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NLO and Fluorescent Behavior of a Novel Schiff Base Derived from 2,4-Diamino-6-phenyl-1,3,5-triazine and 3-(4-methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one and its Metal Complexes

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ABSTRACT

A novel Schiff base *N,N'*-bis(3-(4-methoxyphenyl)-1-(thiophen-2-yl)allylidene)-6-phenyl-1,3,5-triazine-2,4-diamine is synthesized by the condensation reaction of 2,4-diamino-6-phenyl-1,3,5-triazine with chalcone [3-(4-methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one]. Metal complexes of the Schiff base ligand with molecular formula ML_2Cl_2 where, $M=Cu(II)$, $Co(II)$, $Zn(II)$ have been synthesized and characterized on the basis of IR, magnetic susceptibility, UV-Visible, ¹H-NMR, EPR spectral studies. From spectral data of the complexes, it has been tentatively assigned as square planar geometry for $Cu(II)$, $Zn(II)$ complexes and tetrahedral geometry for $Co(II)$ complex. The molar conductance of the metal(II) complexes show the non-electrolytic nature of the complexes. The redox behavior of the copper(II) complex was studied by cyclic voltammetry. All the synthesized compounds may serve as potential photoactive materials as indicated from their characteristic fluorescence spectrum. The ligand–ligand charge transfer is reflected in emission spectra and is due to the presence of phenyl rings in the ligands. The nonlinear optical behaviour of the ligand and the metal(II) complexes are investigated and the second harmonic generation efficiency of the complexes have more activity than the organic ligand. The in-vitro antimicrobial activities of the compound were tested against the microorganisms the bacteria *Klebsiella pneumonia* and the fungi *Candida albicans* by well diffusion method and the result reveals that the ligand and its metal(II) complexes have significant antimicrobial activity.

Keywords: s-triazine, Schiff bases, NLO activity, Fluorescence activity

INTRODUCTION

Development of novel coordination complexes is of great research interest due to their interesting topologies and potential applications in redox system, optoelectronic devices, molecular architectures, material science, etc. [1-3]. Schiff base ligands, owing to their facile syntheses, tunable steric and electronic properties, have been extensively studied for catalysts, fluorescence properties [4,5], electroluminescent materials [6] etc. Of these Schiff bases derived from 1,3,5-triazine derivatives have been demonstrated to be versatile ligands for the synthesis of metal complex materials with a variety of structural architectures. Recently, metal-organic compounds with Nonlinear Optical (NLO) properties have been attracting a great deal of attention [7,8]. Metal-organic complexes have some advantages over the ligand such as tunability of the polarizability by changing the oxidation state of metal atoms or by variation of ligands. 1,3,5-triazine-based ligands make a contribution to optical nonlinearity due to its aromatic triazine core and its metal ions.

Herein, we focus on a novel Schiff base containing 1,3,5- s-triazine moiety and its transition metal(II) complexes regarding the synthesis, structures, fluorescence properties, and nonlinear optical activity.

MATERIALS AND METHODS

Reagents and instruments

All chemicals were obtained from Aldrich chemical & Co. and used without purification. All solvents were of AR grade and purified by standard procedure. The IR spectra in KBr disc was recorded on a Shimadzu Fourier Transform Infra-Red (FTIR) spectrophotometer. Proton Nuclear Magnetic Resonance (¹H-NMR) spectrum was recorded in Deuterated Dimethyl Sulfoxide (DMSO-d₆) solvent using a Bruker 300 MHz NMR spectrometer. The electronic spectra of the complexes and ligand in DMF solutions were recorded in Jasco V-530 UV-Visible spectrophotometer. The EPR spectrum of the Cu complex was recorded at 77 K in Dimethyl formamide (DMF). Cyclic voltammetry

measurements were carried out by model CH 608 C instrument using a three electrode cell containing a reference Ag/AgCl electrode, Pt wire auxiliary electrode and Glassy Carbon (GC) working electrode in DMSO solution with Tetrabutylammonium Perchlorate (TBAP) used as the supporting electrolyte. Fluorescence emission spectra in the UV-Visible range were recorded in Jasco Spectro Fluorimeter FP-8500 between 400-900 nm. The ligand and its complexes were screened for antimicrobial activity through the well diffusion method.

