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Synthesis, Spectral Studies, NLO, and Biological Studies on Metal(II) Complexes of s-Triazine-Based Ligand

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Synthesis, Spectral Studies, NLO, and Biological Studies on Metal(II) Complexes of s-Triazine-Based Ligand

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A series of metal(II) complexes of $[ML.H_2O]$ type [where M=Cu(II), Ni(II), Co(II), and Zn(II); L=2,4-bis(1-(2-hydroxyphenyl)ethylideneamino)-6-phenyl-1,3,5-triazine] have been synthesized and characterized by using analytical and spectral studies. Spectroscopy and other data show octahedral geometry for metal(II) complexes. The redox behavior of the copper(II) complex has been studied by using cyclic voltammetry. The second harmonic generation (SHG) efficiency of the ligand and metal(II) complexes has been found to be higher than that of urea and KDP. The *in vitro* antimicrobial activities of the compounds were tested and the results revealed that metal(II) complexes exhibit higher activity than the ligand.

Keywords antimicrobial activity, hydroxyacetophenone, metal complexes, NLO, triazine

INTRODUCTION

S-triazine and its derivatives display a wide range of pharmacological properties, including antibacterial, antiviral, antimalarial, antiinflammatory activities and exhibit promising anticancer, antileukemia, and anti-HIV activities.^[1–6] Triazine analogues can be utilized as a building block for the construction of multisite ligand systems.^[7,8] During the last few years, the potential of s-triazine derivatives in agrochemical and medicinal properties has been subjected to investigations.^[9–12] The aminosubstituted s-triazine derivatives are associated with a number of pronounced antibacterial activities.^[13]

In recent years, there is a quest to design and develop the nonlinear optical materials to meet the present demand due to their widespread applications such as high-speed information processing, optical communications and optical data storage.^[14] Generally, molecule with conjugated π -electron system can have large nonlinear polarizabilities. Many researchers have shown that the criterion for the compound to exhibit NLO activ-

ity is noncentrosymmetric and the presence of $D-\pi$ -A system. In addition to organic materials, transition metal complexes have also been found to be effective in this regard. In view of the above advantages a lot of attention has been focused especially on s-triazine derivatives because of their high firstorder hyperpolarizabilities and better transparency.^[15] Besides the easily polarizable aromatic π -system, another characteristic of s-triazine is that due to its π -deficient nature, it can act as an auxiliary acceptor in NLO chromophores. Further advantages in considering the s-triazine as central moiety is its symmetric nature by which it will be possible to chemically tune its NLO nature by mono- or di-substitution.^[16-18] Hence s-triazine derivatives are found to be the right choice in this regard.

In order to study the effect of π -conjugated system on NLO activity, we are prompted to synthesize and characterize the metal(II) complexes of ligand 2,4-bis(1-(2-hydroxyphenyl)ethylideneamino)-6-phenyl-1,3,5-triazine derived from s-triazine and 2-hydroxyacetophenone. Because of the presence of π -conjugation between donor and acceptor unit, the present ligand is expected to have largerhyperpolarisability compared to standard. Fluorescence, electrochemical behavior, and biological activity of the ligand and its metal complexes are also examined.

EXPERIMENTAL

Reagents and Measurements

All the chemicals and solvents used were purchased from Aldrich Chemicals & Co. Microanalytical data were recorded at Central Drug Research Institute (CDRI), Lucknow. The mass spectra of the ligand and its metal complexes were recorded at the Indian Institute of Technology, Madras. ¹H NMR spectrum of the ligand was recorded in DMSO-d₆ by employing TMS as internal standard at the Madurai Kamaraj University, Madurai. IR spectra of the samples were recorded on JASCO FT-IR spectrophotometer in 4000–400 cm⁻¹ range using KBr pellet. The UV-Vis spectra were recorded on a JASCO V-530 spectrophotometer using DMSO as a solvent. The ESR spectra of the complexes were recorded at 300 and 77 K at IIT, Mumbai using DPPH (diphenylpicrylhydrazyl) as internal standard. Magnetic susceptibility of the complexes was measured

