SYNTHESIS, CHARACTERIZATION, THEORETICAL STUDIES AND BIOACTIVITY OF Co(II), Ni(II), Cu(II), Pd(II), Pt(IV) AND Cd(II) COMPLEXES WITH BIDENTATE 3-{[(Z)-1H-PYRROL-3-YLMETHYLIDENE]AMINO}-2-THIOXOIMIDAZOLIDIN-4-ONE

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ABSTRACT

Chelation complexes of Co(II), Ni(II), Cu(II), Pd(II), Pt(IV) and Cd(II) were synthesized with new heterocyclic ligand [3-{[(Z)-1H-pyrrol-3-ylmethylidene]amino}-2-thioxoimidazolidin-4-one]. This ligand was characterized by C.H.N.S analysis, FTIR, UV-Vis, ^{1}H NMR, ^{13}C NMR and mass spectral analysis ,the synthesized complexes were identified and their geometrical were suggested in solid state by using (FT-IR) and (UV-Vis) spectroscopy, elemental analysis (C.H.N.S), flame atomic absorption technique, in addition to magnetic susceptibility and conductivity measurements.

Hyperchem-8 program has been used to predict structural geometries of ligand and their metal complexes. The electrostatic potential (E_p) of the ligand was calculated, furthermore the heat of formation (ΔH_f), binding energy ((ΔE_b), vibration spectra and bond length for the ligand and its metal complexes were calculated by PM3 methods. The antimicrobial activity of the ligand and its complexes has been extensively studied in microorganisms such as *Escherichia coli* and *Staphylococcus aureus* and fungi *Candida albicans* and *Aspergillus flavus*.

Key words: Schiff base compounds, Coordination compound of Schiff base, 2-Thioxoimidazolidin-4-one, Spectral data, Antimicrobial activity, Theoretical treatment.

INTRODUCTION

There are a number of heterocycles, which have turned out to be potential chemotherapeutic and pharmacotherapeutic agents. Majority of the heterocyclic compounds,

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which are in the therapeutic field, contains nitrogen as well as other hetero atoms like oxygen and sulphur[1]. At the same time, a large number of heterocyclic compounds contain only nitrogen as the hetero atom. One such heterocyclic moiety is imidazolidin, which is a five membered saturated heterocyclic ring with two nitrogen atoms and contain two groups, thion (C=S) and carbonyl (C=O) at position, 2 and 4, respectively[2]. 2-thioxoimidazolidin-4-one derivatives display a wide range of biological properties such as anticarcinogenic[3], antimicrobial[4], anticonvulsant agents[5], human immunodeficiency virus (HIV)[6] and the leukemia subpanel[7]. The complexes of 2-thioxoimidazolidine-4-one few and well thought enough of such study, Marinova and co-worker[3] synthesized new platinum(II) complexes of (90-fluorene)-spiro-5-(2-thioxoimidazolidin-4-one) and examined cytotoxic activity of ligand and their Pt(II) complexes on the retinoblastoma cell line and cytotoxicity.

EXPERIMENTAL

Instrumentation

Melting points were recorded on a GallenkampMF B600 melting point apparatus. Elemental analyses (C.H.N.S) were obtained using EA-034.mth. for ligand and their metal complexes. Metal contents of complexes were estimated spectrophotometrically using Flame atomic absorption Shimadzu-670 AA Spectrophotometer. Infrared spectra were recorded using FT-IR-8300 Shimadzu in the range of (4000-350) cm^{-1}, samples were measured as (CsI) disc. Magnetic susceptibilities of samples in the solid state were measured by using Magnetic Susceptibility Balance of Sherwood Scietifi. The molar conductivity was measured by using Electrolytic Conductivity Measuring set Model MC-1-Mark V by using platinum electrode (EDC 304) with cell constant (1 cm^{-1}), concentration (10^{-3} M) in dimethylformmide as a solvent at room temperature. Electronic spectra were obtained using UV-1650PC-Shimadzu Spectrophotometer at room temperature, the measurement were recorded using a concentration of (10^{-3} M) of the ligand and its metal complexes.

Materials and methods

All chemical were of highest purity and were used as received.

Synthesis of ligand (L)

Pyrolle carboxyaldehyde (0.0315 mole, 3.0 g) was dissolved in 30 mL absolute ethanole, and then thiosemicarbazide (0.033 mole, 3.0 g) was added. The reaction mixture was refluxed for 4 hrs, then the resulting mixture was poured into crushed ice and stirred for 15 min. from the product (0.01 mole) and chloroethylacetate (0.01 mole, 1.225 g)

were dissolved in 30 mL ethanol. The mixture was stirred for a few minutes, and then (0.02 mole, 1.64 g) sodium acetate was added to the mixture. The mixture was refluxed for 6 hr. after cooling the precipitate was filtered off and recrystallization from ethanol **(Scheme 1)**.
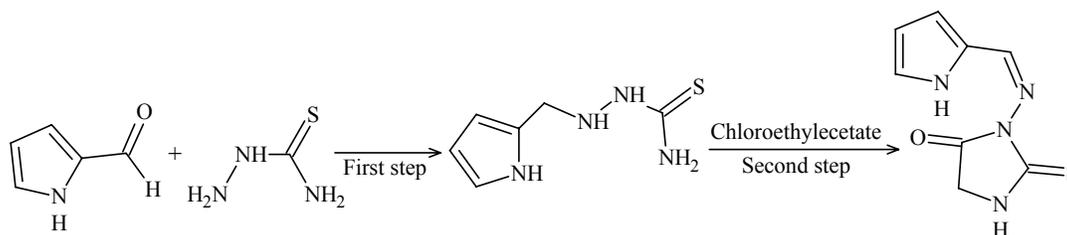
Scheme 1: Synthesis of Ligand (L)

Preparation of metal complexes (S$_1$-S$_6$)

An ethanolic solution of each of the following metal ions salts (0.05 mmol) [CoCl$_2$.6H$_2$O, NiCl$_2$.6H$_2$O, CuCl$_2$.2H$_2$O, H$_2$PtCl$_4$.6H$_2$O, PdCl$_2$.6H$_2$O, and CdCl$_2$.4H$_2$O] was added to an ethanolic solution (0.208 g, 1 mmol) of (L). The reaction mixture was heated under reflux for 2-3 hours, during this time a precipitate was formed. The product was filtered off, washed with hot ethanol, followed by cold water and then dried under vacuum. All complexes were identified by elemental analysis (C.H.N.S), flame atomic absorption, FT-IR and UV-Vis spectrophotometers, magnetic and conductivity measurements.

