metal chelates, thus delocalizing the π -electron over the chelate ring. Accordingly, increasing the lipophilicity of the metal ion, which favors the metal complex permeation through the lipid layers of the bacterial and fungal membranes [17,18].

Cytotoxic activity

Thiourea derivatives play an important role as anticancer agents [19], due to their good inhibitory activity against protein tyrosine kinases (PTKs) [20]. H_2L^1 ligand, also a thiourea derivative, and its metal complexes, were tested for their inhibitory activity towards tumor cell lines of breast (MCF-7) and liver cancer cells (HepG-2). An MTT colorimetric assay was used to plot a dose response curve required to kill 50% of cell population (IC₅₀). The results are

shown in Tables 3 and 4 and Figure 2. The most active against the liver carcinoma cell line (HepG2), showing an IC₅₀ value of 4.8 $\mu\text{g mL}^{-1}$ compared to 4.9 and 18.8 $\mu\text{g mL}^{-1}$ for the known anticancer drugs, 5-flourouracil and cisplatin, respectively. A lower tendency was observed towards breast cancer cells inhibition than those observed for liver carcinoma. The breast cancer cell line (MCF-7) inhibition for the metal complexes was 4a, 3c, 4b, and 4c, in descending order.

Results and Discussion

Keeping in mind the marked significance of sulfonyl and thiourea derivatives in various therapeutics, the synthesis of a ligand (H_2L^1) incorporating both groups makes it very interesting from a structural point of view. The potential sites (N and O) of the prepared ligand H_2L^1 coordinate with the metal ions of Pt (II), Pd (II) and Au (III) producing metal complexes. Characterization of the prepared metal complexes help in more understanding of the mode of chelation of the ligand towards metals. It is also a prerequisite to enable us evaluate the influence of their chemical structure on their biological activities. As a result of microwave-assisted synthesis, homogeneity of reaction mixture was attained by the rotating of reaction platform tray. It was observed that the reaction was completed in a short time, thus reducing synthesis steps. In addition, it was solvent free or reaching minimal, no purification steps required and enhanced % yield. The results were confirmed by the repeated synthesis. All the analytical, physical, and spectroscopic data of the ligand H_2L^1 and its metal complexes are given in Table 1. The complexes are soluble in DMF and DMSO. The formed metal chelates have a 1:1 (Metal: Ligand) stoichiometry.

Infrared spectra

The coordination sites involved in chelation could be interpreted from comparing the IR spectra of the metal complexes obtained with that of the free ligand, Table 2, Figures 2-5. The IR spectra of H_2L^1 show a strong band at 3322 cm^{-1} assigning for stretching vibration of ν (N-H) group. Other H_2L^1 IR spectral bands were at 1380 and 1100 cm^{-1} assigned for ν (S=O) asymmetric and symmetric vibration, 1260 cm^{-1} strong band assigned for ν (C=S) [21-23]. The IR spectral data indicate that the ligand H_2L^1 coordinates through sulfonyl and thionyl groups to PdII and PtII metal ions in a tetradentate square planer manner, while in case of AuIII it takes an octahedral shape. This behavior is supported on the basis of the following evidences: The ν (N-H) group observed band remain unchanged suggesting that the nitrogen atom of the amine group does not participate in coordination.

(1) The band at 1380 cm^{-1} in the spectra of H_2L^1 was shifted to lower frequency and was observed at 1350 cm^{-1} , 1345 cm^{-1} and 1340 cm^{-1} for Au (III), Pd (II) and Pt (II), respectively indicating that metal ions are coordinated through the oxygen atom of the sulfonyl group.

(2) The shift observed in the ν (C=S) frequency in the complexes indicating the participation of thionyl groups in the coordination. The metal-oxygen and metal sulfur bonds are most common in the coordination compounds. Studies of the stretching and the bending models of vibrations of these bonds are important in elucidating the structure of the complex and the type of the chemical bonding.

^1H NMR spectra

These facts were further facilitated by nuclear magnetic resonance (NMR) spectroscopy. The ^1H -NMR spectrum of ligand H_2L^1 (DMSO- d_6) showed a singlet signal at 11.15 and 11.10 ppm Figure 6; attributed to -NH proton and multiplet aromatic proton at (6.52-7.91) ppm.