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FIG. 1. Synthesis of ligand.

by Gouy balance using copper sulphate as calibrant. Effective magnetic moments were calculated using the formula μ_{eff} = 2.28 $(\chi_M T)^{1/2}$, where χ_M is the corrected molar susceptibility. Cyclic voltammetric measurements of copper complexes were carried out at room temperature in acetonitrile under nitrogen atmosphere using three electrode cell containing a Ag/AgCl reference electrode, platinum wire auxiliary electrode, and a glassy carbon working electrode in acetonitrile with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The molar conductance of the complexes was measured using a Systronic conductivity bridge at room temperature in DMSO. Thermogravimetric studies were carried out using a Shimadzu TGA-50 thermal analyser. Fluorescence spectra were recorded with an ELICO SL174 Spectrofluorometer. The antimicrobial activities of the ligand and its metal complexes were carried out by well-diffusion method. The SHG (Second Harmonic Generation) efficiency of the ligand and its complexes were determined by the modified version of powder technique at IISc, Bangalore.

Synthesis of Ligand

A mixture of 2-hydroxy acetophenone (2.72 g, 20 mmol), 2,4-diamino-6-phenyl-1,3,5-triazine (1.87 g, 10 mmol) and piperidine (0.05 cm³) in 25 mL of ethanol was stirred under reflux for 6 h. The solution was concentrated and the white crystalline solid obtained was filtered and recrystallized from ethanol. (Yield: 70%). m.p. $153-155^{\circ}$ C.

Synthesis of Metal(II) Complexes

The metal(II) complexes were prepared by the addition of hot solution of the appropriate metal(II) chloride (1 mmol) [M = Cu(II), Ni(II), Co(II), and Zn(II)] in 25 mL of ethanol to the hot ethanolic solution of the ligand (0.423 g, 1 mmol). The resulting mixture was stirred under reflux for 4 h and the complex pre-

cipitated were collected by filtration, washed thoroughly with ethanol, and dried in vacuum (Yield: 73–78%).

Nonlinear Optical Property

The SHG efficiency of the ligand and its metal(II) complexes were determined by the modified version of the powder technique developed by Kurtz and Perry. The samples were ground into powder and packed between two transparent glass slides. An Nd :YAG laser beam of wavelength 1064 nm was passed through the sample cell. The transmitted fundamental wave was absorbed by a copper(II) sulphate solution, which removes the incident 1064 nm light and Filter BG-38 removing any residual 1064 nm light. Interference filter band width is 4 nm and for



FIG. 2. Suggested structure of metal(II) complexes.

Compounds/Empirical		Element					
Formula	Color	C	Н	Ν	М	$\lambda_m \ (\Omega^{-1} \ cm^2 \ mol^{-1})$	M.P. (°C)
Ligand C ₂₅ H ₂₁ N ₅ O ₂	White	70.92 (70.94)	4.96 (4.97)	16.54 (16.52)			153
$CuL(H_2O) [Cu(C_{25}H_{21}N_5O_2)H_2O] (1)$	Blue	59.46 (59.48)	4.55 (4.52)	13.87 (13.82)	12.59 (12.51)	5.7	209
NiL(H ₂ O) [Ni(C ₂₅ H ₂₁ N ₅ O ₂)H ₂ O] (2)	Green	60.00 (60.04)	4.60 (4.68)	14.00 (14.03)	11.78 (11.74)	8.2	192
$\begin{array}{l} CoL(H_2O) \\ [Co(C_{25}H_{21}N_5O_2)H_2O] (\textbf{3}) \end{array}$	Violet	60.01 (60.05)	4.61 (4.67)	14.01 (14.03)	11.74 (11.78)	7.9	178
$\frac{ZnL(H_2O)}{[Zn(C_{25}H_{21}N_5O_2)H_2O]}$ (4)	White	59.24 (59.29)	4.54 (4.52)	13.82 (13.86)	12.91 (12.96)	9.1	183

 TABLE 1

 Physical characterization, analytical, and molar conductance data of the ligand and metal(II) complexes

central wavelength of 532 nm. Green light is finally detected by the photomultiplier tube and displayed on the oscilloscope. The second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. The efficiency of the sample was compared with microcrystalline powder of KDP (Potassium dihydrogenphosphate) and urea. The input energy used in this particular set-up was 2.2 mJ/pulse.

