

Research Article

Synthesis, Spectroscopic Characterization, and Biological Activities of Metal Complexes of 4-((4-Chlorophenyl)diazenyl)-2-((*p*-tolylimino)methyl)phenol

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Azo Schiff base complexes of VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized from 4-((4-chlorophenyl)diazenyl)-2-((*p*-tolylimino)methyl)phenol (CDTMP). The nature of bonding and the structural features of the complexes have been deduced from elemental analysis, molar conductance, magnetic susceptibility measurements, IR, UV-Vis, ¹H-NMR, EPR, mass, SEM, and fluorescence spectral studies. Spectroscopic and other analytical studies reveal square-planar geometry for copper, square-pyramidal geometry for oxovanadium, and octahedral geometry for other complexes. The EPR spectra of copper(II) complex in DMSO at 300 K and 77 K were recorded, and its salient features are reported. Antimicrobial studies against several microorganisms indicate that the complexes are more potent bactericides and fungicides than the ligand. The electrochemical behavior of the copper(II) complex was studied by cyclic voltammetry. All the synthesized compounds can serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The second harmonic conversion efficiency of the synthesized azo Schiff base was found to be higher than that of urea and KDP (potassium dihydrogen phosphate). SEM image of copper(II) complex implies the crystalline state and surface morphology of the complex.

1. Introduction

Azo compounds are the largest class of industrially synthesized organic dyes due to their versatile application in various fields, such as dyeing textile fiber, biomedical studies, and advanced application in organic synthesis and high technology areas such as laser, liquid crystalline displays, and electrooptical devices [1]. The oxidation-reduction behaviors of these compounds play an important role in its biological activity [2, 3]. The architectural beauty of these coordination complexes arises due to the interesting ligand systems containing different donor sites [4]. Azomethine derivatives are widely applied in biological systems and dyes [5]. In recent years, there is considerable interest in the synthesis and modeling of new organic materials with optical nonlinearities because of their potential use in development of photonic devices [6].

Azo ligands containing salicylaldehyde-based side chains can be used in the production of chemical sensors because they show a significant change of color of the solution and maxima of the absorption band when they interact with transition metal atoms. Transition metal-complexed azomethine compounds have been studied in great detail in the literature for understanding their optical and electronic properties, structure-redox relationships, and mesogenic characteristics [7, 8]. It could be expected that design and synthesis of transition metal complexes derived from azo Schiff base ligands might be a possible way to obtain the applicable nonlinear optical materials [9]. In particular *p*-nitroaniline, *m*-nitroaniline, *p*-nitro-*N,N*-dimethylaniline, and other similar chromophores were found to exhibit rather large NLO properties [10]. Although many Schiff bases derived from aromatic aldehydes and amines and their corresponding metal complexes have been extensively studied, relatively few

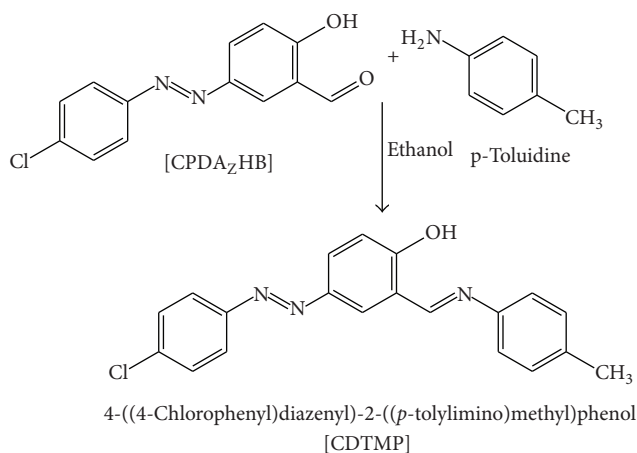
azo-linked Schiff bases and their metal complexes have been reported [11, 12].

1.1. Scope. Design and synthesis of transition metal complexes derived from azo Schiff base ligands might be a possible way to obtain the applicable nonlinear optical materials, endowed with antiviral activity, optical activity, electronic activity, and so forth. The electron-pull and electron-push substituents on the benzene rings have much influence on the electronic structure of azo compounds to possess a larger nonlinear optical susceptibility. Because of the importance of azo-containing compounds and our interest in syntheses of nonlinear optical materials, we report herein the syntheses, spectroscopic studies and biological activities of azo Schiff base derivative 4-((4-chlorophenyl)diazenyl)-2-((*p*-tolylimino)methyl)phenol (CDTMP) which have donor and acceptor property due to electron-pull and electron-push substituents (Cl and CH₃ groups) and their VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes. We are also interested to examine the antimicrobial, fluorescence, NLO, and redox properties of these azo Schiff base compounds.

