

Spectral and Biological Studies: Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) Complexes of 5-Methyl-4-((3-fluoro-4-methoxybenzylidene)amino)-3-thiol-1,2,4-triazole

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Received: 31 August 2020;

Accepted: 6 October 2020;

Published online: 7 December 2020;

AJC-20155

A series of metal-complexes of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Pd²⁺ with new Schiff base named 5-methyl-4-((3-fluoro-4-methoxybenzylidene)-amino)-3-thiol-*s*-triazole have been synthesized and characterized. Schiff base is formed by the condensation of 3-fluoro-4-methoxy-benzaldehyde and 4-amino-3-mercapto-5-methyl-1,2,4-triazoles (AMMT). After synthesis, Schiff base is characterized by IR and NMR techniques. Metal complexes are characterized by different techniques as IR, NMR, ESR, electronic and fluorescence. Elemental analysis and magnetic measurements of metal complexes have also been carried out. Using different techniques, tentative geometry for newly synthesized complexes have been proposed *i.e.* square planar for copper and palladium complexes and octahedral for rest of the metal complexes. The biological activities of all the metal complexes of this series are also examined.

Keywords: Biological, Triazole, Schiff base, Metal-complexes, NMR.

INTRODUCTION

The application of inorganic metal complexes to medicine is a rapidly developing field, new curative and diagnostic complexes are now having a hold on medical practice. From the past few years, triazole derivatives have enticed ample notice due to their chemotherapeutical values [1,2]. Literature studies reveal about extensive pharmacological activities of the triazole derivatives including antimicrobial [3], analgesic [1], anti-inflammatory [4], anti-infective [5], antineoplastic [6], anti-malarial [7], antiviral [8], antiproliferative [9] and anticancer activities [10]. Some of the triazole-based products are existing as medicines [11]. The corrosion inhibition properties of triazoles 4-amino-3-mercapto-5-methyl-1,2,4-triazole (AMMT), 4-amino-3-mercapto-5-ethyl-1,2,4-triazole (AMET), 4-amino-3-mercapto-5-propyl-1,2,4-triazole (AMPT) are also available in literature [12,13]. The simple synthesis procedure, versatility and diverse complexing ability of Schiff bases principally resulting from the carbonyl compounds and heterocyclic rings have attracted major attention of the researchers [14]. The Schiff bases metal-complexes possess considerable contribution in progress of coordination chemistry owing to their important physico-

chemical studies [15] and biological aspects [16-18]. Schiff bases have remarkable tendency to coordinate with various metal ions involving different bonding modes resulting efficacious production of homo- and hetero-metallic complexes having discrete stereochemistry due to which Schiff bases are used in moulding active sites in biological systems [19]. Furthermore, the azomethine metal-complexes have numerous applications in a variety of fields together with antifungal, antiviral, antibacterial, catalysis (homogeneous or heterogeneous) and magnetism [20]. Schiff bases and their metal complexes act as anticancer agents and it has been found that the anticancer activity of metal complexes is superior to their precursor ligands [21]. Among the metal complexes, Schiff bases having nitrogen, oxygen and sulfur donor atoms bonded with metals are of specific importance owing to their capability to have unusual configurations, lability and sensitivity to structural environments [22]. Several Schiff bases based transition metal-complexes derived from substituted triazoles have been reported from our laboratory [23]. In present study, the design (scheme), characterization, antibacterial and antimycotic (antifungal) activities of Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺ and Pd²⁺ complexes of 5-methyl-4-((3-fluoro-4-methoxybenzylidene)amino)-3-thiol-*s*-triazole are reported.

EXPERIMENTAL

AR grade chemicals and solvents have been used. Infrared (IR) spectra of all compounds were monitored using MB-3000 ABB spectrometer with KBr pellets/Nujol mulls. ^1H NMR spectra of synthesized ligand (HL) and divalent zinc (1:1, 1:2) complexes have been monitored using Bruker 400 spectrometer at 400 MHz ($\text{DMSO-}d_6$) with tetramethylsilane as reference. Electronic spectra of respective complexes were recorded on T90 UV/VIS spectrophotometer in DMF solvent from 200-900 nm. Spectrofluorometry of the all the newly synthesized complexes have been monitored on SHIMADZU spectrofluorometer. Cyclic voltammetric (CV) measurements of Cu(II) compounds have been performed using Ivium(IV) Stat Electrochemical Analyzer. Vibrating sample magnetometer (IIC, IIT Roorkee) was used for measurements of magnetic moments of corresponding complexes. For probing the structural environment of copper complexes, electron spin resonance (ESR) spectra were recorded under Varian (E-112) spectrometer (0.3 T magnetic field (H) at 9.1 GHz) at SAIF, IIT Bombay. C, H and N investigations of compounds were carried out using a Perkin Elmer (2400) elemental analyzer. Using alumina powder (reference), thermogravimetric behaviour was investigated on the Perkin Elmer instrument at a heating frequency of $10\text{ }^\circ\text{C min}^{-1}$. Metal contents were determined *via* gravimetrically *i.e.* cobalt as pyridine thiocyanate, nickel as $\text{Ni}(\text{dmg})_2$, copper as CuSCN and zinc as $\text{Zn}(\text{NH}_4)\text{PO}_3$.