Antimicrobial Activity

The *in vitro* biological screening effects of the synthesized compounds were evaluated by well diffusion method. *Staphylococcus aureus, Salmonella typhi, Escherichia coli, and Bacillus subtilis* were used for bacterial test. Antifungal activity was evaluated against *Aspergillus niger* and *Candida albicans*. All the bacterial strains mentioned above were incubated in Nutrient Broth (NB) at 37°C for 24 h and fungal isolates were incubated in PDA broth at 28°C for 2 to 3 days. The wells each of 5 mm in diameter were made in Muller Hinton agar using cork borer. The test solution was prepared in 10^{-3} mL⁻¹ concentration (DMSO) and then 100 μ L of the solution was transferred into each well. The plates were incubated for 24 h at 37°C and examined for clear inhibition zone around the well.

TABLE 2 Characteristic of IR bands (cm⁻¹) of the ligand and its metal(II) complexes

inetai(ii) complexes								
	Vibrational frequencies (cm ⁻¹)							
Compounds	(C=N)	ν(C=N) triazine ring	ν (OH)	$\nu(OH)$ of H ₂ O	ν (M-N)	ν (M-O)		
Ligand	1646	1425	3188		_			
$[Cu(L)H_2O]$ (1)	1635	1408	_	3380	420	540		
$[Ni(L)H_2O]$ (2)	1632	1411	_	3406	460	520		
$[Co(L)H_2O]$ (3)	1630	1417	_	3392	442	515		
$[Zn(L)H_2O]$ (4)	1639	1415	—	3410	438	528		

RESULTS AND DISCUSSION

The ligand is synthesized by the condensation of 2,4diamino-6-phenyl-1,3,5-triazine and 2-hydroxyacetophenone (Figure 1). The metal(II) complexes of copper(II), nickel(II), cobalt(II), and zinc(II) of general formula [ML.H₂O] were obtained in good yield through the reaction of ligand with the corresponding metal chlorides (Figure 2). The analytical data and physical properties of the ligand and metal(II) complexes are listed in Table 1. The molar conductance of the metal(II) complexes were measured to establish the charge of the metal(II) complexes and implies that all the complexes are nonelectrolytes.^[19] The metal(II) complexes are stable in air and nonhygroscopic in nature. They are freely soluble in organic solvents such as DMSO, DMF, and acetonitrile.

IR Spectra

Important IR spectral bands of the free ligand and metal complexes are listed in Table 2. The IR spectrum of the ligand shows a broad band centered at 3188 cm⁻¹ which is characteristic of ν (OH). This band disappears in all the complexes, which can be attributed to the involvement of phenolic -OH in coordination.^[20] The involvement of deprotonated phenolic moiety in complexes is confirmed by the shift of ν (C–O) stretching band observed at 1212 cm⁻¹ in the free ligand to a lower frequency^[21,22] to the extent of 10 to 20 cm⁻¹. The shift of ν (C–O) band at 1212 cm⁻¹ to a lower frequency suggests the weakening of ν (C-O) and formation of stronger M-O bond. The band observed at 1646 cm⁻¹ in the ligand is assigned to ν (C=N) mode. The shift of ν (C=N) vibration in all the complexes to a lower frequency suggests the coordination of azomethine nitrogen to the metal ion.^[23,24] The ligand shows a strong band at 1425 cm⁻¹ which is a characteristic of the ν (C=N) group in s-triazine. This band which is shifted to lower frequency of 1417–1408 cm⁻¹ upon complexation indicates that the above group is one of the coordinating atoms in the ligand.^[25] The presence of coordinated water in the complexes is confirmed by a broad band