2. Experimental

The chemicals and solvents were purified by standard methods. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. Molar conductance of the complexes was measured in DMSO at room temperature using a Systronic Conductivity Bridge 304. Magnetic susceptibility of the complexes was performed on a Sherwood MSB mark 1 Gouy balance. Infrared spectral studies were carried out on a Shimadzu FT IR 8000 spectrophotometer using KBr discs. UV-Vis spectra were obtained using a Thermo Spectronic 6 Hexios α , and fluorescence spectra were determined with an Elico SL174 Spectrofluorometer. NMR spectra were recorded on Bruker DRX-300, 300 MHz NMR Spectrometer using TMS as reference. EPR spectra of the Cu(II) and VO(II) complexes were recorded in Varian E-112 machine at 300 and 77 K using TCNE (Tetracyanoethylene) as the g-marker. Cyclic voltammetric measurements for Cu(II) and VO(II) complexes in DMSO were carried out on Electrochemical Analyzer CH Instruments (USA) using a three-electrode cell containing an Ag/AgCl reference electrode, Pt wire auxiliary electrode, and glassy carbon-working electrode with tetrabutylammonium perchlorate as supporting electrolyte. Electron-ionization (EI) mass spectra were recorded by JEOL-GC Mass Spectrometer MATE-2.

2.1. Synthesis of Azo Ligand (CDTMP). The diazonium salt, 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (CPDA_ZHB) [13] (2.3 g, 8.7 mmol), was condensed with *p*-toluidine (0.94 g, 8.7 mmol) in ethanol and refluxed for 3 h. After the reaction was over, the reaction mixture was concentrated to one-half of the volume and refrigerated for one day. The obtained bright orange-colour solid product was filtered and recrystallized from ethanol. The yield obtained was 77%, m.p. 212°C. (Scheme 1).



SCHEME 1: Synthesis of azo Schiff base ligand.

2.2. Synthesis of Metal(II) Complexes. To a solution of (0.70 g, 2 mmol) 4-((4-chlorophenyl)diazenyl)-2-((*p*-tolylimino)methyl)phenol (CDTMP) in 20 mL ethanol was added 1 mmol of metal salts (VOSO₄·5H₂O, MnCl₂·4H₂O, CoCl₂·6H₂O, NiCl₂·6H₂O, CuCl₂·2H₂O, and ZnCl₂). The solution was stirred for 1 h at room temperature, and the coloured complexes precipitated upon concentration was filtered, washed with ethanol, and dried under vacuum. The oxovanadium complex was synthesized from the ligand and oxovanadium sulfate by adopting the above method under reflux for 3 h and concentrating the solution through rotoevaporation. The yield obtained was 60–70%.

3. Results and Discussion

The analytical data and physical properties of CDTMP and metal(II) complexes are presented in Table 1. The complexes are partially soluble in ethanol, chloroform, and acetonitrile but soluble in polar coordinating solvents such as DMF and DMSO. The molar conductivities of all the complexes are in the 8.9–11.2 Ω⁻¹ cm² mol⁻¹ range indicating a nonelectrolytic nature. The obtained data showed that the stoichiometry of the chelates is 1 : 2 (M : Ligand) and the analytical data of the complexes are in good agreement with the general formula ML₂ for Cu(II), VO(II), and ML₂·2H₂O for Mn(II), Ni(II), Co(II), and Zn(II) complexes.

3.1. Mass Spectral Studies. The mass spectra of the ligand CDTMP (L₁) and its complexes were recorded at room temperature, and they are used to compare their stoichiometry composition. The azo Schiff base shows a molecular ion peak at 349 *m/z*. Molecular ion peak for the nickel complex observed at 790 *m/z* confirms the stoichiometry of metal chelates as [ML₂·2H₂O] type, whereas the molecular ion peak for the Cu(II) and VO(II) complexes observed at *m/z* 759, 764 confirms the stoichiometry of metal chelates as [ML₂] type. The mass spectra of the ligand and its nickel(II) complex are shown in Figure 1.

TABLE 1: Physical characterization, analytical and molar conductance data of the ligand (CDTMP, **L**₁), and its metal(II) complexes.