Synthesis of ligand: 3-Mercapto-5-methyl-4-amino-triazole (AMMT) was synthesized by a reported procedure [24]. The ethanolic solution of AMMT (0.239 g, 1.84 mmol) and 3-fluoro-4-methoxybenzaldehyde (0.284 g, 1.84 mmol) was mixed and the formed mixture was refluxed on heating mantle for 4 h. The development of the reaction was checked using TLC. The prepared ligand 5-methyl-4-((3-fluoro-4-methoxybenzylidene)amino)-3-thiol-1,2,4-triazole (HL) (Fig. 1), was filtered, washed with alcohol, recrystallized and then kept in desiccator for drying.

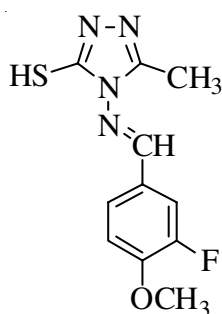


Fig. 1. 5-Methyl-4-((3-fluoro-4-methoxybenzylidene)amino)-3-thiol-1,2,4-triazole (m.p.: 206, Colour: Cream)

Synthesis of metal-complexes

(M:HL) metal-complexes: The mixing of hot solutions of ligand (0.15 g, 5.6 mmol) with the alcoholic solutions of respective acetates of Co (0.140 g, 5.6 mmol), Ni (0.143 g, 5.6 mmol), Cu (0.113 g, 5.6 mmol), Zn (0.124 g, 5.6 mmol) and Pd (0.127 g, 5.6 mmol), resulted in desired complexes.

The resulted solid products have been filtered and washed using hot water, alcohol, acetone and then dried out.

1:2{M:(HL)₂} metal complexes: The alcoholic solutions of ligand (0.30 g, 2.2 mmol) and acetates of Co (0.141 g, 1.1 mmol), Ni (0.141 g, 1.1 mmol), Cu (0.113 g, 1.1 mmol), Zn (0.124 g, 1.1 mmol) and Pd (0.127 g, 1.1 mmol) were mixed. Immediate precipitation occurred and precipitated products were separated, filtered and washed using hot water, alcohol, acetone and finally dried out.

Biological valuation: Schiff base and its complexes were evaluated *via* Agar well diffusion method to determine the *in vitro* minimum inhibitory concentrations (MICs) against a variety of bacteria including *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *Candida albicans*. Standard drugs ciprofloxacin and amphotericin B were used to compare the activity of prepared compounds [25]. These analyses have suggested the enhancement in activity for complexes compared to prepared ligand. Microbial cultures that were used in testing were induced from Microbial Type Culture Collection; IMTECH, Chandigarh. The activities were tapered in terms of zone of inhibition appearing that comes into view around the well against bacteria and fungus. The method was operated in three replicate plates.

RESULTS AND DISCUSSION

The newly synthesized Schiff base and its 1:1 and 1:2 metal complexes are moisture insensitive. Each metal-complex exhibits distinct colour. The prepared Schiff base possess solubility in wide range of organic solvents but its coordinated metal-complexes showing insolubility in general organic solvents but dissolve preferably in DMSO and DMF. The purity of the ligand as well as metal-complexes was tested using TLC. Table-1 includes the analytical data of all the compounds.

IR study: IR frequencies of synthesized compounds were detailed in $4000\text{-}200\text{ cm}^{-1}$ region. Table-2 summarises important IR frequencies of prepared compounds. IR spectrum of HL possess specific band witnessed at 1597 cm^{-1} analogous to azomethine $\nu(\text{-HC=N})$ moiety [26], that shifts by $30\text{-}40\text{ cm}^{-1}$ lower wavenumber in the complexes, demonstrating a bonding of metal with nitrogen of azomethine group (-HC=N) [27]. The weaker peak appeared at 2733 cm^{-1} corresponds to $\nu(\text{SH})$ group of prepared base, became extinct in the metallic complexes, which indicates the metal bonding to sulphur atom due to deprotonation of thiol group. A wide-ranging band in metal complexes, appeared in $3700\text{-}3200\text{ cm}^{-1}$ region owing to $\nu(\text{OH/H}_2\text{O})$, which is attributed to associated water molecules of the complexes. Presence of acetate group can be observed by band in range $1744\text{-}1730\text{ cm}^{-1}$ for 1:1 metal complexes. The metal-ligand bonding through the nitrogen atom and sulfur donor atoms of azomethine is further supported by (M-N) and (M-S) bands in the range $486\text{-}480$ and $345\text{-}325\text{ cm}^{-1}$, respectively [28].

^1H NMR analysis: ^1H NMR spectra of HL and its both the Zn(II)(1:1,1:2) compounds have been noted down in $\text{DMSO-}d_6$ and displayed in Table-3. In Schiff base, a signal at 9.86 ppm corresponds to azomethine proton that appears at 10.71 and 9.25 ppm for 1:1 and 1:2 divalent zinc complexes, respectively showing complexation *via* nitrogen atom of azo-