Programs used in theoretical calculation

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its' quality, flexibility and ease of use[9,10]. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation. This information is useful in determining reactivity and correlating calculation results with experimental data.

Computational methods

Semi-empirical quantum mechanical, Molecular mechanics and Mopac 2000.

Types of calculations

The types of prediction possible of molecules are[11,12]:

Geometry optimization calculations employ energy minimization algorithms to locate stable structures, Bond distances, molecular dynamics, which provide the thermodynamic calculations and dynamic behavior of molecules, Plot the electrostatic potential field (HOMO and LUMO), and vibrational spectrum (I.R and Raman spectra).

Study of biological activities for ligand (L) and their metal complexes (S_1 –S_6)

The biological activities of the ligand (L) and their respective complexes (S_1-S_6) were studied against selected types of bacteria, which include (*Escherichia coli*) and (*staphylococcus aureus*) cultivated in Nutrient agar medium, DMSO was used as a solvent and as a control, the concentration of the compounds in this solvent were (10^{-3}M). The new metal complexes (S_1-S_6) were tested for their *in vitro* growth inhibitory activity against further pathogenic fungi, i.e., [*Candida albicans* and *Aspergillus flavus*] on potato dextrose agar medium and incubated at 30°C for 72 hours. DMSO was used as a solvent and as a control for both techniques. The concentrations of the compounds in this solvent were (10^{-3}M). The inhibition of fungal growth expressed in percentage terms, were determined on the growth in test plates compared to the respective control plates.

RESULTS AND DISCUSSION

Part (I) study ligand and their complexes in solid state

Elemental analyses

The physical and analytical data of the ligand (L) and metal complexes (S_1-S_6) are given in Table 1.

Table 1: Some physical properties and elemental analysis of ligand and its metal complexes (S_1-S_6)

Comp. symbol	General formula	M.wt. g.mol^{-1}	Color	M.P. (°C)	Elemental analysis (%) Found (calc.)				
					C	H	N	S	M
(L_1)	$C_8H_8N_3O_4S$	208	Pale pink	240-242	45.10 (46.14)	3.79 (3.87)	27.71 (26.90)	15.67 (15.40)	-
S_1	[Co(L_1)$_2$(H$_2$O)$_2$]Cl$_2$	581.93	Brown	250-252	33.68 (32.99)	3.79 (3.44)	19.99 (19.25)	11.49 (10.99)	10.55 (10.13)
S_2	[Ni(L_1)$_2$Cl$_2$]	545.69	Orange	273 dec	35.67 (35.25)	3.11 (2.93)	21.03 (20.52)	12.08 (11.93)	10.94 (10.76)

| Comp. symbol	General formula	M.wt. g.mol^{-1}	Color	M.P. (°C)	Elemental analysis (%) Found (calc.)				
					C	H	N	S	M
S$_3$	[Cu(L$_1$)$_2$]Cl$_2$·H$_2$O	568.546	Dark brownish	360 dec	33.89 (33.77)	3.36 (3.17)	20.11 (19.69)	11.76 (11.26)	12.03 (11.18)
S$_4$	[Pt(L$_1$)$_2$Cl$_2$]Cl$_2$	753.078	Redish-brown	170-172	26.03 (25.49)	2.33 (2.12)	15.58 (14.87)	9.11 (8.49)	25.83 (25.90)
S$_5$	[Pd(L$_1$)$_2$]Cl$_2$	593.42	Orange	342dec	33.01 (32.35)	3.33 (2.69)	19.36 (18.87)	11.05 (10.78)	18.20 (17.93)
S$_6$	[Cd(L$_1$)$_2$]Cl$_2$	599.41	white	232-234	32.66 (32.03)	2.48 (2.69)	19.01 (18.69)	10.73 (10.68)	18.58 (18.75)

The results obtained from elemental analysis are in satisfactory agreement with the calculated value. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The new (S$_1$-S$_6$) complexes colored crystalline solid were soluble in (CH$_2$Cl$_2$, CHCl$_3$, DMF and DMSO). They are thermally stable and unaffected by atmospheric oxygen and moisture.

Mass spectrum of Ligand (L)