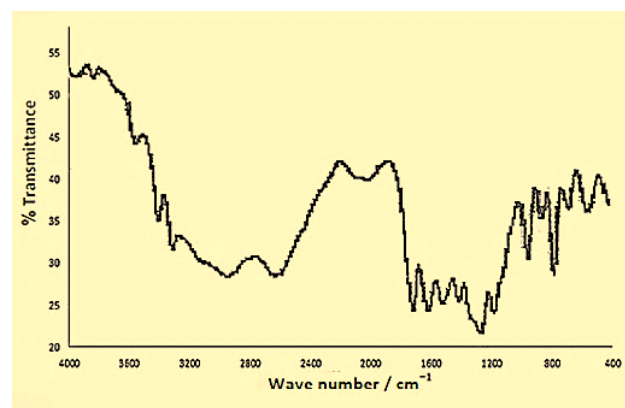


Figure 2. IR Spectrum of H_2L^1

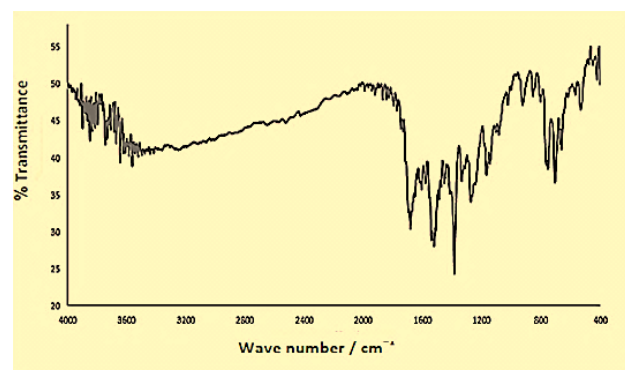


Figure 3. IR Spectrum of Pd- H_2L^1

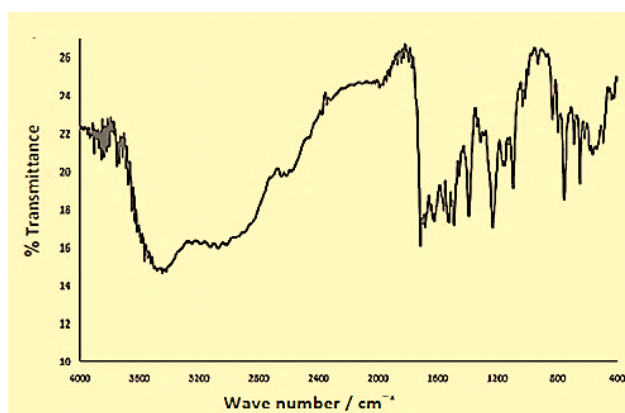


Figure 4. IR Spectrum of Pt- H_2L^1

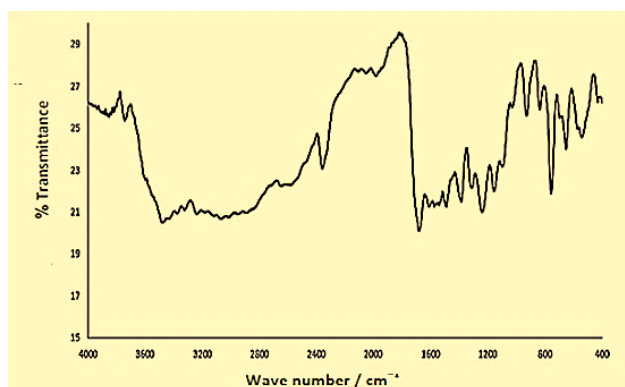
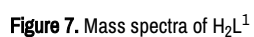


Figure 5. IR Spectrum of Au- H_2L^1



The mass spectra of H_2L^1 Figure 7; show multi peak representing successive degradation of the ligand. The spectra show the peak $m/e = 326.85$ represent the molecular ion peak ($\text{C}_{13}\text{H}_{11}\text{N}_2\text{O}_2\text{S}_2\text{Cl}$) with 9.70% abundance. The base peak 100% with $m/e = 81$.

The mass spectral studies of three of the representative compounds, Pd-H₂L¹, Pt-H₂L¹ and Au-H₂L¹ indicate their monomeric nature. The molecular ion peaks of Au-H₂L¹ appear at m/z 503 t with 10.09% abundance has confirming the formation of metal complexes in 1:1. The base peak 100% with m/e =155 and metal peak at m/e =107 with different peaks Figure 8.