TABLE-1
ANALYTICAL DATA OF THE SYNTHESIZED COMPOUNDS

Compounds	Colour	Yield (%)	Elemental analysis (%): Found (calcd.)			
			C	H	N	M
Schiff base (HL)	Cream	83	46.79 (49.61)	3.49 (4.16)	21.87 (21.00)	–
Co(L)(OAc)·3H ₂ O	Grey	78	33.40 (35.70)	4.11 (4.38)	11.70 (12.18)	12.11 (13.48)
Co(L) ₂ ·2H ₂ O	Brown	80	41.50 (42.24)	2.99 (3.87)	17.11 (17.91)	7.99 (9.43)
Ni(L)(OAc)·3H ₂ O	Green	79	31.12 (35.72)	3.88 (4.38)	10.56 (12.82)	13.44 (13.43)
Ni(L) ₂ ·2H ₂ O	Dark green	80	41.12 (42.26)	3.43 (3.87)	16.52 (17.92)	8.56 (9.39)
Cu(L)(OAc)·H ₂ O	Brown	76	36.48 (38.47)	2.89 (3.72)	11.95 (13.80)	13.78 (15.66)
Cu(L) ₂	Yellowish green	81	43.22 (44.48)	3.33 (3.39)	17.95 (18.86)	8.78 (10.79)
Zn(L)(OAc)·3H ₂ O	Dull white	74	33.78 (35.19)	3.59 (4.32)	12.32 (12.63)	13.44 (14.73)
Zn(L) ₂ ·2H ₂ O	Yellow	77	40.35 (41.81)	2.89 (3.83)	17.47 (17.73)	9.67 (10.35)
Pd(L)(OAc)·H ₂ O	Brown	75	30.20 (34.79)	2.63 (3.37)	10.20 (12.48)	21.87 (23.71)
Pd(L) ₂	Brick red	82	40.32 (41.48)	2.89 (3.16)	16.99 (17.59)	15.55 (16.71)

TABLE-2
IMPORTANT IR SPECTRAL DATA (cm⁻¹) OF THE LIGAND AND ITS METAL-COMPLEXES

Compounds	v(N=CH)	v(C-S)	v(S-H)	v(OCOCH ₃)	v(H ₂ O/OH)	v(M-S)	v(M-N)
Schiff base, HL	1597	–	2733	–	–	–	–
C ₁₁ H ₁₁ FN ₄ OS							
Co(L)(OAc)·3H ₂ O	1562	761	–	1738	3394	331	480
Co(L) ₂ ·2H ₂ O	1556	705	–	–	3414	340	480
Ni(L)(OAc)·3H ₂ O	1561	761	–	1730	3212	344	485
Ni(L) ₂ ·2H ₂ O	1570	761	–	–	3408	327	484
Cu(L)(OAc)·H ₂ O	1569	761	–	1735	3399	339	486
Cu(L) ₂	1556	761	–	–	–	342	485
Zn(L)(OAc)·3H ₂ O	1567	791	–	1738	3310	336	483
Zn(L) ₂ ·2H ₂ O	1576	761	–	–	3324	345	486
Pd(L)(OAc)·H ₂ O	1584	761	–	1744	3222	325	485
Pd(L) ₂	1564	704	–	–	–	335	483

TABLE-3
¹H NMR SPECTRAL DATA OF SYNTHESIZED LIGAND AND DIVALENT ZINC COMPLEXES IN DMSO-*d*₆

Compounds	δ (ppm)
Schiff base (HL)	13.74 (s, -SH, 1H), 9.86 (s, -N-CH, 1H), 7.82 (s, Ar-H, 1H), 7.72 (d, Ar-H, 1H), 7.27 (d, Ar-H, 1H), 3.83 (s, O-CH ₃ , 3H), 2.35 (s, triazole-CH ₃ , 3H)
Zn(L)(OAc)·3H ₂ O	10.71 (s, -N-CH, 1H), 7.68 (s, Ar-H, 1H), 7.49 (d, Ar-H, 1H), 7.28 (d, Ar-H, 1H), 2.35 (s, triazole-CH ₃ , 3H), 3.83 (s, OCH ₃ , 3H), 2.29 (s, OCOCH ₃ , 3H)
Zn(L) ₂ ·2H ₂ O	9.25 (s, -N-CH, 1H), 7.79 (s, Ar-H, 1H), 7.68 (d, Ar-H, 1H), 7.29 (d, Ar-H, 1H), 3.83 (s, O-CH ₃ , 3H) 2.35 (s, triazole-CH ₃)

methine [29]. In the spectrum of Schiff base, the signal of SH proton appears at 13.74 ppm that disappeared indicating the complexation *via* S atom of thiol group in Zn (II) complexes [30]. The peak appearing at 2.35 ppm analogous to methyl group of triazole ring remained unshifted in metal complexes. The aromatic protons appear in the range of 7-8 ppm in the ligand and both Zn(II) complexes.

Fluorescence analysis: To determine the fluorescent nature of ligand (HL) and its metal complexes with divalent metals, fluorescence spectra have been monitored in DMSO at the excitation wavelength of 225 nm. The prepared base exhibits weaker fluorescence at 440 nm. The synthesized metal complexes (1:1 and 1:2) exhibit strong fluorescence compared to the ligand except copper complexes. It observed that the metal complexes demonstrate improved fluorescence intensity in the sequence as HL ~ Cu(II) < Ni(II) < Co(II) < Pd (II) < Zn(II) in 1:1 metal complexes (Fig. 2a) and in 1:2 the order is HL~Cu(II) < Co(II) < Ni(II) < Pd(II) < Zn(II) (Fig. 2b). Zinc(II)

complex possesses highest fluorescence intensity. The fluorescence of ligand is possibly reduced by phenomenon of photo-induced electron transfer (PET) [31,32] that is prohibited by coordination of ligand with metals; thus the luminescence intensity may be significantly improved by complexation thus rigidity of ligand is increased and energy loss through vibrations is reduced [33]. Augmentation of fluorescence through coordination is of much concern as it shows the possibility of these complexes to be used in photochemical applications [34]. The stoke shift for all the complexes is above 200 nm and a higher stoke shift (> 70) indicates a good chance of photochemical properties.