The mass spectrum of ligand (L) (Fig. 1), showed the mother ion peak at (*m/z* = 208), as a base peak, which is corresponds to (M$^+$). The others fragments and their relative abundances and fragmentation pathways[13] are shown in **Scheme 2**.
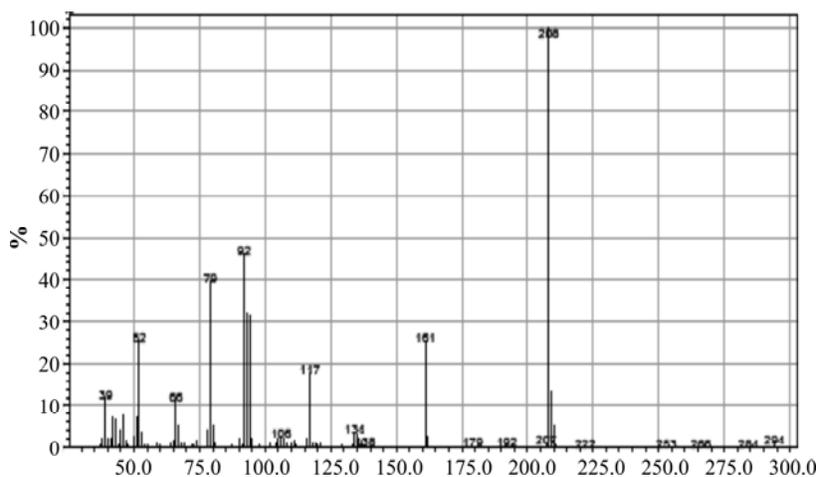
Fig. 1: Mass spectrum of Ligand (L)
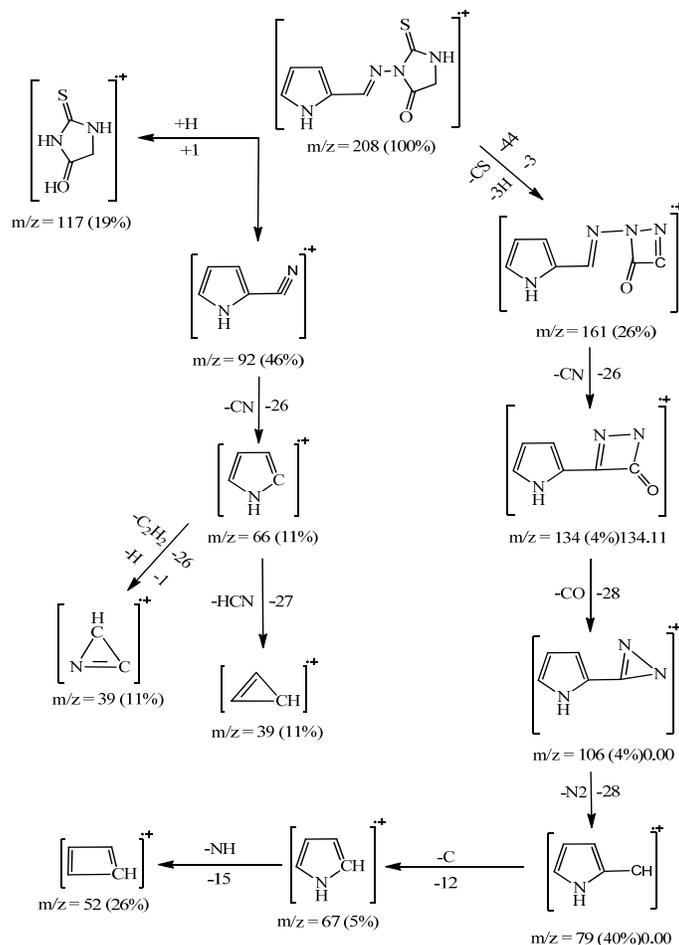
Scheme 2: Proposed fragmentation pathways of ligand (L)

^{1}H-NMR Spectrum of ligand (L)

^{1}H-NMR spectrum of ligand, Fig. 2, in DMSO-d_6 showed signals at (11.97 ppm, 1H, 11.13 ppm, 1H, 8.65 ppm, 1H, 6.97 ppm, 3H, and 4.00 ppm, 2H) assigned to NH of imidazolidine ring, (NH) group proton of pyrolle ring, proton of Schiff bass, protons of pyrolle ring, and protons of CH$_2$ group of imidazolidine ring, respectively[14].

^{13}C-NMR spectrum of ligand

^{13}C-NMR spectrum of ligand, Fig. 3, in DMSO-d_6 exhibited chemical shifts, at (174.22, 161.55, 147.99 and 32.96 ppm) assigned to carbonyl carbon atom, carbon of (C=S) group of imidazolidine ring, carbon atom of (C=N) group of azomethane ring and carbon

atom of (CH$_2$) group respectivlly[14], chemical shifts at (128.03, 123.03, 114.11, 109.51) attributed to carbon atoms of pyrolle ring.
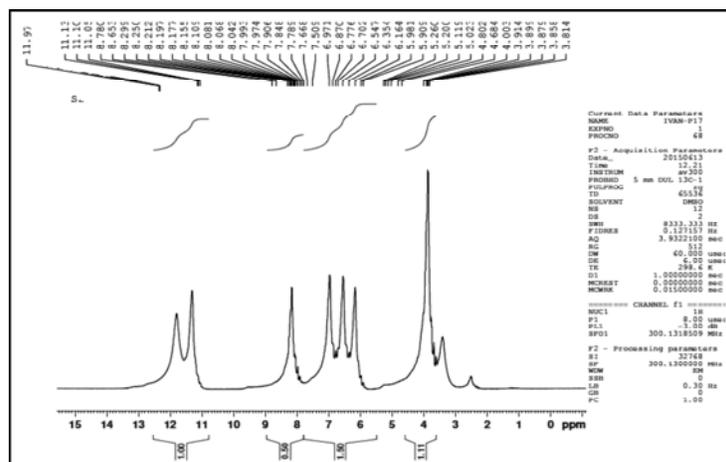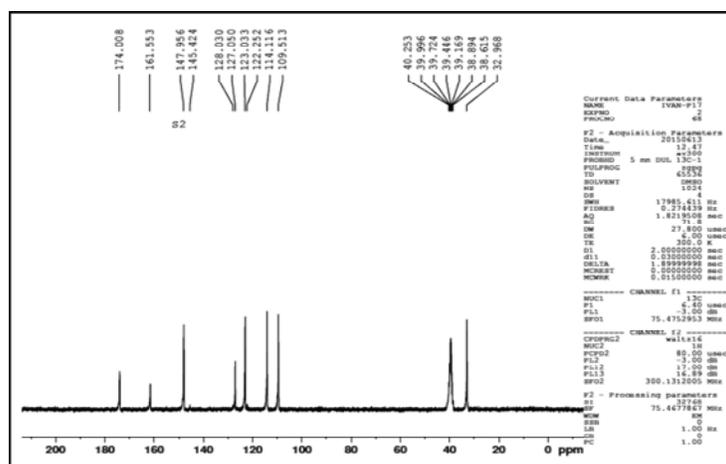

Fig. 2: ^{1}H-NMR spectrum of (L) in DMSO-d$_6$

Fig. 3: ^{13}C-NMR spectrum of (L) in DMSO-d$_6$

FTIR Spectra of ligand (L) and their metal complexes (S$_1$-S$_6$)

FTIR spectra of the ligand and its complexes and important vibration modes are listed in Table 2.