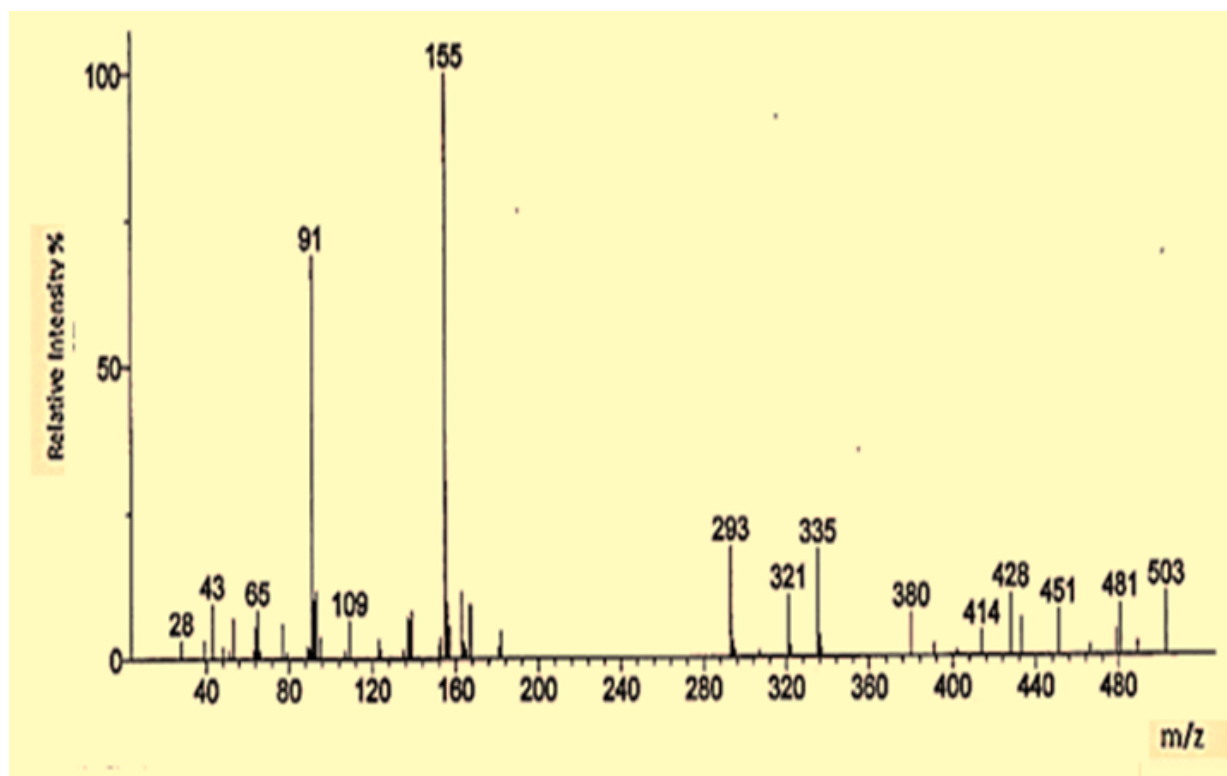
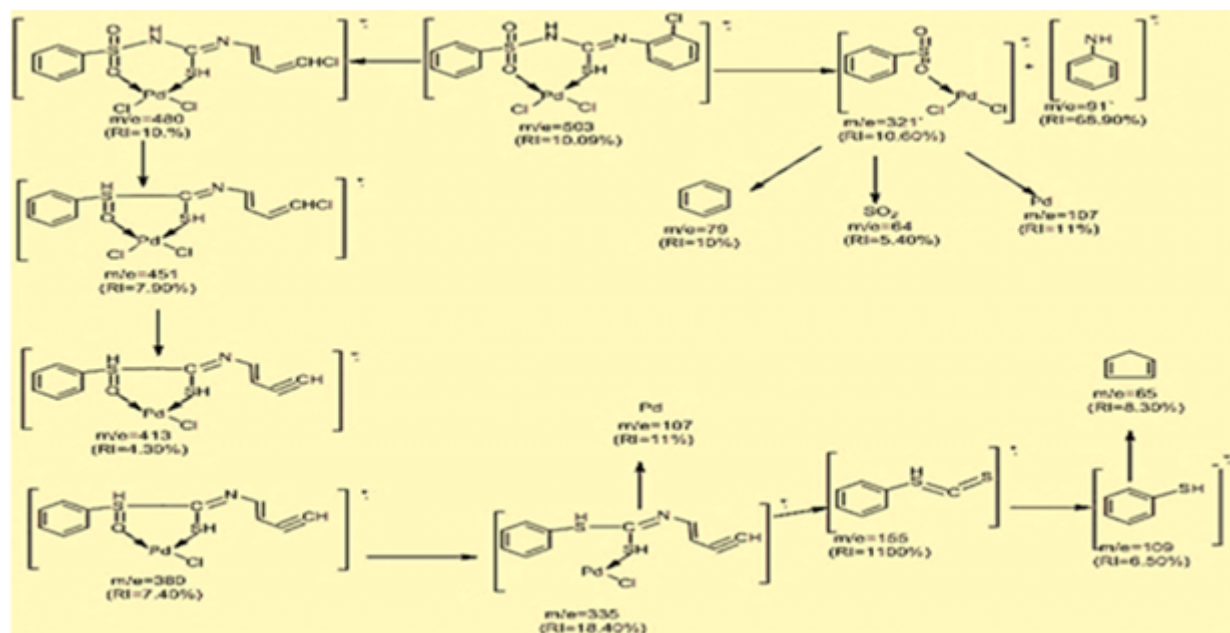


Figure 8. Mass Spectra of Pd- H_2L^1

UV reflectance

Mass fragmentation is shown in scheme 1.