Compounds	Frequency (nm) (ε , M ⁻¹ cm ⁻¹)	Assignment	Geometry	μ_{eff} (B.M.)
$[Cu(L)H_2O] (1)$	447 (210)	ILCT*	Distorted octahedral	1.86
	852 (78)	$^{2}\text{E}_{g} \rightarrow ^{2}\text{T}_{2g}$		
$[Ni(L)H_2O]$ (2)	999 (68)	$^{3}A_{2g} \rightarrow ^{3}T_{2g}$	Distorted octahedral	3.23
	749 (105)	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$		
	410 (132)	${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$		
$[Co(L)H_2O]$ (3)	1040 (128)	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$	Distorted octahedral	4.78
	630 (183)	${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$		
	525 (222)	${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$		

 TABLE 3

 Electronic absorption spectral data (nm) and magnetic susceptibility data of metal(II) complexes

*Intraligand charge transfer.

around 3400 cm⁻¹ and weak band around 850 cm⁻¹ indicating the binding of water to the metal.^[26] The lower ν (C=N) frequency also indicates stronger M–N bonding. In the IR spectra of the complexes, a band observed between 420 and 460 cm⁻¹ is attributed to the ν (M–N) stretching vibrations.^[27] Another band appeared between 515 and 540 cm⁻¹ which is assigned to the interaction of phenolic oxygen to the metal atom, *i.e.*, the stretching vibrations of ν (M–O).^[28]

¹H NMR Spectra

The ¹H NMR spectra of ligand and nickel(II), zinc(II) complexes recorded in DMSO-d₆ show well-resolved signals. The ¹H NMR spectrum of ligand shows that a singlet at 2.57 ppm is due to six methyl protons, singlet at 6.6–8.3 ppm corresponding to aromatic protons, and singlet at 11.5 ppm observed for phenolic hydroxyl group. The ¹H NMR spectra of both the complexes show the resonance with expected integrated intensities. In both complexes, no signal is recorded for phenolic hydrogen in the 11.5 ppm region. This indicates deprotonation of the orthohydroxyl group on complexation. The singlet at 3.45–3.72 ppm shows the presence of water molecule in the metal complexes.^[29] No appreciable changes were found in other signals of the complex.

The ¹³C NMR spectrum of the ligand that exhibits a singlet peak at 172 ppm is attributed to three equivalent carbons of triazine ring and aromatic carbons are observed in the region 117–167 ppm and azomethine carbon at 170 ppm. From the ¹³C NMR spectrum of the Co(II) complex, the signal for C₃ and C₄ carbon showed an upfield shift to 109, 152 ppm, respectively,

 TABLE 4

 Ligand field parameters of metal(II) complexes

Complexes	v_2/v_1	B (cm ⁻¹)	β	eta_0	10 Dq
$\frac{[Ni(L)H_2O] (2)}{[Co(L)H_2O] (3)}$	1.38	478	0.46	54	10010
	1.64	704	0.72	28	10562

on complexation compared with the free ligand. C_{17} and C_{19} show a downfield shift to 189 ppm on complexation. The other ring carbons did not show significant shifts.

Electronic Absorption Spectra and Magnetic Susceptibility

The electronic absorption spectral regions, assignments, and the proposed geometry of the complexes are given in Table 3. The electronic absorption spectrum of the ligand displayed bands at 219 nm and 400 nm which can be assigned to Intraligand charge transfer transition. The electronic absorption spectrum of the copper(II) complex (1) displayed bands at 447 nm and 852 nm which are assigned as an intra-ligand charge transfer band (ILCT) and a d-d band due to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition, respectively.^[30] This band strongly favors an octahedral geometry; the same is further supported by the magnetic susceptibility value (1.86 B.M.).^[31,32] The nickel(II) complex (2) exhibits three d-d bands at 999 nm, 749 nm, and 419 nm which can be assigned to ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$, ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(F)$, and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ transitions, respectively.^[33] Moreover, the ratio ν_2/ν_1 is (1.38) indicative of octahedral geometry for nickel(II) complex.[34] The magnetic moment for nickel(II) complex is 3.23 B.M. which is well within the range expected for octahedral geometry around the central metal ion.^[35] The electronic spectrum of cobalt(II) complex (3) exhibits three d-d bands at 1040 nm, 630 nm, and 525 nm due to the ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2}g(F)$, and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ transitions, respectively, and has magnetic moment value 4.78 B.M.^[36] These transitions suggest octahedral geometry and the assignments are in good agreement with the reported values.^[37]