ESR study: Powder ESR spectra of both the copper complexes were monitored. The perceived parameters for Cu:L (1:1) and Cu:(L)₂ (1:2) are $g_{||} = 2.15$ and 2.22, $g_{\perp} = 2.05$ and 2.09, $g_{av} = 2.09$ and 2.13, $G = 2.70$ and 2.40, respectively. The spectrum of each complex have shown axial features ($g_{||} > g_{\perp} > 2.00233$) and suggested that $d_{x^2-y^2}$ orbital exists as ground

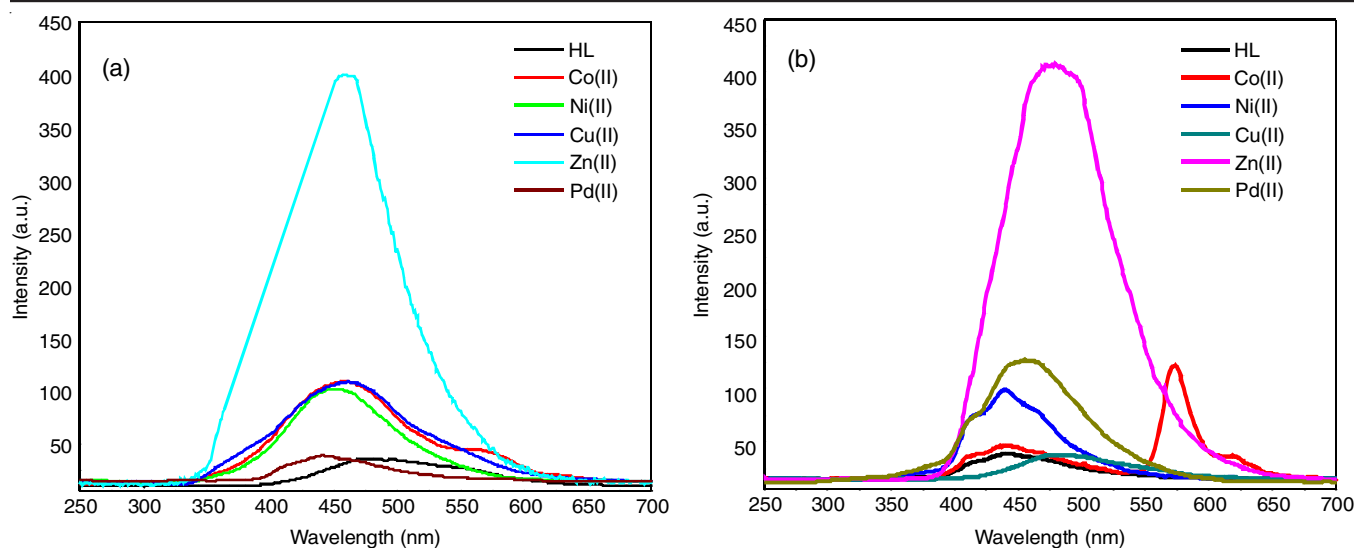


Fig. 2. Fluorescence emission spectra of Schiff base [HL] and its (a) 1:1 and (b) 1:2 metal-complexes

state, which is a feature of square-planar (distorted) structure in divalent copper complexes. Metal-ligand bonds possess significant covalent character for $g_{||}$ value lesser than 2.3 whereas a value more than 2.3 implies the ionic nature [35]. For both the complexes (Fig. 3), $g_{||} < 2.3$ point out adequate covalent nature of Cu-L bonds [36]. The G value (axial symmetry parameter) is fewer/smaller than 4 for both the complexes that suggest the presence of substantial exchange interactions in divalent copper complexes [37].

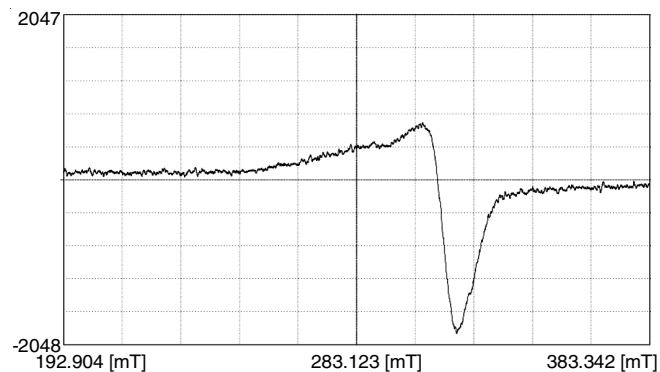


Fig. 3. X-band electron spin resonance spectra of Cu(L)(OAc)·H₂O

Electronic spectra: The electronic spectra of all the newly synthesized complexes have been recorded at room temperature

in DMF solvent to understand the type of M-L bonds.