Scheme 1. Mass fragmentation of Pd- H_2L^1

The electronic spectrum is a good tool to deduce the magnetism of the ligand around the metal ion. The electronic spectra of H_2L^1 Table 2, Figure 9 revealed two bands at 244 and 375 nm, assigned to the ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions of the ligand; usually $n \rightarrow \pi^*$ transitions occur at lower energy than ($\pi \rightarrow \pi^*$) transitions.

The electronic absorption spectra of Pd (II)- H_2L^1 complex Figure 10; shows three electronic spectral bands at 470-520, 380-465 and 350-430 nm. These are tentatively assigned to $^1A_{1g} \rightarrow ^3A_{2g}$, $^3B_{2g}$, $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow$

$^1B_{1g}$ transitions, respectively. Additionally, another band appears at 360 nm attributed to ($^1A_{1g} \rightarrow ^1E_g$) transition.

The diamagnetic behaviors as well as electronic spectral data confirm the square planar geometrical structure of the Pd (II) complexes. The electronic spectra of Pt (II)- H_2L^1 complex Figure 11; exhibits two broad bands at 579 and 530 nm related to $^1A_{1g} \rightarrow ^3T_{2g}$ and $^1A_{1g} \rightarrow ^1T_{1g}$ transitions, respectively.

Another broad band was observed at 777 nm attributed to $^1A_g \rightarrow ^3T_{1g}$ transition. It is a diamagnetic complex, therefore square planar geometry has been suggested also for Pt (II) complex.

Concerning Au- H_2L^1 complex, Figure 11; it shows five bands at 270-290 (assigned to the intra ligand $\pi \rightarrow \pi^*$ transition), 310-370 (assigned to the intra

ligand $n \rightarrow \pi^*$ transition), 380-420 nm (attributed to Au (III) complex charge transfer).

The last two bands at 445 and 778 nm due to $^1A_{1g} \rightarrow ^3B_{1g}$ and $^1H_{1g} \rightarrow E_g$ transitions. The diamagnetic behavior indicated the presence of Au (III) complex in octahedral geometry (Figure 12).