FTIR spectrum of the ligand showed bands at (3286 cm^{-1}) and (3271 cm^{-1}) in FTIR spectrum due to υ(N-H) vibration of pyrrole and thioxoimidazolidine ring, respectively, also

observed[14,15] at complexes spectra, this mean that this group does not participates in coordinatio, spectrum of the ligand showed band at (1701 cm^{-1}) attributed to υ(C=O) vibration. This band not change in all complexes of ligand, at same time this group variation in its shape and intensity. Various changes have occurred at frequencies of υ(C=N) vibrations of Schiff base and thione group, were the first observed at (1627 cm^{-1}) in the spectrum of free ligand shifted by (13-27) cm^{-1} to a lower frequencies in the spectra of complexes as shown in Table 2, The υ(C=S) vibration, which observed at (1096 cm^{-1}) in free ligand shifted by (21-43) cm^{-1} to a lower frequencies, These two different behaviors indicated the involvement of (C=N) group of Schiff and thion group in the coordination with metal ions. The frequencies of υ(M–N) and υ(M–S) in the spectra of complexes were observed at (535-528) cm^{-1} and (460-455) cm^{-1}, respectively[16].

Table 2: FTIR spectral data (cm^{-1}) of ligand and its metal complexes

Comp.	L	S$_1$	S$_2$	S$_3$	S$_4$	S$_5$	S$_6$
υ(N-H) Pyrrol	3286	3294	3381	3290	3282	3288	3289
υ(N-H) Imidazolidine	3271 (m)	3280	3333	3250	3240	3240	3248
υ(C=O)	1701 (s)	1699 (s)	1701 (s)	1701 (s)	1701 (s)	1701 (s)	1699 (s)
υ(C=N) Schiff	1627 (s)	1608	1612	1608	1608	1600 (m)	1606
υ(C=S)	1093 (m)	107 2 (s)	1053 (w)	1066 (m)	1066 (s)	1062 (m)	1070
υ(M–N)	--------	530 (w)	528 (w)	532 (w)	530 (w)	535 (w)	530 (w)
υ(M–S)	-------	460 (w)	455 (w)	458 (w)	455 (w)	460 (w)	458 (w)

Where : S = strong, W = weak, M = medium

Electronic absorption spectra, magnetic susceptibility, and conductivity measurements

The (U.V-Vis) spectrum of ligand, in absolute ethanol exhibited three absorption bands at (243 nm, 41152 cm^{-1}), (275 nm, 36363 cm^{-1}) were assigned to ($\pi \rightarrow \pi^*$) transitions, and band at (310 nm, 39063 cm^{-1}) assigned to (n $\rightarrow \pi^*$) transitions[14,17]. Complexation of (L) with metal ions appearance a new bands in the visible and UV. These bands were attributed to M-L charge transfer and to ligand field transitions[17]. Table 3 describes bands of maximum absorption of (S$_1$-S$_6$) complexes in chloroform with their assignments.

The electronic spectrum of the (S_1) complex showed two transitions at (660 nm, 15151 cm^{-1}) and (555 nm, 18018 cm^{-1}), which might be assigned to the transition $^4T_1g \rightarrow$ $^4A_2g_{(F)}$ (v_2) and $^4T_1g \rightarrow {}^4T_1g_{(P)}$ (v_3), respectively[18-20], these indicate an octahedral geometry. On the basis of theses assignment it was possible to calculate (v_1) for d^7 of (Tanaba-Sugano) diagram, the calculated value of (v_1) to be (7212) cm^{-1} due to the transition $^4T_1g \rightarrow {}^4T_2g_{(F)}$. The magnetic susceptibility and molar conductivity measurement indicated that the complex to be a paramagnetic (4.18 B.M) and conducting.

The electronic spectrum of (S_2) complex, shows two bands, (690 nm, 14492.75) and (445 nm, 22471.9 cm^{-1}) assigned to $^3A_2g \rightarrow {}^3T_1g_{(F)}$ (v_2) and $^3A_2g \rightarrow {}^3T_1g_{(P)}$ (v_3) transitions, respectively[19,20]. These bands indicate an octahedral geometry around Ni(II) ion, the calculated value of (v_1) to be (11569) cm^{-1}, may be attributed to the transition $^3A_2g \rightarrow {}^3T_2g_{(F)}$[20,22]; The magnetic value (3.29 B.M) for Ni(II) is observed and it is within the range of (2.8-3.5 B.M)[20,21]. This agree with octahedral geometry around Ni(II) ion. The conductance measurements indicate the non-ionic behavior of this complex.

The electronic spectrum of (S_3) complex shows one broad band at (692 nm, 14450.8 cm^{-1}), which corresponds to $^2B_1g \rightarrow {}^2A_1g$ transition, and a shoulder band at (435 nm, 22988.5 cm^{-1}), which assigned to $^2B_1g \rightarrow {}^2B_2g + {}^2Eg$ transition[18,20,21]. The position of these bands is in a good agreement with square planner configuration. The value of magnetic moment at room temperature was found to be (1.83 B.M), which agree well with square planer geometry around Cu (II) complex[20,22]. Conductivity measurement in DMF showed that the complex has electrolytic nature.