Compound	FW (g/mol ⁻¹)	Found (Calcd) (%)				m.p. (°C)	Λ_M (Ω ⁻¹ cm ² mol ⁻¹)
		M	C	H	N		
C ₂₀ H ₁₆ ClN ₃ O (CDTMP) (L ₁)	349.10	—	68.69 (68.67)	4.58 (4.61)	12.00 (12.02)	212–214	—
[VO(CDTMP) ₂] (L ₁ 1)	763.84	6.62 (6.66)	62.83 (62.84)	3.90 (3.92)	10.97 (10.99)	285–287	10.8
[Mn(CDTMP) ₂ ·2H ₂ O] (L ₁ 2)	787.16	6.98 (6.97)	60.94 (60.92)	4.36 (4.35)	10.63 (10.66)	282–284	8.9
[Co(CDTMP) ₂ ·2H ₂ O] (L ₁ 3)	791.15	7.45 (7.44)	60.59 (60.61)	4.30 (4.32)	10.61 (10.60)	312–314	11.9
[Ni(CDTMP) ₂ ·2H ₂ O] (L ₁ 4)	790.14	7.40 (7.41)	60.61 (60.63)	4.31 (4.33)	10.64 (10.61)	287–289	9.6
[Cu(CDTMP) ₂] (L ₁ 5)	759.11	8.33 (8.35)	63.13 (63.12)	3.91 (3.94)	11.03 (11.04)	298–300	10.5
[Zn(CDTMP) ₂ ·2H ₂ O] (L ₁ 6)	796.07	8.19 (8.18)	60.12 (60.13)	4.27 (4.29)	10.53 (10.52)	305–307	9.9

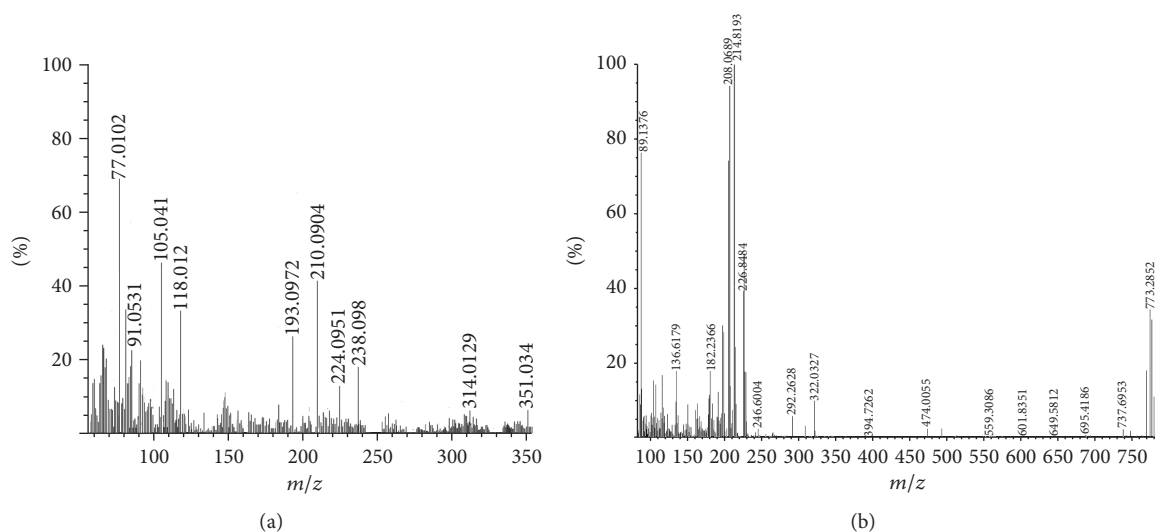
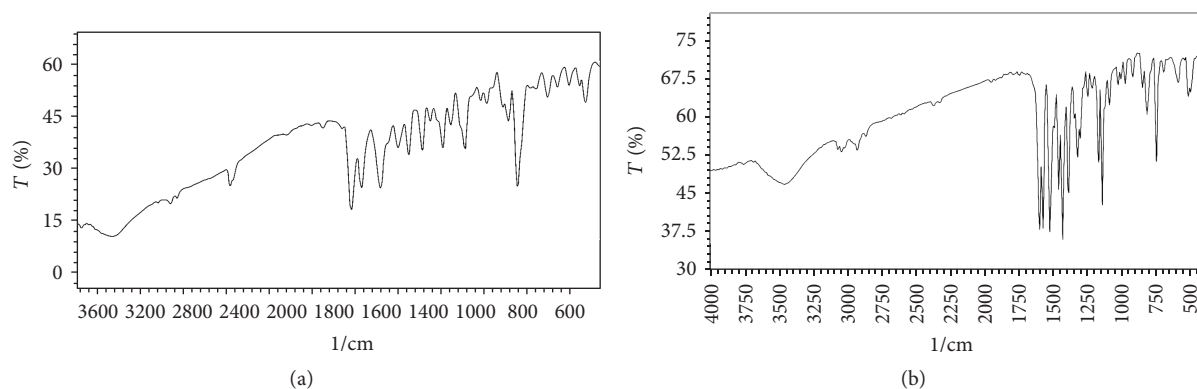
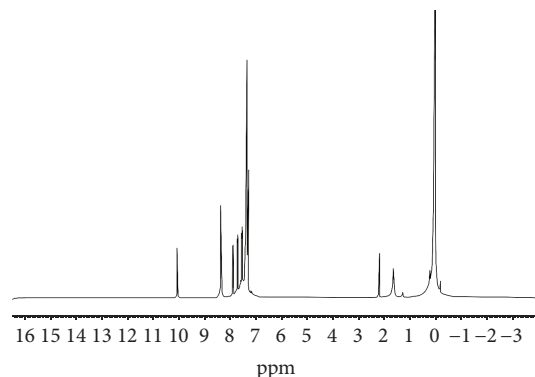
FIGURE 1: Mass spectra of (a) [CDTMP], (b) [Ni(CDTMP)₂·2H₂O].FIGURE 2: IR spectra of (a) [CDTMP], (b) [Co(CDTMP)₂·2H₂O].