Cobalt complexes: For cobalt(II) octahedral (high spin) complexes, two transitions appeared are assigned as ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) while ν_2 is missing. However, ν_2 can be determined with equation $\nu_2 = \nu_1 + 10Dq$ that lies close to ν_3 transition [38-40]. Two absorption bands are observed in 12642-12787 cm^{-1} (ν_1) and 21929-22883 cm^{-1} (ν_3) region and transition energy ratio of 2nd to 1st is 1.7-2.1 for Co^{2+} octahedral (high spin) complexes. Band-fitting relation was applied to determine various ligand field parameters including Dq , B , β , $\beta\%$ (Table-4) [40]. The observed Racah parameter (B value) is 703-761 cm^{-1} ($< 971 \text{ cm}^{-1}$), signifying the presence of overlapping between M-L orbitals. The value of nephelauxetic ratio (β) is found to be less than one for both cobalt (1:1 and 1:2) complexes demonstrating the partial covalent character of M-L bonds. The experimental ligand field parameters indicated the octahedral environment of Co(II) in the complexes [41].

Nickel complexes: Three bands at 10111-10209, 16025-16233 and 25947-26109 cm^{-1} corresponding to excitation (spin-allowed) from ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3T_{1g}(F)$ (ν_2) and ${}^3T_{1g}(P)$ (ν_3) correspondingly, were detected in absorption spectra of divalent nickel complexes (Table-4). These characteristic bands correspond to the octahedral environment around Ni(II) in the complexes [42,43]. The ligand field parameters indicated significant overlapping of the metal-ligand orbitals with some covalent

TABLE-4
ELECTRONIC TRANSITIONS AND OTHER IMPORTANT PARAMETERS DATA OF METAL-COMPLEXES

Complex	Transitions (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})	ν_2/ν_1	β	$\beta\%$	μ (BM)
	ν_1	ν_2	ν_3						
Co(L)(OAc)·3H ₂ O	12642	26549	21929	1390	703	1.7	0.72	28	4.5
Co(L) ₂ (OAc)·3H ₂ O	12787	26906	22883	1411	761	2.1	0.78	21	4.7
Ni(L)(OAc)·3H ₂ O	10111	16025	25974	1011	777	1.58	0.74	26	3.2
Ni(L) ₂ (OAc)·3H ₂ O	10209	16233	26109	1020	781	1.59	0.75	24.9	3.3
Cu(L)(OAc)·H ₂ O		19801		–	–	–	–	–	1.9
Cu(L) ₂		20661		–	–	–	–	–	2.1
Pd(L)(OAc)·H ₂ O	20040	22371	32679	–	–	–	–	–	–
Pd(L) ₂	21161	23419	30769	–	–	–	–	–	–

character in bonds [40]. The crystal field splitting energy (Dq) value is 1011 and 1020 cm^{-1} for 1:1 and 1:2 complexes, respectively indicating the octahedral environment around nickel in complexes. Further, ν_2/ν_1 ratios (~ 1.5) and β % (24.9-26) also support the formation of Ni^{2+} octahedral complexes.

Copper complexes: In spectra, band observed for copper(II) complexes (19801-20661 cm^{-1}) (Table-4), is attributed to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition, signify square planar arrangement around divalent copper ion [44].

Palladium complexes: Three bands were detected in absorption spectra of divalent palladium complexes. Three transitions detected in 20040-21161, 22371-23419 and 32679-30769 cm^{-1} region and are allocated to corresponding ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$ transitions. These electronic transitions of complexes specify the square planar environment of palladium(II) and the data obtained correspond to earlier reported values used for the square planar geometry [45,46].

Thermal analysis (TG/DTG): Thermal behaviour of the metal complexes $\text{Co}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot 3\text{H}_2\text{O}$, $\text{Ni}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot 3\text{H}_2\text{O}$, $\text{Cu}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot \text{H}_2\text{O}$, $\text{Pd}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot \text{H}_2\text{O}$ were studied by thermo gravimetric analysis in the range of room temperature to 600 $^\circ\text{C}$ under N_2 atmosphere with a heating frequency of 10 $^\circ\text{C}/\text{min}$ taking alumina as reference. The TG/DTG plots have been shown in Fig. 4.

Cobalt(II) complex decomposes primarily in four steps [47]. Both TG and DTG studies demonstrate the thermal dehydration of complex over the 60-120 $^\circ\text{C}$ temperature range (Table-5). At 203 $^\circ\text{C}$ (DTG), partial decomposition of ligand begins with removal of acetate. This is accompanied by decomposition of remaining organic moiety in the range 270-388 $^\circ\text{C}$. Finally, decomposition of the triazole moiety takes place in 400-550 $^\circ\text{C}$ range resulting cobalt metal oxide as end product and as evident by DTG peak at 473 $^\circ\text{C}$. The nature of chemical change and weight loss percentage with the temperature range is given in Table-5.

$\text{Ni}(\text{C}_{11}\text{H}_{10}\text{N}_4\text{OSF})\text{OAc}\cdot 3\text{H}_2\text{O}$ decomposes in three main steps. The weight loss in first step, involves elimination of water molecules in 50 to 120 $^\circ\text{C}$ temperature range. In second step, the weight loss indicates the elimination of organic moiety in 220 to 350 $^\circ\text{C}$ range. The weight loss in third step corresponds to the elimination of the triazole ring (at 380-490 $^\circ\text{C}$). NiO is estimated as the final residue [48].