Preparation of ligand

Synthesis of tridentate Schiff base involves refluxing 1 equivalent of 2,4-diamino-6-phenyl-1,3,5-triazine with two equivalent of chalcone in ethanol solution. An ethanolic solution of 2,4-diamino-6-phenyl-1,3,5-triazine (0.01 mol) is refluxed with 3-(4-methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one (0.02 mol) in ethanol for about 9 h and then keep it for a day. The yellow solid is filtered and recrystallized with ethanol and dried in vacuum over anhydrous calcium chloride (Figure 1). M.p. 180°C. Yield: 67%.

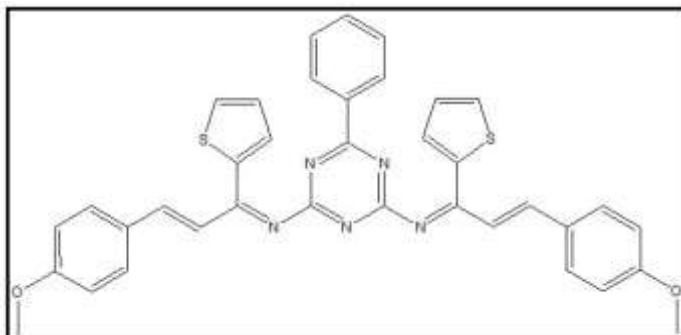


Figure 1: Structure of ligand(L)

Preparation of metal(II) complexes

To the ethanolic solution of the ligand (1 mmol), metal chloride ($MCl_2 \cdot xH_2O$, 1 mmol) in ethanol is added drop wise with constant stirring. The resulting mixture was stirred for about 3 h at room temperature. The chelate separated out was filtered and dried. Yield 76%.

RESULTS AND DISCUSSION

The results of elemental analysis (Table 1) and 1H -NMR spectrum of the ligand are consistent with the formula in Figure 1. The 1H -NMR spectra of the Schiff base ligand in DMSO- d_6 shows a singlet at 3.87 ppm for $-OCH_3$ (6H, s) proton, multiplet at 7.40-7.53 ppm for aromatic protons, doublet at 8.30 ppm for $-CH$ proton. Molar conductivity of the metal(II) complexes in DMSO were in the range 3.0-6.50 $S \cdot cm^2 \cdot mol^{-1}$ indicating the non-electrolytic nature of the complexes.

Table 1: Physical characteristics of the ligand and metal(II) complexes

Compounds	Color	Found (calcd) (%)				M.p. (°C)	Molar conductance ($S \cdot cm^2 \cdot mol^{-1}$)
		C	H	N	M		
Ligand(L)	Pale yellow	69.48	4.53	10.95	-	180	-
		69.43	4.49	10.98	8.01		3.03
CuLCl ₂ (1)	Green	57.39	3.74	9.04	8.2	128	
		57.43	3.7	8.99	7.56		3.04
CoLCl ₂ (2)	Blue	57.74	3.77	9.1	7.67	111	
		57.69	3.71	8.98	8.38		6.5
ZnLCl ₂ (3)	Yellow	57.26	3.74	9.02	8.44	194	
		57.22	3.71	9.03			

IR spectra

IR spectra for ligand and metal(II) complexes are given in Table 2. On comparing the IR spectra of the ligand with their metal complexes, stretching band at 1452 cm^{-1} corresponding to $\nu(C=N)$ group in triazine ring is found to be shifted by $60-62 \text{ cm}^{-1}$ in complexes indicating the coordination of $C=N$ in the triazine nitrogen in coordination [9]. A red shift is observed in complex for (C-S) stretching vibration around 5 cm^{-1} indicates thiophene sulphur in coordination with metal [10]. The appearance of weak non-ligand band in the far IR region at $561-553 \text{ cm}^{-1}$ can be assigned to $\nu(M-N)$ vibration and confirm the interaction between the metal and the ligand [11].

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

Compound	$\nu(C=N)$ (triazine)	$\nu(C=N)$	$\nu(C-S)$	$\nu(M-N)$
Ligand (L)	1452	1589	823	-
CuL.Cl ₂ (1)	1512	1584	819	561
CoL.Cl ₂ (2)	1514	1589	819	553
ZnL.Cl ₂ (3)	1514	1589	819	553