The electronic spectrum of (S_4) complex, shows bands, (525 nm, 19047.61 cm^{-1}), (440 nm, 22727.2 cm^{-1}) and (338 nm, 29585.7 cm^{-1}) assigned to $^1A_1g \rightarrow {}^3T_1g$, $^1A_1g \rightarrow {}^3T_2g$ and (L $\rightarrow$ M$_{CT}$), respectively[19,21,23]. The complexes may have an octahedral coordination of the central metal ion by the surrounding ligands. The magnetic value (1.18 B.M) for Pt(IV) is observed, this agree with octahedral geometry around Pt(IV) ion[22-24]. The conductance measurements indicate the ionic behavior of this complex.

The electronic spectrum of (S_5) complex, shows two bands, (488 nm, 20491.8 cm^{-1}) and (408 nm, 24509.8 cm^{-1}) assigned to $^1A_1g \rightarrow {}^1B_1g$ and $^1A_1g \rightarrow {}^1Eg$ transitions, respectively[19,23-25]. The complex may have a square-planar coordination of the central metal ion by the surrounding ligands. The magnetic moment data of Pd(II) complexes indicate that this complex is diamagnetic. This agree with square-planar geometry around Pd(II) ion[19,24]. The conductance measurements indicate the ionic behavior of this complex.

According to the electronic spectrum of (S_6) complex, no **d-d** transition is located as

it belongs to d^{10}. The prepared complexes are off white in color with the diamagnetic being expected,The U.V-Vis spectrum of (S_6), in $CHCl_3$, displayed three bands at (257 nm, 38910 cm^{-1}), (293 nm, 34129 cm^{-1}) and (335 nm, 29850 cm^{-1}), respectively, assigned to ($\pi \rightarrow \pi^*$), ($n \rightarrow \pi^*$) and ($L \rightarrow M_{CT}$) transitions[18,19,25]. The conductivity measurements indicate ionic conducting behavior of the complex.

Table 3: Electronic spectra, magnetic moment (B.M) and conductance in (DMF) for (S_1-S_6) complexes

No.	Maximum absorption υ_{max} (cm^{-1})	Band assignment	B`	β	10Dq	Molar Cond. S.cm^2.mol^{-1}	μeff. B.M	Suggested geometry
(S_1)	15151	$^4T_1g \rightarrow {}^4A_2g$ (F)	601	0.62	7183	170.33	4.18	O.h
	18018	$^4T_1g \rightarrow {}^4T_1g$ (P)						
	7212	$^4T_1g \rightarrow {}^4T_2g$ (F)) (calc.)						
(S_2)	14492.75	$^3A_2g \rightarrow {}^3T_1g$(F)	503	0.45	11066	18.63	3.29	O.h
	22471.9	$^3A_2g \rightarrow {}^3T_1g$(P)						
	11569	$^3A_2g \rightarrow {}^3T_2g$(F)						
(S_3)	14450.8	$^2B_1g \rightarrow {}^2A_1g$	----	-----	-----	169.21	1.83	S.p
	22988.5	$^2B_1g \rightarrow {}^2B_2g + {}^2Eg$						
(S_4)	19047.6	$^1A_1g \rightarrow {}^3T_1g$	-----	------	------	175.00	1.18	O.h
	22727	$^1A_1g \rightarrow {}^3T_2g$						
	29585.7	LMCT						
(S_5)	20491.8	$^1A_1g \rightarrow {}^1B_1g$	-	-	-	173.03	0.0	S.p
	24509.8	$^1A_1g \rightarrow {}^1Eg$						
(S_6)	38910	$\pi \rightarrow \pi^*$	----	----	---	168.9	0.0	T.h
	34129	$n \rightarrow \pi^*$						
	29850	MLCT						

Suggested chemistry structure of metal complexes (S_1-S_6)