TABLE 2: IR spectral data of [CDTMP] and its metal(II) complexes (cm^{-1}).

Compound	ν (C=N)	ν (C-O) phenolic	ν (N=N)	ν (M-N)	ν (M-O)
$\text{C}_{20}\text{H}_{16}\text{ClN}_3\text{O}$ (CDTMP) (L₁)	1616	1284	1483	—	—
$[\text{VO}(\text{CDTMP})_2]$ (L₁1)	1607	1309	1482	536	461
$[\text{Mn}(\text{CDTMP})_2 \cdot 2\text{H}_2\text{O}]$ (L₁2)	1601	1312	1483	567	452
$[\text{Co}(\text{CDTMP})_2 \cdot 2\text{H}_2\text{O}]$ (L₁3)	1602	1305	1481	594	430
$[\text{Ni}(\text{CDTMP})_2 \cdot 2\text{H}_2\text{O}]$ (L₁4)	1608	1317	1483	590	425
$[\text{Cu}(\text{CDTMP})_2]$ (L₁5)	1606	1300	1482	584	490
$[\text{Zn}(\text{CDTMP})_2 \cdot 2\text{H}_2\text{O}]$ (L₁6)	1600	1295	1482	525	450

3.2. IR Spectral Studies. The characteristic IR spectral data of the ligand and its complexes are given in Table 2. The detected band at 1616 cm^{-1} is assigned to the stretching vibration of the azomethine group of the ligand CDTMP. This band is shifted in the complexes toward lower frequencies ($1608\text{--}1600\text{ cm}^{-1}$) because of the participation of the nitrogen atom to coordinate with metal ion. This fact can be explained by the withdrawing of electrons from nitrogen atom to the metal ion due to coordination process [14]. The bands around 3130 cm^{-1} and 1284 cm^{-1} are assigned to (O-H) vibration and the phenolic C-O vibration, respectively. However, in the spectra of the metal complexes the C-O bands underwent a shift towards higher frequencies $\sim 33\text{ cm}^{-1}$, and this shift confirms the participation of oxygen in the C-O-M bond. Mn(II), Co(II), Ni(II), and Zn(II) complexes show a broadband at $\sim 3400\text{ cm}^{-1}$ due to the vibrations of coordinated water molecules [15]. The band at 1483 cm^{-1} is assigned to the stretching vibration of the diazo group of the azo-linked Schiff base ligand, and the spectra of the complexes did not show any frequency shift of the -N=N- band, which may be explained by nonparticipation of azo group in complex formation [16]. The band of medium intensity observed for the complexes in the region $525\text{--}594\text{ cm}^{-1}$ is attributed to ν (M-N) and in the region $425\text{--}490\text{ cm}^{-1}$ to ν (M-O) [17]. All the IR data of the Schiff base and its metal complexes imply that the Schiff base behaves as bidentate and is bonded to the metal ion through phenolic oxygen and imino nitrogen of azomethine group. The IR spectra of the ligand and cobalt complex are depicted in Figure 2.