Electronic spectra

The electronic spectrum of the ligand shows a strong intense band at 28818 cm⁻¹ due to $\pi \rightarrow \pi^*$ transition. The electronic spectrum of Cu(II) complexes (Table 3) exhibits a band at 22935 cm⁻¹ which can be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition suggests square planar geometry [12]. The electronic absorption spectrum of the cobalt (II) complex shows absorption bands at 16447 cm⁻¹ (v3), 9836 cm⁻¹ (v2) which corresponds to the transitions ${}^4A_2(F) \rightarrow {}^4T_1(P)$, ${}^4A_2(F) \rightarrow {}^4T_1(F)$ suggests tetrahedral geometry [12]. Bands v2 and v3, show a structure which is believed to be mainly due to splitting of d orbitals caused by a lowering of symmetry [13]. From the electronic spectra of the complexes, it is tentatively assigned that square planar geometry for Cu(II) complex and tetrahedral geometry for Co(II) complex (Figure 2).

Table 3: Electronic spectral data of the ligand and its metal(II) complexes

Compound	Frequency (cm ⁻¹)	Assignments	$\epsilon M^{-1}cm^{-1}$	Geometry
Ligand	28818	$\pi \rightarrow \pi^*$	-	-
CuL.Cl ₂ (1)	22935	${}^2B_{1g} \rightarrow {}^2A_{1g}$	52.5	Square planar
CoL.Cl ₂ (2)	16447	${}^4A_2(F) \rightarrow {}^4T_1(P)$	25.1	Tetrahedral
	9836	${}^4A_2(F) \rightarrow {}^4T_1(F)$	40.3	

EPR spectra

The EPR spectrum of Cu(II) complex (1) at LNT shows four well resolved peaks. The anisotropic signals exhibits with $g_{\parallel}=2.292$ and $g_{\perp}=2.06$ which is comparable with those observed for square planar geometry. The $g_{\parallel}/A_{\parallel}$ value calculated for complex (1) (138 cm) lies between 90 and 140 cm indicating a square planar structure around the Cu (II) ion [14]. The trend, $g_{\parallel} (2.292) > g_{\perp} (2.06) > g_e (2.0023)$ shows that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital of the copper(II) ion. The exchange interaction parameter G is estimated from the expression $G=(g_{\parallel}-2.0023)/(g_{\perp}-2.0023)$. The observed G value is greater than 4 ($G=4.8$) for the Cu(II) complex demonstrates the negligible exchange interaction between the copper(II). The covalence parameters α^2 was calculated using the following Equations:

$$\alpha^2 (Cu)=(A_{\parallel}/p) + (g_{\parallel}-2.0023) + 3/7(g_{\perp}-2.0023) + 0.04$$

The calculated α^2 value (0.7269) of the complex is less than unity, which indicates the complex has some covalent character in the ligand environment [15]. The spin orbit coupling constant value $\lambda(-571 \text{ cm}^{-1})$, calculated using the relations $g_{av}=1/3(g_{\parallel} + 2 g_{\perp})$ and $g_{av}=2(1-2\lambda/10Dq)$, is less than the free Cu(II) ion (-832 cm^{-1}) which also supports the covalent character of M-L bond in the complex [16].