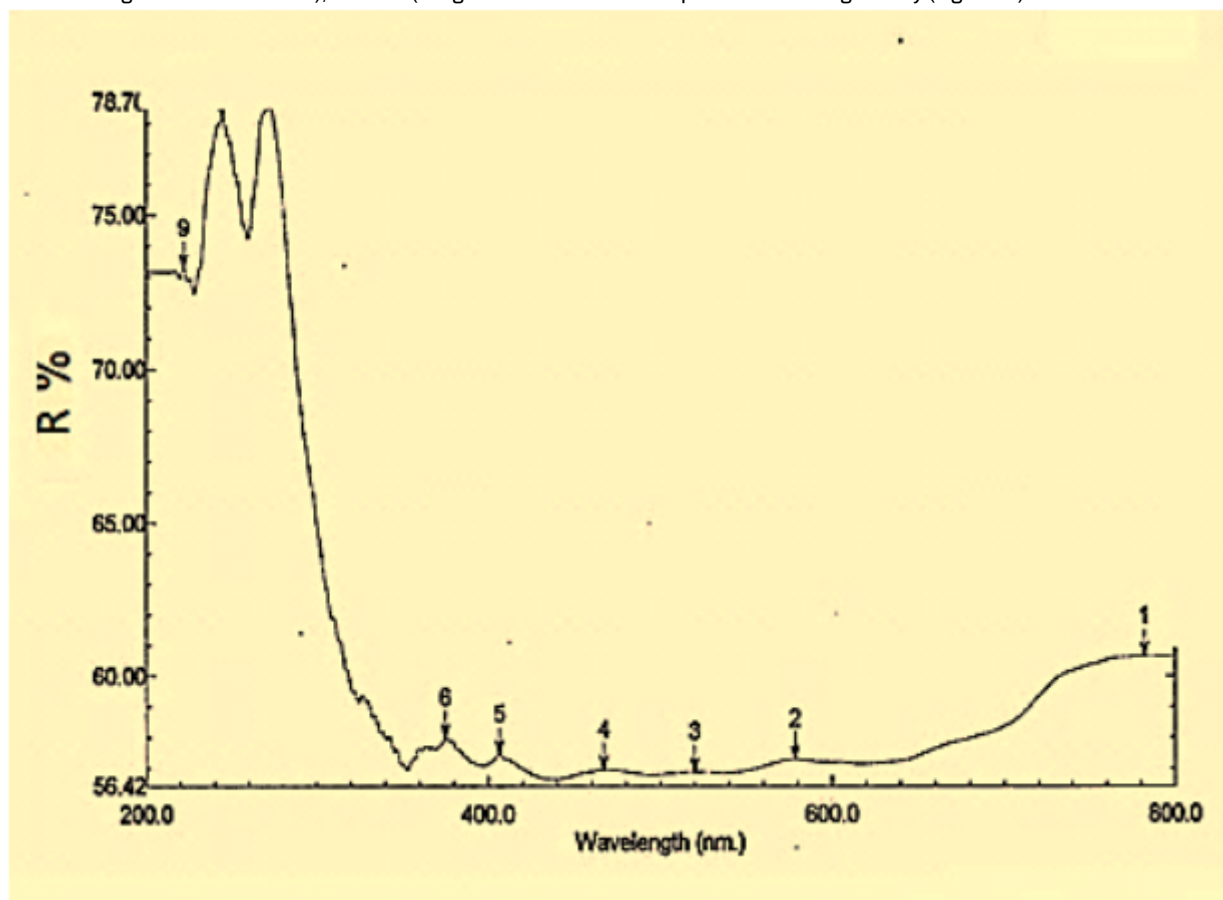


Figure 9. UV reflectance of H_2L^1

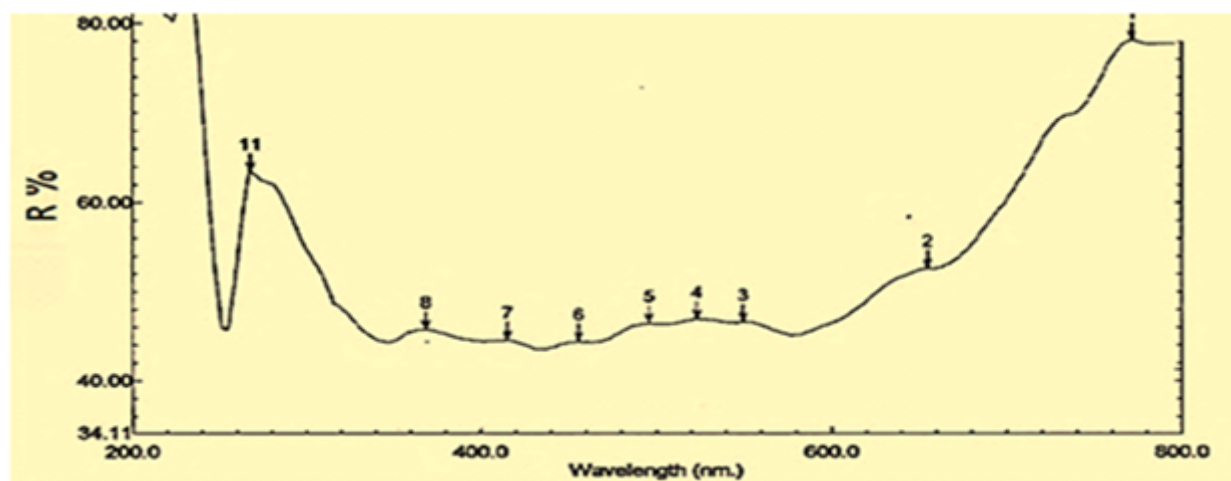
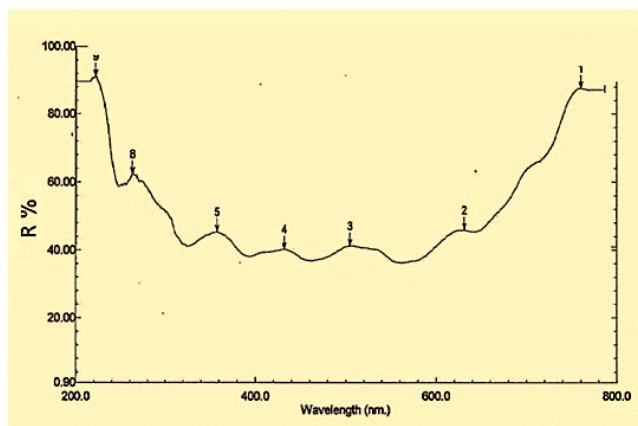
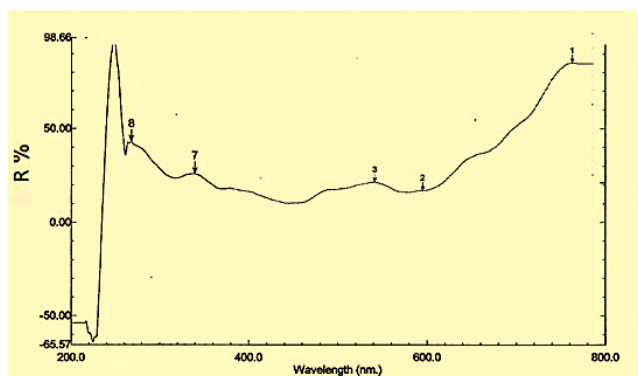