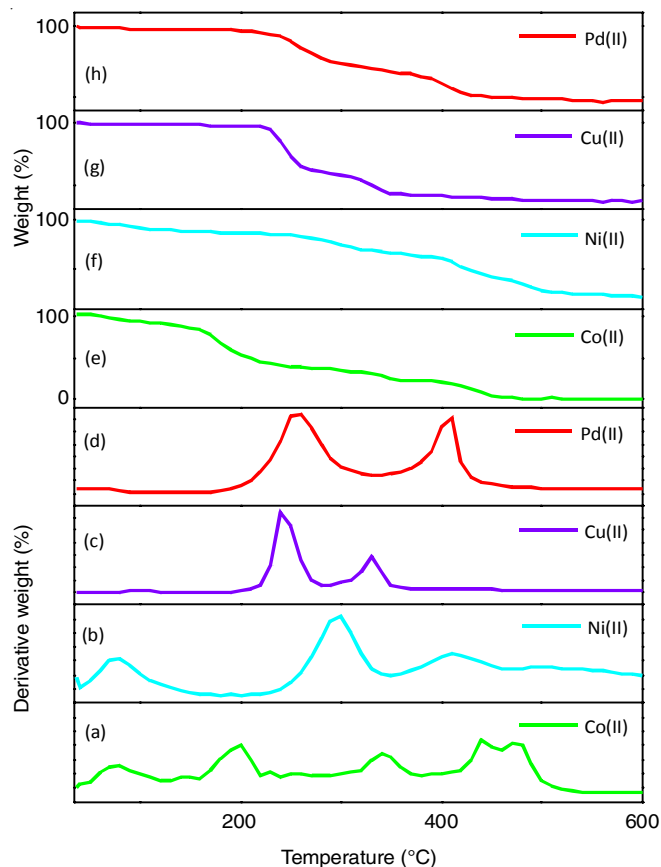


Fig. 4. DTG and TG plot of $\text{Co}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot 3\text{H}_2\text{O}$ (a,e), $\text{Ni}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot 3\text{H}_2\text{O}$ (b,f), $\text{Cu}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot \text{H}_2\text{O}$ (c,g), $\text{Pd}(\text{C}_{11}\text{H}_{10}\text{FN}_4\text{OS})\text{OAc}\cdot \text{H}_2\text{O}$ (d,h) complexes, respectively

Mainly two steps are involved in decomposition of copper and palladium complexes. First step resulted in elimination of organic moiety in temperature range 201-320 $^\circ\text{C}$ and 193-341 $^\circ\text{C}$, respectively for $\text{Cu}(\text{II})$ and $\text{Pd}(\text{II})$ complexes. This is also characterized by DTG peak at 242 $^\circ\text{C}$ [$\text{Cu}(\text{II})$] and 259 $^\circ\text{C}$ [$\text{Pd}(\text{II})$]. Second stage includes the elimination of triazole ring leaving respective metals oxide as residue in temperature range 330-525 $^\circ\text{C}$.

Electrochemistry: To study redox behaviour of copper complexes cyclic voltammetry experiment was performed in DMSO solution with 100 mV/s within the ± 1 V range versus

TABLE-5
THERMOGRAVIMETRIC CHARACTERISTICS OF METAL COMPLEXES

Complex	T.G. plateau ($^\circ\text{C}$)	D.T.G. ($^\circ\text{C}$)	Mass loss (%)		Decomposed moiety	Metallic residue
			Cald.	Found		
$\text{Co}(\text{C}_{11}\text{H}_{10}\text{N}_4\text{OSF})\text{OAc}\cdot 3\text{H}_2\text{O}$	60-120	82	12.33	11.80	H_2O	CoO
	166-227	203	13.41	12.77	Organic moiety	
	270-388	343	31.35	29.41	Organic moiety	
	400-550	473	29.04	29.40	Triazole moiety	
$\text{Ni}(\text{C}_{11}\text{H}_{10}\text{N}_4\text{OSF})\text{OAc}\cdot 3\text{H}_2\text{O}$	50-120	82	12.38	12.01	H_2O	NiO
	220-350	300	45.11	43.66	Organic moiety	
	380-490	410	29.78	28.22	Triazole moiety	
$\text{Cu}(\text{C}_{11}\text{H}_{10}\text{N}_4\text{OSF})\text{OAc}\cdot \text{H}_2\text{O}$	201-320	242	48.5	46.1	Organic moiety	CuO
	330-510	370	31.2	31.1	Triazole moiety	
$\text{Pd}(\text{C}_{11}\text{H}_{10}\text{N}_4\text{OSF})\text{OAc}\cdot \text{H}_2\text{O}$	193-341	259	43.97	43.88	Organic moiety	PdO
	360-525	420	28.29	27.60	Triazole moiety	