According to the results obtained from elemental and spectral analysis as well as magnetic moment and conductivity measurements, the structure of the above mentioned compounds can be illustrated as follows, Fig. 4.
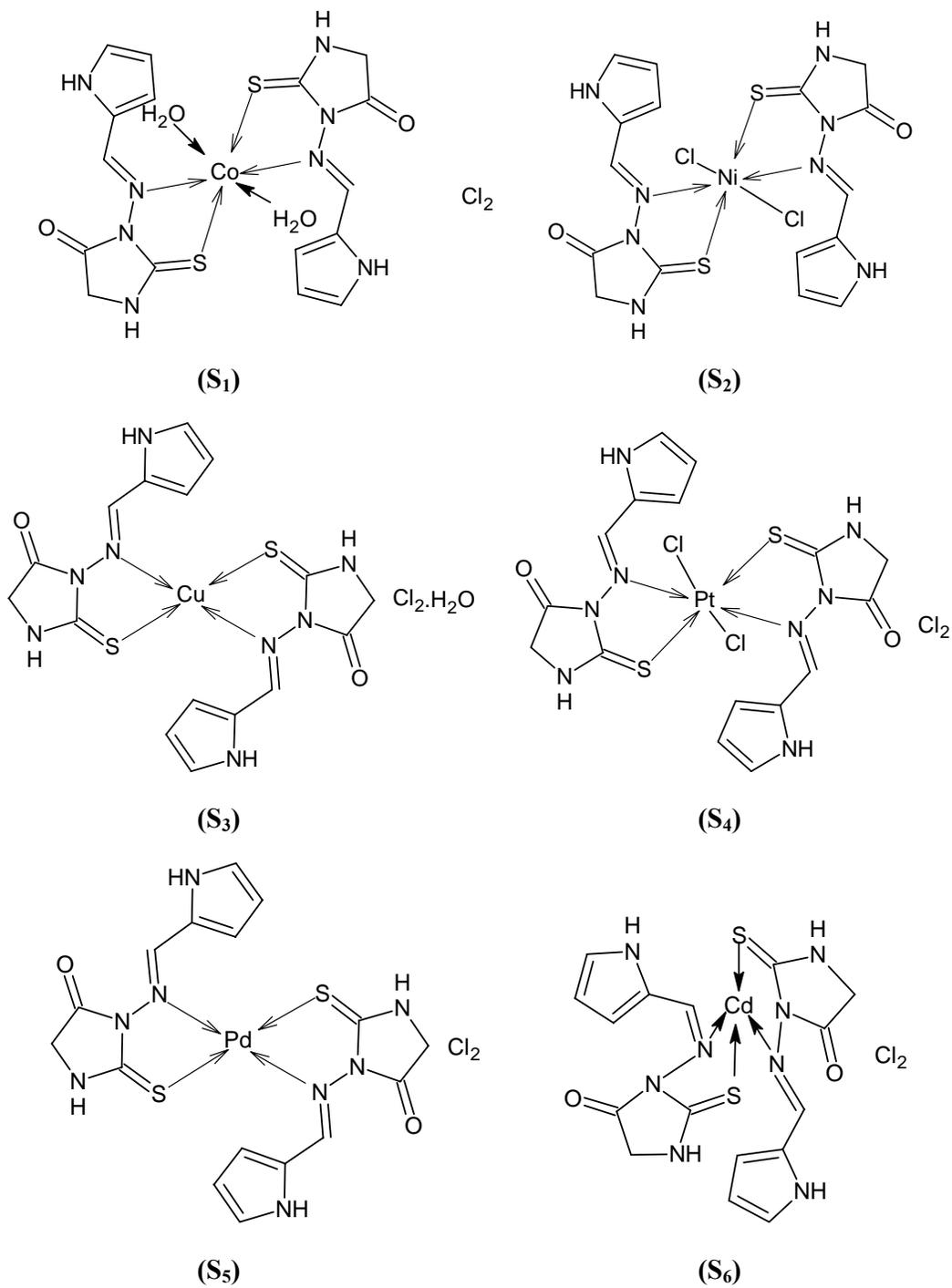
Fig. 4: Suggested chemistry structure of metal complexes (S₁-S₆)

Biological studies

The free ligand (L) and its complexes (S$_1$-S$_6$) were screened *in vitro* for their ability to inhibit the growth of representative [(*E.coli*) as gram negative] and [(*Staph. aureus*) as gram positive] are shown in Table 4. Also the study was done against (*Candida albicans* and *Aspergillus flavus*) fungus, in DMSO as a solvent, Table 4. As a result from the above mentioned studies, the following points were concluded:

1. (L) was active against *E.coli.*

2. All complexes (S$_1$-S$_6$) showed highly active against two types of bacteria compared with the ligand (L).

3. Results of the antifungal activity of the new compounds, Table 4 showed that the metal ion chelates (S$_1$-S$_6$) were more toxic compared with their parent ligand (L) toward the same micro-organism and under the identical experimental conditions. The increase in the antifungal activity of metal chelates may be due to the effect of the metal ion on the normal cell process. These activities may be explained by Tweedy's Chelation theory[26]. According to which chelation reduces the polarity of the metal atom mainly, because of the partial sharing of its positive charge with the donor groups of the ligand, which favours permeation of the complexes through the lipid layer of cell membrane[26-29].

Table 4: Antibacterial and antifungal activities for ligand (L) and their metal complexes (S$_1$-S$_6$) (10^{-3} µgm.mL^{-1})

Comp. No.	*E. coli*	*Staph. aureus*	*Cand.albic*	*Asper.flav*
Control DMSO	-	-	-	-
(L)	6	-	38	33
(S$_1$)	8	6	25	22
(S$_2$)	8	10	29	30
(S$_3$)	10	8	22	30
(S$_4$)	10	12	20	18
(S$_5$)	12	16	22	28
(S$_6$)	16	12	18	16

Part (II) study complexes in gas stat (Theoretical studies)

Electrostatic potentials

Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack)[11,12,24]. The (E.P) of the free ligand (L) was calculated and plotted as 2D contour to investigate the reactive sites of the molecules, Fig. 5. Also one can interpret the stereochemistry and rates of many reactions involving "soft" electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of transition metal ions prefer to react with the HOMO of two-donor atoms of sulfer of thion group and nitrogen of the azomithane group for free ligand (L).
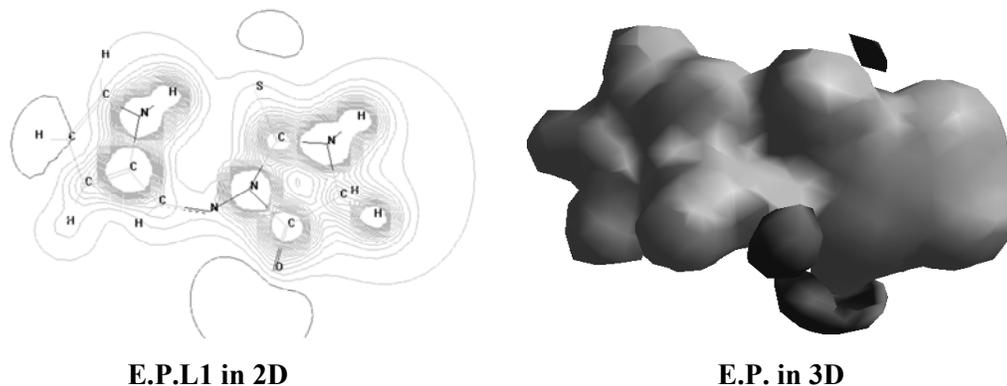

E.P.L1 in 2D   **E.P. in 3D**

Fig. 5: Electrostatic potential as 2D&3D counters for ligand L

Optimized energies

The program hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f^o), binding energy (ΔE_b) and total energy (ΔE_T) for free ligand (L) and their metal complexes(S_1-S_6) were calculated, Table 5.