The coordination field parameters 10Dq, B, and β and β_0 were calculated using the secular equation given by E. Konig^[38] for nickel(II) and cobalt(II) complexes and the results are given in Table 4. Observed ν_2/ν_1 values are in agreement with the calculated ones. This indicates that the assignments are reasonable and are additional evidence for octahedral structure.^[39] In addition, the β value for cobalt(II) complex is ≈ 0.7 showing that the bonding is moderately covalent.^[40]



FIG. 3. Mass spectrum of ligand.

Mass Spectra

The EI mass spectra of the ligand and copper(II) complex were recorded. Mass spectrum of the ligand shows a molecular ion peak at m/z 423 and the molecular ion peak for copper(II) complex (1) is observed at 504 m/z confirms the stoichiometric composition of the metal(II) complexes as being of the [ML.H₂O] type. Mass spectra of the ligand and copper(II) complex are given in Figures 3 and 4.

Electrochemical Behavior

The redox behavior of the copper(II) complex was studied using cyclic voltammetry at 10^{-3} M concentration in DMSO. The Cyclic voltammogram of copper(II) complex (1) shows one reduction peak at -0.385 V in cathodic side and oxidation peak at 0.377 V in anodic side. The peak separation, $\Delta E_p = 0.762$ V which is greater than required for reversible process (59 mV) indicates that the redox couple is irreversible^[41] and the ratio of cathodic to anodic peak current corresponds to a simple one electron process. The cyclic voltammogram of the copper(II) complex (1) is shown in Figure 5.

ESR Spectra

The ESR spectrum of copper(II) complex (1) was recorded at 300 K and 77 K. The spin Hamiltonian parameters calculated for the copper(II) complex is given in Table 5. The "g" tensor values of this copper(II) complex can be used to derive the ground state. The observed spectral parameters show $g|| > g \perp$ value that is characteristic of an axially elongated octahedral geometry. The covalent character of metal-ligand bond is inferred from the g_{iso} value 2.094, which support the fact that the unpaired electron lies predominantly in the d_{x2-y2} orbital. The geometric parameter G is estimated from the expression $G=g|| - 2.0023/g \perp - 2.0023$. The observed value for the exchange interaction parameter for the copper(II) complex (G = 6.45) suggest that no appreciable exchange coupling is present. Kivelson and Nielson pointed out that g|| value is moderately sensitive function of metal-ligand



FIG. 4. Mass spectrum of copper(II) complex.



FIG. 5. Cyclicvoltammogram of [Cu(L)H₂O].

covalency. The observed g|| value is less than 2.3 which is an indication of a strong covalent environment in the copper(II) complex.

The spin-orbit coupling constant, λ value calculated using the relations,

$$g_{av} = 1/3 (g|| + 2 g \perp)$$

 $g_{av} = 2(1 - 2\lambda)/10Dq$

is less than that of free Cu(II) ion (-832 cm^{-1}) which supports covalent character of metal-ligand bond in the complex. The covalency parameter α^2 is calculated using the following equation.

$$\alpha^{2} = -(A||/0.036) + (g||-2.0023) + 3/7(g \perp -2.0023) + 0.04$$

The observed value of $\alpha^2 = 0.75$ of the complex is less than unity, which indicates that the complex has some covalent character in the ligand environment.^[42] The calculated value of g||/A|| (145 cm) for the complex indicates that the structure is strongly distorted.