3.3. ^1H -NMR Spectral Studies. The ^1H -NMR spectrum of CDTMP (**L₁**) recorded in CDCl_3 is assigned as follows: the characteristic singlet at (8.23δ) is due to the azomethine proton ($-\text{CH}=\text{N}$), and multiplets around ($7.4\text{--}7.8\delta$) are assigned to aromatic protons, and signal at (2.31δ) is ascribed to methyl group. A singlet at (10.1δ) is attributed to the phenolic -OH of the Schiff base. The absence of this peak noted for the zinc(II) complex indicates deprotonation of the ligand and coordination to the metal. The azomethine protons signal in the spectrum of the zinc complex is shifted downfield (8.31δ) compared to the free ligand, suggesting deshielding of the azomethine group due to the coordination with metal ion. There is no appreciable change in other signals

FIGURE 3: ^1H NMR spectrum of [CDTMP].

of this complex. ^1H NMR spectrum of CDTMP is shown in Figure 3.

3.4. Electronic Spectral and Magnetic Susceptibility Studies. The electronic spectra of CDTMP (**L₁**) and its complexes were recorded in DMSO. The absorption spectrum of the ligand shows strong peaks at 26100 and 33670 cm^{-1} which may be assigned to $n \rightarrow \pi^*$ (transitions of the $-\text{CH}=\text{N}$ - and $-\text{N}=\text{N}-$ groups) and $\pi \rightarrow \pi^*$ (transition of $-\text{N}=\text{N}-$ azo group) transitions, respectively. The spectral data of the ligand and its complexes with molar extinction coefficient or molar absorption coefficient ϵ ($\text{L mol}^{-1}\text{ cm}^{-1}$) are calculated and given in Table 4.

The UV-Vis spectrum of the vanadyl(II) complex (**L₁1**) exhibits three d-d bands observed at 12013 , 17182 , and 24128 cm^{-1} assignable to $^2\text{B}_2 \rightarrow ^2\text{E}$, $^2\text{B}_2 \rightarrow ^2\text{B}_1$, and $^2\text{B}_2 \rightarrow ^2\text{A}_1$ transitions which are the characteristic of square-pyramidal geometry, and the magnetic moment value 1.75 B.M. [18] and the molar extinction coefficient (ϵ) values also support the geometry. The electronic absorption spectrum of the Co(II) complex (**L₁3**) exhibits three d-d bands at 9267 cm^{-1} , 11560 cm^{-1} , and 18115 cm^{-1} assignable to $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{F})$ (ν_1), $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{A}_{2g}(\text{F})$ (ν_2), and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}(\text{P})$ (ν_3) transitions [19], respectively, and the magnetic moment value of the cobalt(II) complex 4.82 B.M. confirms the octahedral geometry [20]. The molar intensities are in the range of hundreds indicating the strong metal-ligand interactions.

TABLE 3

For Co(II) complexes	For Ni(II) complexes
$10Dq = 1/2[(2v_1 - v_3) + (v_3^2 + v_1v_3 - v_1^2)^{1/2}]$	$10Dq = v_1$
$15B = v_3 - 2v_1 + 10Dq$	$15B = (v_2 + v_3) - 3v_1$
$\beta = B/B_0$ [B_0 (free ion) = 971]	$\beta = B/B_0$ [B_0 (free ion) = 1030]
$\beta_0 = (1 - \beta) \times 100$	$\beta_0 = (1 - \beta) \times 100$

TABLE 4: Electronic spectral data of [CDTMP] and its metal(II) complexes.