(c) Optimized vibrational spectra for ligand (L)

The vibrational spectra of the free ligand (L) and their metal complexes (S_1-S_6) have been calculated, Table 6. The theoretically calculated wave numbers for this ligand showed

that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations[10,11,30]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligand (L) and metal complexes (S1-S6), which are included in Table 6 and their respective experimental vibrational modes are shown in the same table. The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, Tables 6.

Table 5: Conformation energetic (in KJ.mol^{-1}) for the L and their metal complexes

Compound	PM3			AMBER
	ΔH^{o}_{f}	ΔE_{b}	ΔE_{T}	ΔE_{T}
L	608.541	-9264.17	-211469.61	----------
S$_1$	115.25	-21427.26	-561617.41	----------
S$_2$	-394.59	-20812.09	-585463.34	----------
S$_3$	1504.50	17578.219	-536718.39	----------
S$_4$	-----	-----	------	1144.56
S$_5$	1023.80	-19897.79	-523420.81	----------
S$_6$	1893.41	-17963.67	-424538.60	----------

Table 6: Comparison between the experimental and theoretical vibational frequencies (cm^{-1}) for free ligand (L) metal complexes

Compd.	υN-H	υC=N	υC=O	υC=S	υM-N	υM-O	υM-S
L	3271*	1627*	1701*	1093*	-	-	-
	3295**	1766**	1819**	1043**			
	0.728***	7.9***	6.5***	4.8***			
	3286*						
	3404**						
	3.46***						
S$_1$	3269*	1614*	1705*	1078*	530*	522*	460*
	3247**	1625**	1885**	1082**	559**	547**	475**
	1.45***	1.03***	9.5***	0.36***	5.18***	4.57***	3.15***

Cont…

| Compd.	υN-H	υC=N	υC=O	υC=S	υM-N	υM-O	υM-S
S$_2$	3333*	1614*	1718*	1078*	528*	-	455*
	3380**	1620**	2000**	1034**	510**		445**
	1.39***	0.37***	15.05***	1.83***	3.52***		2.24***
S$_3$	3250*	1602*	1701*	1066*	532*	-	458*
	3171**	1527**	1692**	1059**	565**		441**
	2.49***	5.30***	-0.53***	0.66***	5.84***		3.88***
	3290*						
	3280**						
	0.30***						
S$_4$	3240*	1608*	1701*	1066*,1080*	530*	-	455*
	3172**	1556**	1693**	1060**,1077**	565**		466**
	-2.14***	3.34***	0.47***	0.6***,0.3***	6.19***		2.36***
	3282*						
	3280**						
	-0.06***						
S$_5$	3207*	1606*	1701*	1062*	535*	-	460*
	3238**	1750**	1855**	1041**	582**		457**
	0.061***	8.57***	8.30***	1.82***	8.07***		-0.65***
	3288*						
	3376**						
	2.60***						
S$_6$	3176*	1606*	1705*	1070*	530*	-	458*
	3286**	1645**	1855**	1046**	542**		452**
	3.34***	2.37***	8.09***	-2.29***	2.12***		-1.32***

Where: *Experimental frequencies, **Theoretical frequencies, ***Error %

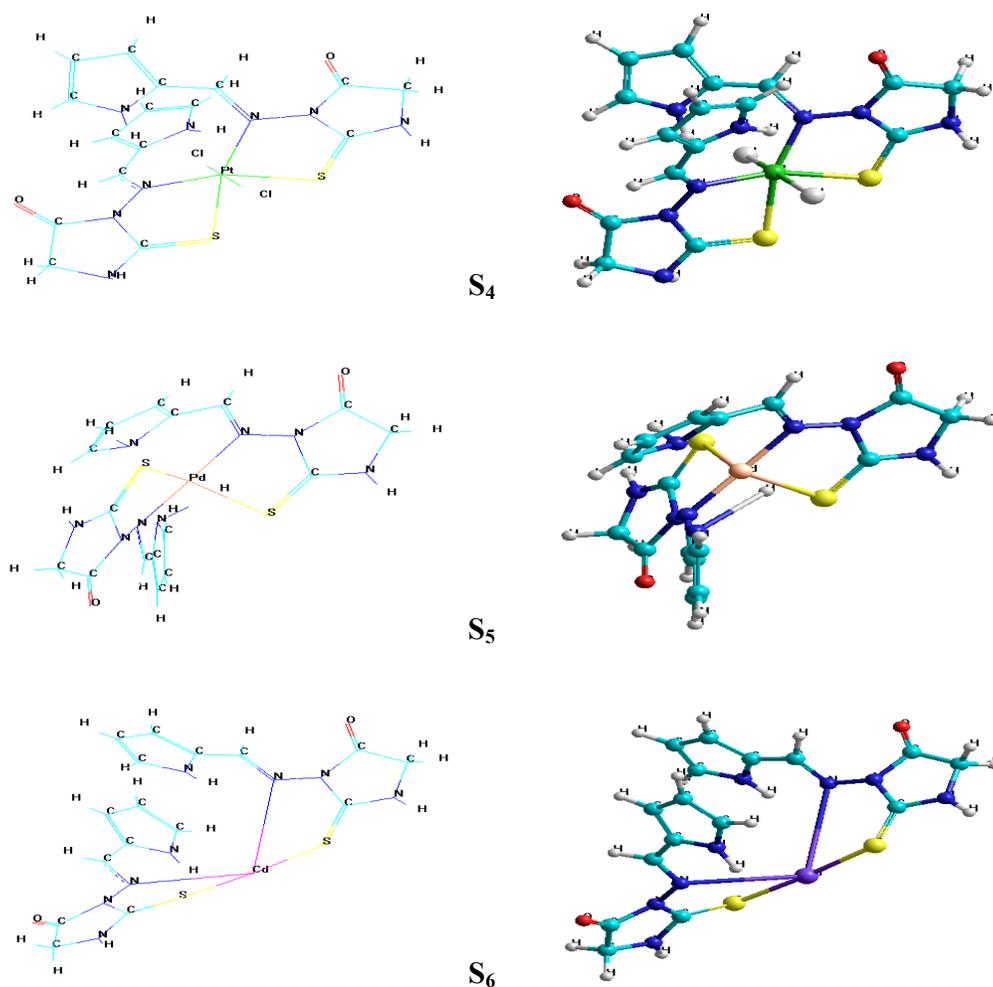## (d) Optimized geometries of ligand (L) and their metal complexes