NLO Property

Thus, the second-order nonlinear optical property of ligand and all the four complexes were investigated using modified version of powder technique developed by Kurtz and Perry.^[43] The efficiency of the ligand and metal(II) complexes were compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup is 2.2 mJ/ pulse. From the experimental data, ligand shows 1.3 and 5.8 times more activity than urea and KDP, respectively. Metal(II) complexes show SHG intensity as high as 1.8–3.5 times as that of urea and 5.2–6.9 times than that of KDP, which concludes that metal(II) complexes exhibit better SHG efficiency than the ligand. The second order nonlinearity for the metal(II) complexes follows the order (1) > (2) > (4) > (3). Thus, among the metal(II) complexes, (1) has the largest hyperpolarisabilty. The magnitude of the optical nonlinearities depends on the strengths of the donor-acceptor groups and also the nature of π -bonding sequence.

Fluorescence Studies

The ligand displays a fluorescence excitation maximum at λ_{ex} =496 nm and an emission maximum at λ_{em} =501 nm in DMSO solvent. The Cu(II), Ni(II), and Co(II) complexes exhibit emission bands at 540 nm, 544 nm, and 471 nm upon photo excitation at 535 nm, 538 nm, and 465 nm, respectively (Table 6). Usually, metal(II) complexes showed a decrease in fluorescence intensities compared to the ligand due to the delocalization of π -electrons within the system.^[44] However, the increase in fluorescence intensity may be explained by metal to ligand charge transfer. The fluorescence quantum yields of the ligand and its metal(II) complexes were obtained using the following relation,^[45]

$$\Phi_{\rm S} = A_{\rm s}/A \times ({\rm Abs})_{\rm R}/({\rm Abs})_{\rm s} \times \Phi_{\rm R}$$

Where Φ_s and Φ_R are the fluorescence quantum yield of the sample and reference respectively, A_S and A_R are the area under the fluorescence spectra of the sample and reference and $(Abs)_S$ and $(Abs)_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation. The closed shell Zn(II) ion is known to be nonquenching in nature as it does not allow a fluorophore-metal oxidative photoelectron transfer.^[46] The emission spectrum of ligand is given in Figure 6.

Thermal Analysis

Thermogravimetric studies of ligand, Cu(II), and Ni(II) complexes were carried out in the temperature range 30 to 800°C (Table 7). The TG curve for ligand shows weight change between 120 to 150°C. This is in conformity with indefinite stability of ligand at room temperature compared to metal(II)

 TABLE 5

 ESR spectral data of the copper(II) complex (1)

			1					
Compound	g	g⊥	g iso	$A_{\parallel} (10^{-4} \text{ cm}^{-1})$	$A \perp (10^{-4} \text{ cm}^{-1})$	α^2	β^2	g _∥ /A _∥ cm
[Cu(L)H ₂ O] (1)	2.26	2.043	2.095	156.93	80.25	0.75	1.70	145



FIG. 6. Fluorescence spectrum of ligand.

complexes. In the nickel(II) complex, the TG curve is indicative of 3.57% weight loss in the temperature range 30 to 140°C which could be ascribed to the elimination of water molecule. The dehydrated product remains stable between 140 and 320°C. The second step corresponds to removal of two hydroxyacetophenone moiety in the temperature range 320 to 506°C and the third step corresponds to lose of triazine moiety at 432 to 685°C leaving NiO residue.