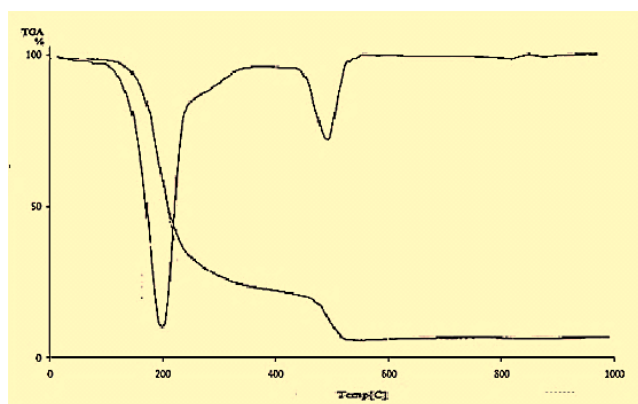
Figure 10. UV reflectance of Pd- H_2L^1 complex.

Figure 11. UV reflectance of Pt- H_2L^1 complexFigure 12. UV reflectance of Au- H_2L^1 complex

Thermal analysis of H_2L^1 and its metal complexes

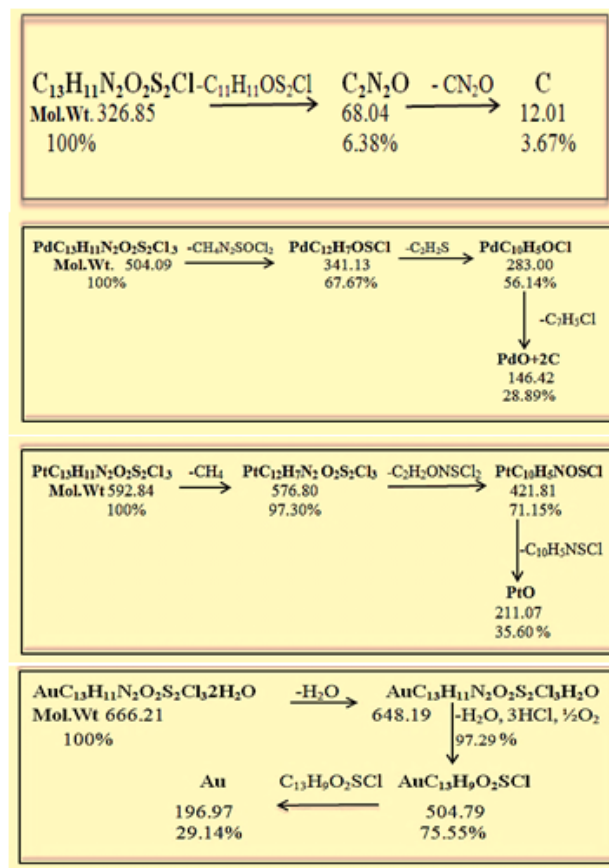
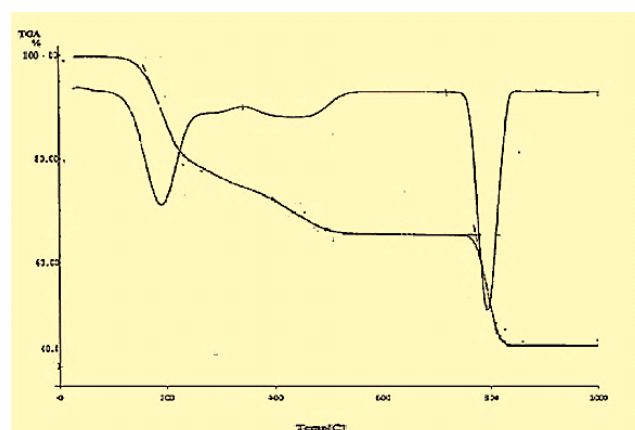
The thermal analysis helps in evaluating the thermal stability of the formed metal complexes. The obtained thermo grams show no loss in weight up to 353°C, 136°C and 133°C in case of Pd- H_2L^1 , Pt- H_2L^1 and Au- H_2L^1 complexes, respectively. Above these temperatures, decomposition of ligand molecules started, with observed mass losses in subsequent steps.

TGA curve of H_2L^1 $C_{13}H_{11}N_2O_2S_2Cl$, Figure 13, Scheme 2; refers to two steps of mass losses at a temperature range of 27-998°C leaving 3.67% as residue. The thermo grams for complexes Pd- H_2L^1 , Figure 14; Pt- H_2L^1 and Au- H_2L^1 , each revealed a three steps decomposition behavior Scheme 2.