Theoretically probable structures of metal complexes with ligand have been calculated to find the most possible model building stable structure for ligand and thire metal complexes are shown in Fig. 6.
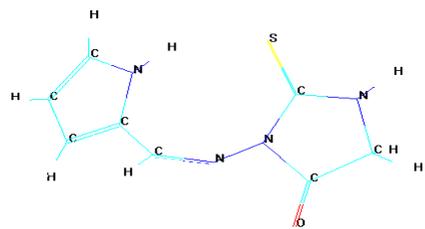
L
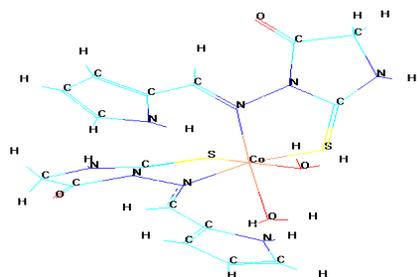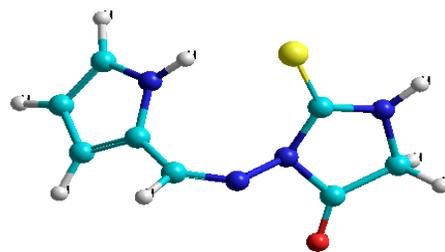
S₁
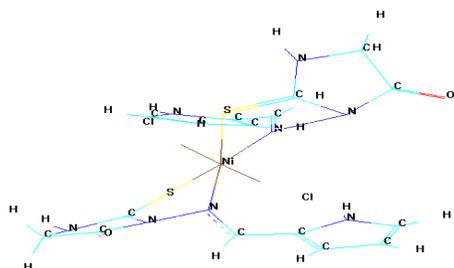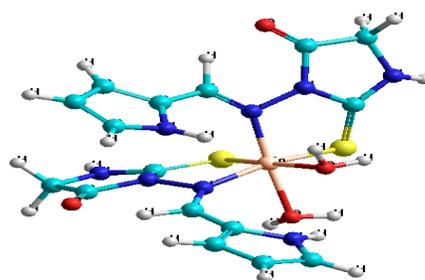
S₂
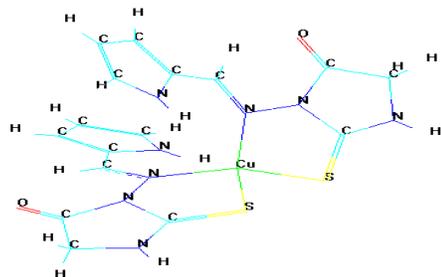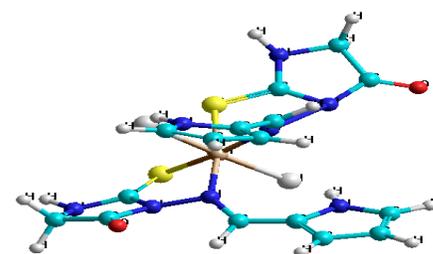
S₃
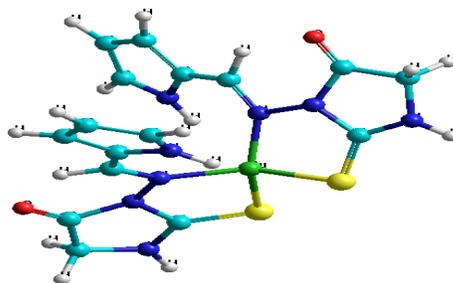
Cont…

Fig. 6: Conformation structure of Ligand (L) and their metal complexes using Hyperchem 8

(e) Bond lengths measurements for (L) and their metal complexes

The Gaussian suite of software was employed throughout this study optimizations were carried out for the model systems represented in Table 7. The initial state for structure didn't give bond lengths naturally so that the geometry optimization was used for correct bond lengths, calculation parameters were optimized of bond lengths for the free ligands and its metal complexes by using the semi-empirical (PM3) method at geometry optimization (0.001 Kcal/mol), to give excellent agreement with the experimental data[9,11,30].

Table 7: Bond length of ligands and their metal complexes using hyperchem.-8.7 program

Compound	C=N	C=S
L	1.1016	1.6335
S_1	1.3449	1.7242
S_2	1.3296	1.6455
S_3	1.3482	1.7236
S_4	1.2939	1.682
S_5	1.3138	1.7069
S_6	1.3245	1.7322

CONCLUSION

The new 2-Thioxoimidazoliine (L) ligand and its metal complexes were successfully synthesized and characterized. The mode of bonding and overall structure of the complexes was determined through physio-chemical and spectroscopic methods. Hyperchem-8 program has been used to predict structural geometries of all compounds in gas phase. The free ligand (L) and its metal complexes show significant antimicrobial activity. The all complexes are found more effective than the free ligand.

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