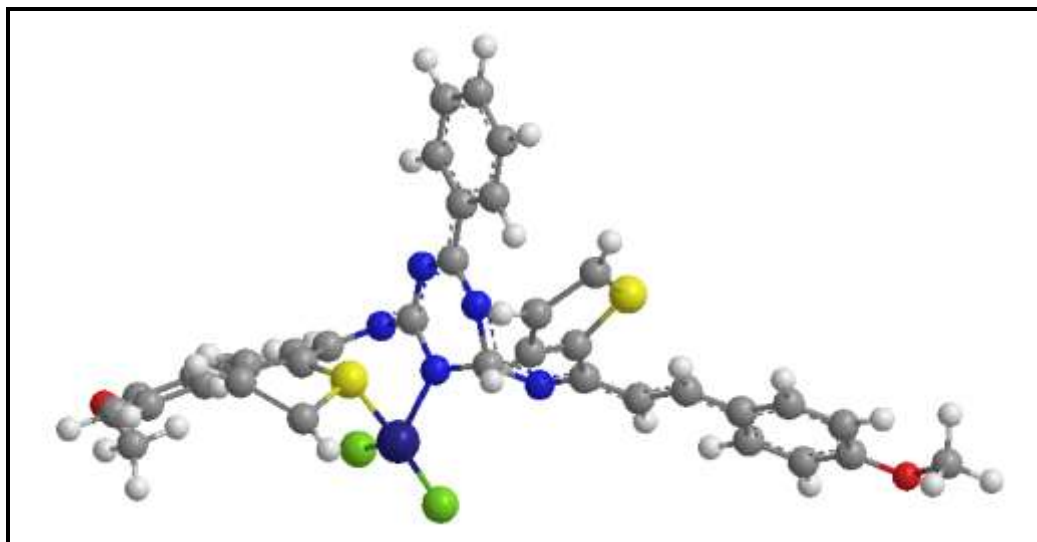


Figure 2: Proposed structure of Co(II) complex

Electrochemical behaviour

The redox behavior of Cu(II) complex in DMSO have been studied by cyclic voltammetry using glassy carbon as the working electrode, platinum wire as counter electrode, Ag/AgCl as reference electrode and Tertiary Butyl Ammonium Perchlorate (TBAP) as supporting electrolyte. The cathodic current function values were independent of scan rate. The repeated scan as well as different scan rate shows that dissociation does not take place in the complex. The cyclic voltammogram of Cu(II) complex (Figure 3) shows a well-defined redox process corresponding to the formation of the Cu(II)/Cu(I) couple at 0.44V and another at -0.641V which is attributable to the reduction of Cu(I)/Cu(0). During the reverse scan, it shows two anodic oxidation peaks at 0.71V and 1.08V which are attributable to the oxidation of Cu(0)/Cu(I) and Cu(I)/Cu(II) respectively. The ratio of cathodic to anodic peak $I_c/I_a=1$ corresponding to a single one electron process [17].

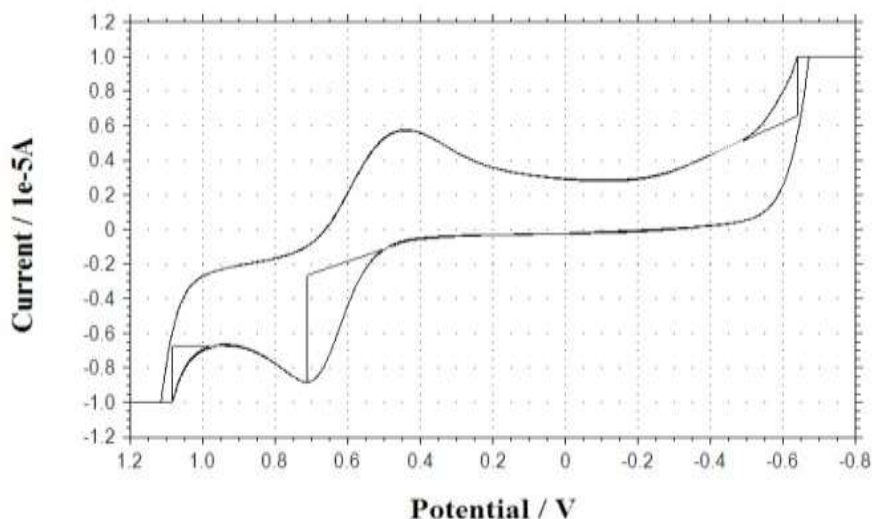


Figure 3: Cyclic voltammogram of Cu (II) complex

Nonlinear optical activity

NLO property of the material was confirmed by Kurtz powder technique to study the second harmonic generation efficiency. A comparison of the Second Harmonic Generation (SHG) signal emitted by the sample with the standard KDP under the same experimental conditions, shows that the ligand is 0.25 times that of KDP and the Cu(II) complex is 0.5 times that of KDP. The NLO properties of a molecule are related to the energy gap between Highest Energy Occupied Molecular Orbital (HOMO) and Lowest Energy Unoccupied Molecular Orbital (LUMO). The small HOMO-LUMO gap indicates small excitation energy and hence high NLO properties are predicted.

Fluorescence studies

Fluorescence is particularly favored in molecules that possess rigid structures. Therefore, influence in rigidity has been invoked to account for increase in fluorescence when complexed with metal ions. Ligand and the complexes are photoluminescent in DMF solvent at room temperature, as shown in Figures 4 and 5, which may be due to intra-ligand $\pi \rightarrow \pi^*$ emission. The ligand upon excitation at 354 nm displays two broad emission bands, centered at 360 nm and 437 nm with the quantum yield of 0.8226. Complex 2, displays a relatively weak emission with λ_{max} at 684 nm in DMF solvent at room temperature with the quantum yield of 0.677. Significant differences in the positions of emission maximum of ligand and its complexes establish the coordination of the metal ion to the ligand [18].