Figure 13. TGA curve of H_2L^1

These TG steps are related to exothermic events attributed to the pyrolysis of organic byproducts. The thermo grams also exhibited completion of the decomposition at 1000°C.

The residual for complex (1) was 28.89% (obs.), corresponding to the formation of $PdO+2C$ as residue (calculated. 28.26%). The residual for complex (2) was 35.60% (obs.), corresponding to the formation of PtO (calculated. 34.77%) and 29.14% (obs.), corresponding to the formation of Au as residue (calculated. 29.30%) in case of complex.

Scheme 2. The sequence of decomposition steps for the ligand H_2L^1 and its metal complexes.Figure 14. TGA curve of Pd- H_2L^1

Applications

Anti-microbial activity

The spectrum, Figure 15 and Table 3; reveals a noticeable growth inhibition of Gram-positive, Gram-negative bacteria and fungi examined at concentrations as low as 5 μ g/mL.

Table 3. Antimicrobial result of H_2L^1 Free and its related metal complexes.

Comp	Growth inhibition against					
	Gram-positive bacteria		Gram-negative bacteria		Fungi	
	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>	<i>Salmonella.sp.</i>	<i>Escherichia coli</i>	<i>Aspergillus fumigatus</i>	<i>Candida albicans</i>
H_2L^1	17	12	19	20	16	13
Pd- H_2L^1	13	19	16	19	13	18
Pt- H_2L^1	15	18	14	15	12	19
Au- H_2L^1	11	18	14	17	15	17
Gentamycin	23	32	–	–	–	–
Ampicillin	–	–	17	19	–	–
Amphoteric.B	–	–	–	–	23	25
DMF	–	–	–	–	–	–

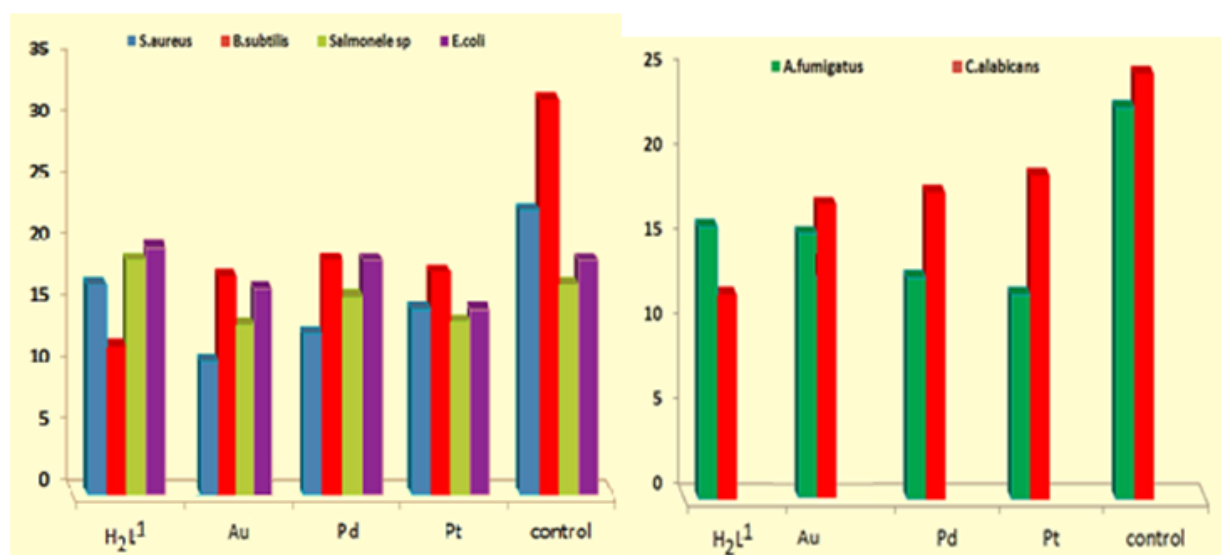


Figure 15. Activity of H_2L^1 and its metal complexes against bacteria and fungi

Anticancer activity

The free ligand H_2L^1 , H_3L^2 may have a promising potential as an anticancer agent, attributed to the ligands possible alternative modes of cytotoxic action. The cytotoxicity activities of Au- H_2L^1 was tested against (MCF-7) and (HepG-2) human tumor cell lines. The reported results in terms of IC₅₀ value was recorded in Table 4, Figures 16 and 17 for comparison, the cytotoxicity of Cisplatin, as standard antitumor drug was evaluated and produced (IC₅₀ mL) under the same conditions, Au- H_2L^1 > H_2L^1 against

breast carcinoma cells; H_2L^1 > Au- H_2L^1 against Hepatocellular carcinoma cells.

From the obtained results;

Au- H_2L^1 has more efficiency than H_2L^1 on the breast carcinoma cells.