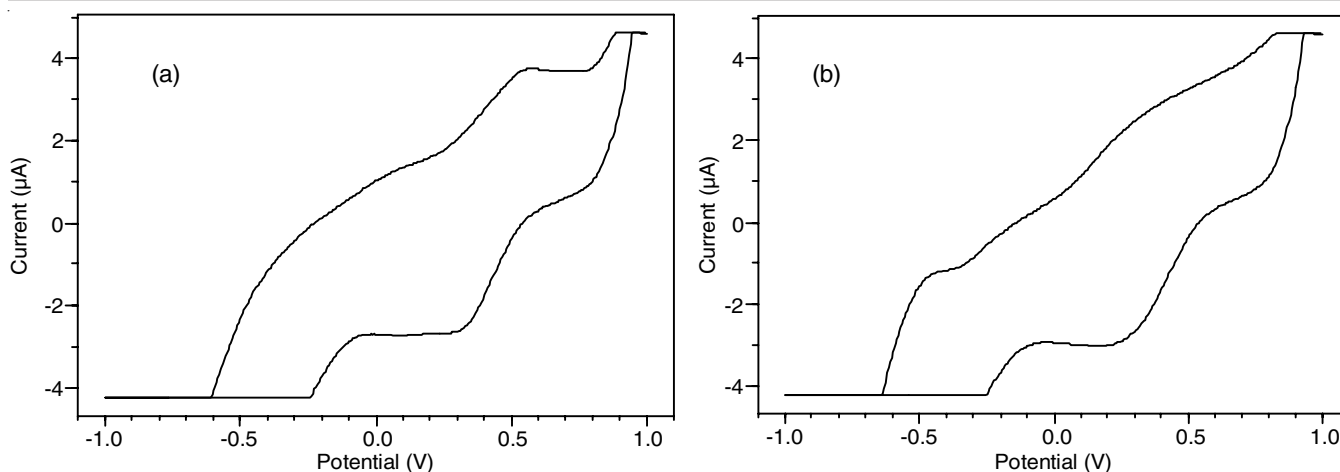


Fig. 5. Cyclic voltammogram of (a) Cu(L)(OAc)·H₂O and (b) Cu(L)₂

platinum wire electrode at room temperature using a three electrode configuration. Tertbutylammoniumperchlorate (TBAP) was used as auxiliary electrolyte. Cyclic voltammogram (CV) of both Cu complexes is shown in Fig. 5. Cu(L)(OAc)·H₂O exhibits reduction and oxidation peak at $E_{pc} = 0.28$ V and $E_{pa} = 0.57$ V, respectively for Cu(II) to Cu(I) and for Cu(1:2) the corresponding maxima appear at $E_{pc} = 0.26$ V and $E_{pa} = 0.32$ V. ΔE for these processes is very high, which is consistent with the quasi reversible process. The ratio of cathodic to anodic peak current (I_c/I_a) is 0.71, which corresponds to one electron process [49].

Antimicrobial: Schiff base and its metal complexes were evaluated *via* Agar well diffusion method against a variety of bacteria including gram \pm bacteria [*S. aureus*, *B. subtilis* (G +ve), (*E. coli*, *P. aeruginosa* (G -ve)] and yeast (*C. albicans*). The activity of coordinated metal complexes was found enhanced than that of ligand. The antimicrobial action of the compounds depends on the level of its liposolubility. Due to ligand and metal coordination the charge on metal ion get overlapped with ligand's donor atom orbitals, which increase the lipophilic character of the percolation of metal ion *via* cell membrane of microbes that prohibit their growth due to blocking of their

active sites. Diameter of growth of inhibition zone of all newly synthesized compounds against two Gram-positive and two Gram-negative bacteria and one yeast is summarized in Table-6 and their respective MIC values in Table-7. Figs. 6 and 7 depicts the bar diagram including the zone of inhibition and MIC of compounds and standard drugs, respectively. It can be concluded from antibacterial studies of the 1:1 and 1:2 complexes of Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) that most of these possess good antibacterial activities. Ni(C₁₁H₁₀FN₄OS)OAc·3H₂O and Cu(C₁₁H₁₀FN₄OS)(OAc)·H₂O showed maximum barrier to *B. subtilis*.

Conclusion

From the above discussion, it can be concluded that the synthesized azomethine base coordinates in bidentate fashion *via* N and S atoms. The bivalent metal complexes of Co²⁺, Ni²⁺ and Zn²⁺ possess octahedral environment in both 1:1 and 1:2 molar ratios whereas square planar arrangement can be suggested around the newly synthesized Cu²⁺ and Pd²⁺ complexes. The possible structures are shown in Fig. 8. The antimicrobial and antifungal investigation illuminates us to conclude that some of the newly synthesized complexes possess good activity than that of ligand.

TABLE-6
ANTIMICROBIAL AND ANTIFUNGAL ACTIVITIES (*in vitro*) OF PREPARED SCHIFF BASE AND METALS-COMPLEXES EVALUATED USING AGAR WELL DIFFUSION METHOD

S. No.	Compounds	Diameter of growth of inhibition zone (mm)				
		Gram positive bacteria		Gram negative bacteria		Fungi
		<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>C. albicans</i>
PS	HL	15	16	10	12	–
Ps-1	Co(L)(OAc)·3H ₂ O	10	18	12	15	–
Ps-2	Co(L) ₂ ·2H ₂ O	12	12	10	15	10
Ps-3	Ni(L)(OAc)·3H ₂ O	18	22	18	12	12
Ps-4	Ni(L) ₂ ·2H ₂ O	10	15	10	12	12
Ps-5	Cu(L)(OAc)·H ₂ O	20	22	10	10	10
Ps-6	Cu(L) ₂	10	12	8	10	12
Ps-7	Zn(L)(OAc)·3H ₂ O	12	10	12	16	10
Ps-8	Zn(L) ₂ ·2H ₂ O	12	13	10	12	–
Ps-9	Pd(L)(OAc)·H ₂ O	18	20	15	16	10
Ps-10	Pd(L) ₂	10	12	8	12	8
Cf	Ciprofloxacin	24	26.6	25	22	–
At	Amphotericin-B	–	–	–	–	16.6