Biological Activity

Antimicrobial activity of the compounds were tested *in vitro* by well diffusion method^[47] against the bacteria *Staphylococcus aureus, Salmonella typhi, Escherichia coli, Bacillus subtilis,* and antifungal activity against the fungi *Candida albicans* and *Aspergillus niger.* Amikacin and Ketokonazole were used as references for antibacterial and antifungal studies. All the bacterial strains were incubated in Nutrient Broth (NB) at 37°C for 24 h and fungal isolates were incubated in PDA broth at 28°C for 2 to 3 days. The wells each of 5 mm in diameter were made in Muller-Hinton agar using cork borer. The stock solution was

TABLE 6 Fluorescence spectral parameters of the ligand and metal(II) complexes

Compounds	λ_{exc} (nm)	$\lambda_{em} (nm)$	Quantum yield	
Ligand	496	501	0.29	
$[Cu(L)H_2O](1)$	535	540	0.72	
$[Ni(L)H_2O]$ (2)	538	544	0.96	
$[Co(L)H_2O]$ (3)	465	471	0.95	

prepared in 10^{-3} mL⁻¹ concentration (DMSO) and then 100μ L of the solution was transferred into each well. The plates were incubated for 24 h at 37°C and examined for clear inhibition zone around the well. The inhibition zone was developed and it was measured. Zone of inhibition of the investigated compounds against the bacteria and fungi are summarized in Table 8. The biospectrum of ligand and its metal complexes are shown in Figure 7.

All the tested compounds showed a remarkable biological activity against different types of bacteria and fungi species. On comparing the biological activity of the ligand and its metal(II) complexes with the standard, it is inferred that, the metal(II) complexes have shown potential antibacterial activity against all the bacterial strains. In case of antifungal activity, all the metal(II) complexes were found to be highly active than the free ligand. In general, all the metal(II) complexes possess higher

 TABLE 7

 Thermal analysis data of metal(II) complexes

Metal complex	Temperature, (°C)	% Weight loss	Decomposition product	
[Ni(L)H ₂ O]	30–140	3.57	H ₂ O	
	320-506	53.17	$2(C_8H_8NO)$	
	432-685	30.75	$C_9N_3H_5$	
	>685	residue	NiO	
$[Cu(L)H_2O]$	90-186	3.59	H_2O	
	276-318	54.22	$2(C_8H_8NO)$	
	318-800	31.07	$C_9N_3H_5$	
	>800	residue	CuO	



FIG. 7. Graphical representation of antimicrobial activity of ligand and metal(II) complexes.

antimicrobial activity than ligand and this may be due to the change in structure due to coordination and chelation tends to make metal complexes act as more powerful and potent bacteriostatic agents, thus inhibiting the growth of the microorganisms.^[48] Moreover, coordination reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups within the chelate ring system formed during the coordination.^[49] This process, in turn increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the microorganism, thus destroying them more aggressively. The mode of action of ligand and complexes may involve the formation of a hydrogen bond through the azomethine nitrogen

TABLE 8 Antimicrobial activity data of the ligand and metal(II) complexes

		· · · ·						
		Zone of inhibition (mm)*						
Compounds	S. aureus	S. typhi	E. coli	B. subtilis	C. albicans	A. niger		
Ligand	10	10	14	15	14	13		
$[Cu(L)H_2O]$ (1)	12	11	16	16	18	15		
$[Ni(L)H_2O]$ (2)	16	13	17	17	21	20		
$[Co(L)H_2O]$ (3)	15	11	16	17	20	16		
$[Zn(L)H_2O]$ (4)	13	12	14	R	17	19		
Standard	17	14	20	18	25	23		

*The test was done using 10^{-3} M concentration of synthesized compounds by well diffusion technique. The values are mean of three replications.

atom with the active centre of the cell constituents resulting in interference with normal cell process.^[50]

CONCLUSIONS

The metal(II) complexes of Cu(II), Ni(II), Co(II), and Zn(II) obtained from 2,4-bis(1-(2-hydroxyphenyl)ethylideneamino)-6-phenyl-1,3,5-triazine were synthesized and characterized by spectral and analytical methods. The spectral and analytical data confirm the bonding of ligand to metal(II) ions and the octahedral geometry of metal(II) complexes. The ligand and its metal(II) complexes were found to exhibit appreciable nonlinear optical property in comparison with KDP and urea, hence the compound can be studied for optical sensing material. Ligand and its metal(II) complexes are fluorescent in nature. Most of the metal chelates show better antimicrobial activity than ligand, particularly Ni(II) complexes.

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