Au- H_2L^1 has less efficiency than H_2L^1 on the Hepatocellular carcinoma cell.

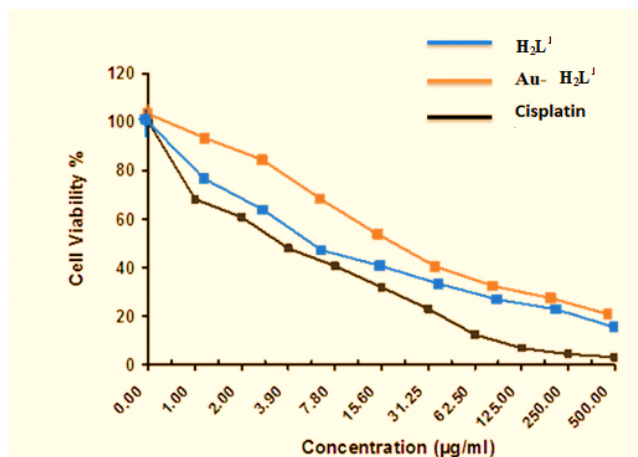


Figure 16. Cytotoxicity of Au- H_2L^1 , H_2L^1 against (HepG-2)

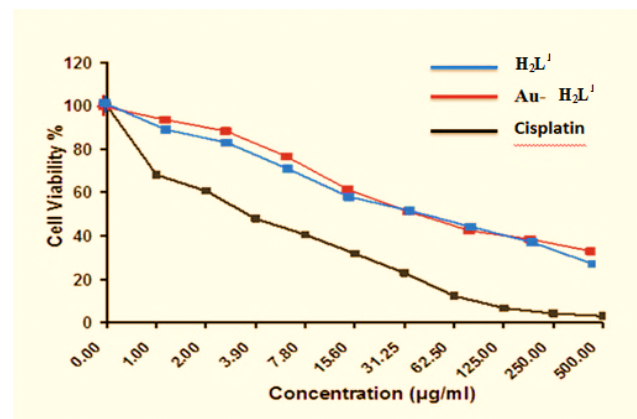


Figure 17. Cytotoxicity of Au- H_2L^1 , H_2L^1 against (MCF-7)

Table 4. Anticancer result of H_2L^1 Free and its related metal complexes

Compounds	IC ₅₀ cytotoxicity (µg/mL) (MCF-7)	IC ₅₀ cytotoxicity (µg/mL) (HepG-2)
Cisplatin	5.71	3.76
H_2L^1	37.1	12.6
Au- H_2L^1	30.1	29.5

The proposed structure of the metal complex shown in Figure 18.

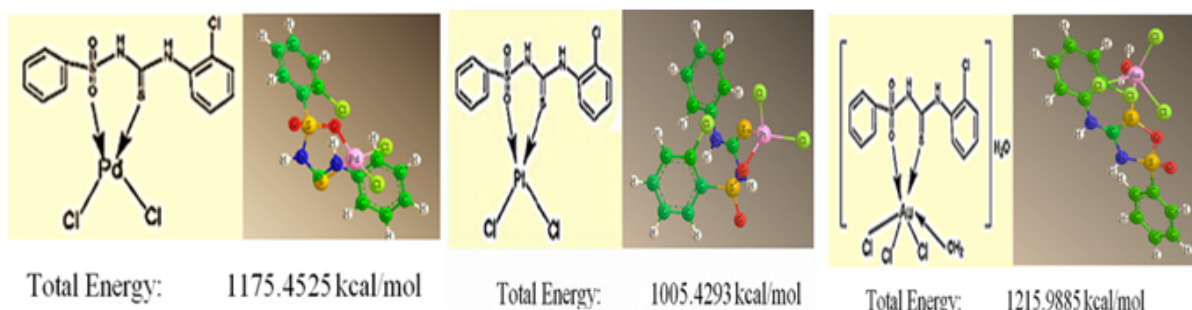


Figure 18. Proposed structure of the metal complex.

Conclusion

The prepared metal complexes have been characterized by elemental analysis, FT-IR, 1H NMR, UV-Vis, thermal analysis and magnetic susceptibility. They were tested for their antibacterial activity against Gram positive, Gram-negative bacteria as well as fungi. Also anti-cancer assay was applied against two cell lines; breast cancer cells (MCF-7) and liver cancer cells (HepG-2). The IR spectral data indicate that the ligand H_2L^1 coordinates to metal ions through sulfonyl and thionyl groups in a tetradentate square planer manner for Pd^{II} and Pt^{II} ions while in case of Au^{III} it takes an octahedral shape. Based on spectrophotometric investigations, it is suggested that $Pd(II)$, $Pt(II)$ and $Au(III)$ form 1:1 complexes. The molecular compositions of the complexes were proposed on the basis of chemical analyses and spectrophotometric evidences.

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