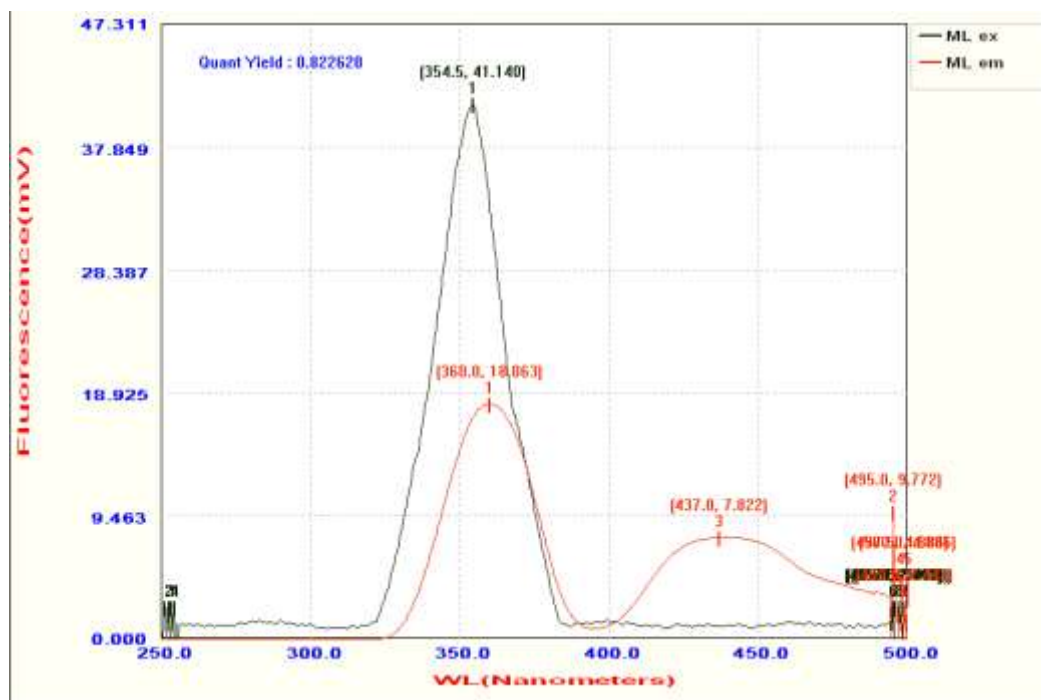


Figure 4: Fluorescence spectrum of ligand

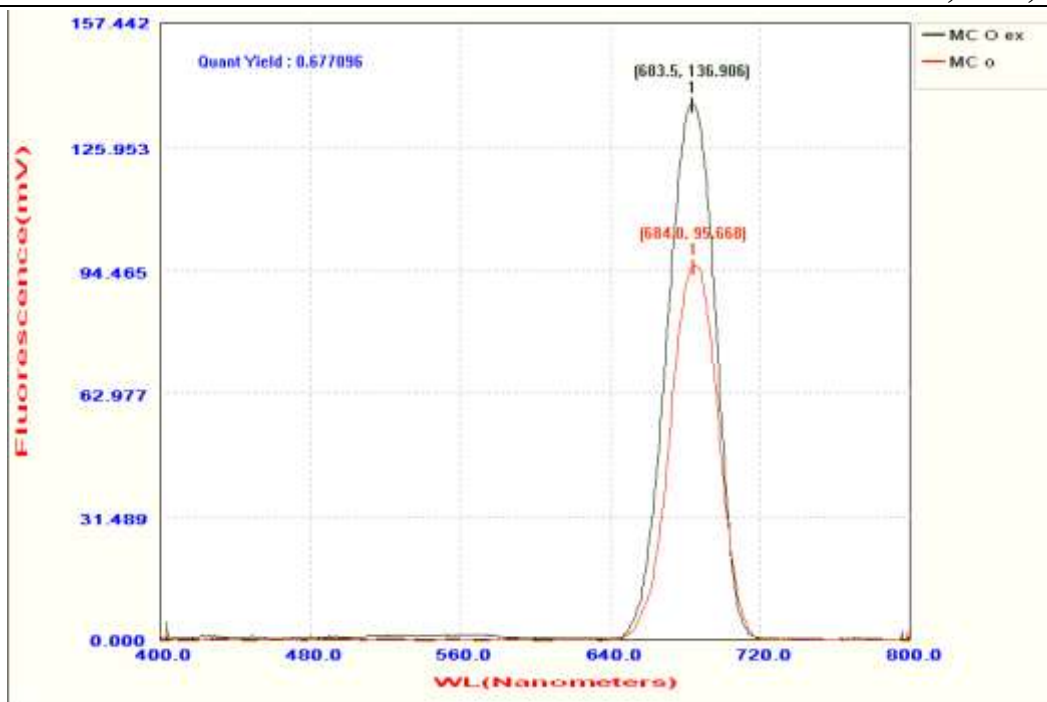


Figure 5: Fluorescence spectrum of complex 2

Antimicrobial activity

The antimicrobial activity of the ligands and their metal complexes were tested against the bacteria (*Klebsiella pneumonia*) and fungi species (*Candida albicans*) by the well diffusion method. The test solutions were prepared in DMSO. Amikacin and ketoconazole were taken as the standard antibacterial and antifungal drugs. *In vitro* antibacterial data reveals that the newly synthesized ligand and its complexes displayed moderate antibacterial activity. All the synthesized compounds show significant antifungal activity in comparison to the standard drugs used (Figure 6). The metal(II) complexes shows more potent activity than the free ligand due to chelation effects.

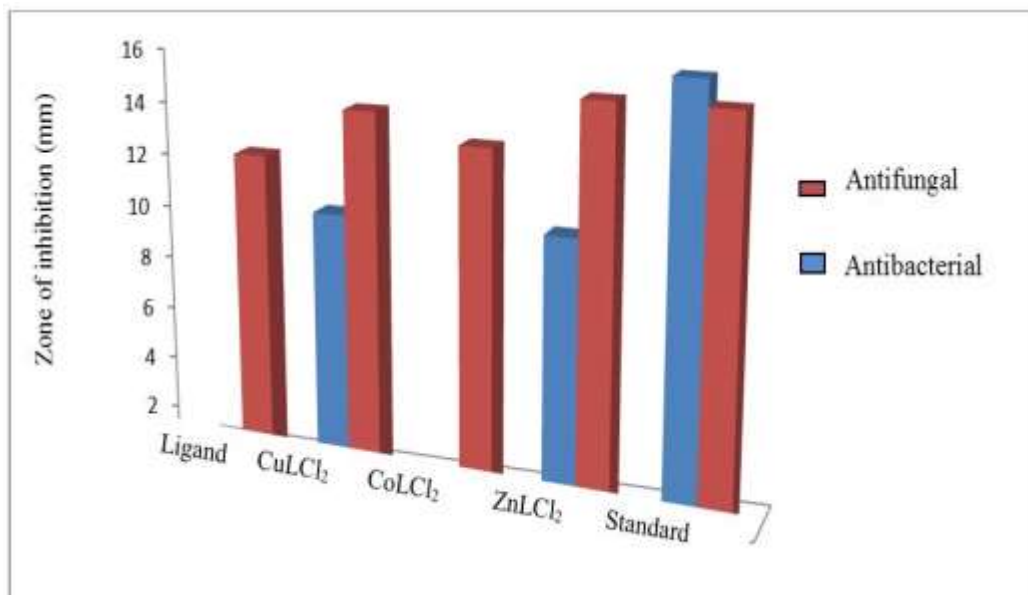


Figure 6: Zone of inhibition of the ligand and its complexes (mm)

CONCLUSION

A novel tridentate Schiff base ligand have been prepared by condensation of 2,4-diamino-6-phenyl-1,3,5-triazine and -3-(4-methoxyphenyl)-1-(thiophen-2-yl)prop-2-en-1-one and characterized by spectroscopic studies. From spectral data of the complexes, it have been tentatively assigned as square planar geometry for Cu(II), Zn(II) complexes and tetrahedral geometry for Co(II) complex. Molar conductance of the complexes reveals that the prepared complexes are found to be non-electrolytes. Electrochemical studies of the Cu(II) complexes shows that Cu(II)/Cu(I) redox system is reversible in nature. *In-vitro* antimicrobial activity data also reveals that the newly synthesized compound displayed significant activity in comparison to the standard. The synthesized ligand and the ccomplexes are photoluminescent in DMF solvent at room temperature. The ligand and copper(II) complex shows significant NLO properties when compared with standard KDP. Enriched NLO activity of the Cu(II) complex than the free ligand is due the decrease in energy gap between HOMO and LUMO.

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