TABLE-7
MIC VALUES OF SYNTHESIZED COMPOUNDS

S. No.	Compounds	<i>B. subtilis</i>	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>C. albicans</i>
PS	HL	50	25	–	50	–
Ps1	Co(L)(OAc)·3H ₂ O	–	25	50	50	–
Ps2	Co(L) ₂ ·2H ₂ O	50	50	–	50	–
Ps3	Ni(L)(OAc)·3H ₂ O	25	12.5	25	50	50
Ps4	Ni(L) ₂ ·2H ₂ O	–	50	–	50	50
Ps5	Cu(L)(OAc)·H ₂ O	12.5	12.5	–	–	–
Ps6	Cu(L) ₂	–	50	–	–	50
Ps7	Zn(L)(OAc)·3H ₂ O	50	–	50	25	–
Ps8	Zn(L) ₂ ·2H ₂ O	50	50	–	50	–
Ps9	Pd(L)(OAc)·H ₂ O	–	12.5	50	25	–
Ps10	Pd(L) ₂	–	50	–	50	–
Cf	Ciprofloxacin	6.25	6.25	6.25	12.5	–
At	Amphotericin-B	–	–	–	–	25

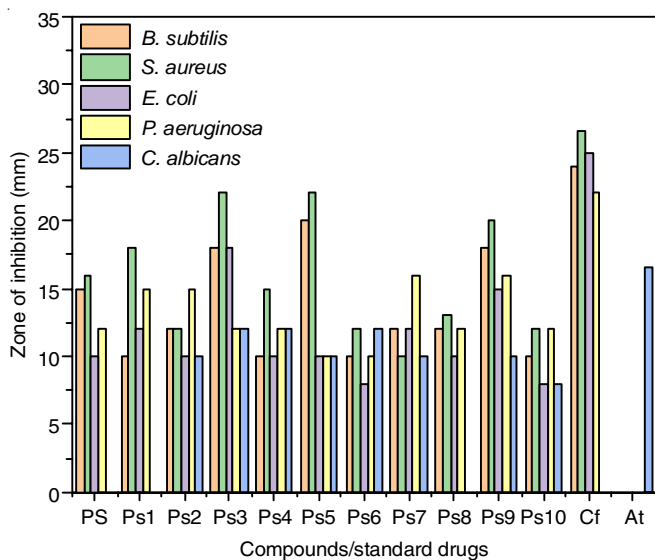


Fig. 6. Antimicrobial activity of compounds/standard drugs showing zone of inhibition

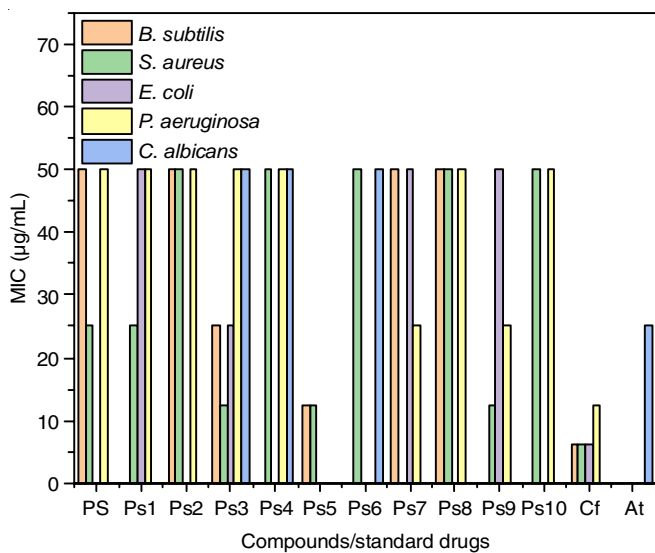


Fig. 7. Comparison of MIC of compounds with standard drugs

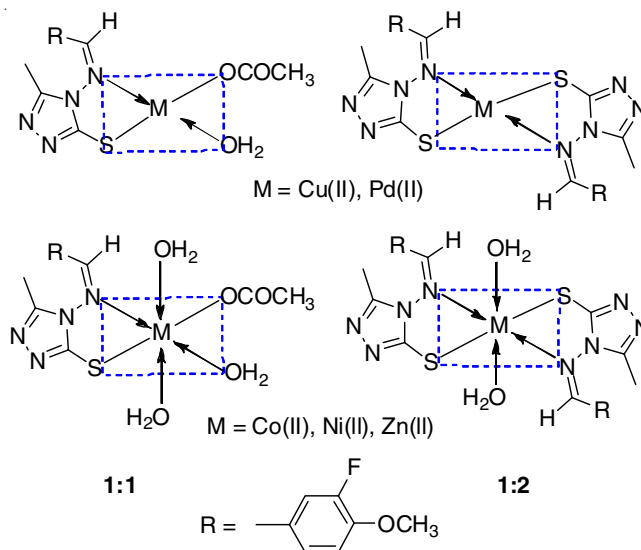


Fig. 8. Proposed structures of synthesized metal-complexes

ACKNOWLEDGEMENTS

One of the authors (Preeti Siwach) thank UGC, New Delhi, India for the economic support in the form of Junior Research Fellowship (JRF).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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