Compound	λ_{\max} (cm ⁻¹) ϵ (L mol ⁻¹ cm ⁻¹)	Transition	Geometry	μ_{eff} (B.M.)
CDTMP (L₁)	26100 (610) 33670 (5900)	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	—	—
[VO(CDTMP) ₂] (L₁1)	12013 (121) 17182 (234) 24128 (510)	${}^2B_2 \rightarrow {}^2E$ ${}^2B_2 \rightarrow {}^2B_1$ ${}^2B_2 \rightarrow {}^2A_1$	Square pyramidal	1.75
[Co(CDTMP) ₂ ·2H ₂ O] (L₁3)	9267 (199) 11560 (175) 18115 (392)	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$	Octahedral	4.82
[Ni(CDTMP) ₂ ·2H ₂ O] (L₁4)	10384 (156) 15822 (113) 22883 (119)	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	Octahedral	3.02
[Cu(CDTMP) ₂] (L₁5)	14265 (1100) 22573 (1800) 25706 (1845)	${}^2B_{1g} \rightarrow {}^2A_{1g}$ INCT* INCT	Square planar	2.01

* Intraligand charge transfer.

The nickel(II) complex (**L₁4**) exhibits three d-d bands at 10384, 15822, and 22883 cm⁻¹, due to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ [ν_1], ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ [ν_2], and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ [ν_3] transitions which arises from an octahedral structure [21]. The Ni(II) complex reported has magnetic moment of 3.02 B.M. which indicates that the Ni(II) complex is six coordinate and probably octahedral [22, 23]. The absorption at 14265 cm⁻¹ with high molar intensity (1100 L mol⁻¹ cm⁻¹) of copper(II) complex (**L₁5**) is tentatively assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition suggesting square planar geometry [24]. An additional band appears at 22573 and 25706 cm⁻¹ which may be due to intraligand charge transfer (INCT) in the UV region, and the molar extinction coefficient (1800, 1845 L mol⁻¹ cm⁻¹) of charge transfer transitions is higher than the d-d transition. The magnetic moment value 2.01 B.M. falls within the range normally observed for square planar Cu(II) complexes [25].

The Zn(II) complex (**L₁6**) has been found to be diamagnetic in nature. On the basis of analytical, conductance, and spectral data, the Zn(II) complex of CDTMP is assigned to octahedral geometry [26]. The Mn(II) complex (**L₁2**) under study has the magnetic moment value of 5.84 B.M. which supports an octahedral geometry around the metal ion [27]. The ligand-field-splitting energy (10Dq), interelectronic repulsion parameter (B), and covalency factor (nephelauxetic ratio) (β) for the octahedral Co(II) and Ni(II) complexes have been calculated using the secular equation given by Konig are shown in Table 3 [28].

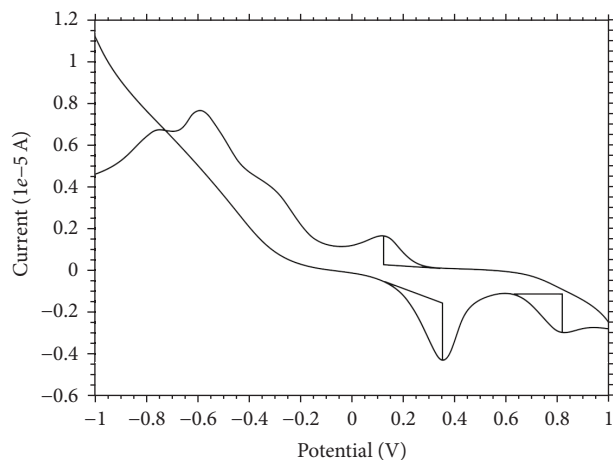
The ligand-field parameters of Ni(II) and Co(II) complexes are shown in Table 5, and the values support the proposed geometry for the synthesized Ni(II) and Co(II) octahedral complexes. The covalent factor β equal to B/B' for the complexes is less than one suggesting considerable amount of covalent character of the metal-ligand bonds.

3.5. Electrochemical Behavior. The redox behavior of the copper(II) complex (**L₁5**) was performed in DMSO solution at room temperature with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte; glassy carbon as working electrode; Pt wire as auxiliary electrode; Ag/AgCl as reference electrode in order to monitor spectral and structural changes accompanying electron transfer. The copper(II) complex exhibited one-step reduction peak at 0.122 V and two oxidation peaks at 0.812 and 0.352 V at the scan rate of 100 mV as shown in Figure 4. It has been observed that the E_{pc} and E_{pa} values change with scan rate as shown in Table 6. The ΔE_p values increase with increase in scan rate and is found to be greater than 400 mV which indicates that the nature of the electron transfer process is irreversible [29, 30].

3.6. EPR Spectral Studies. The EPR spectrum of the copper(II) complex (**L₁5**) was recorded at 300 K and 77 K, and the spin Hamiltonian parameters of the Cu(II) complex are listed in Table 7. The observed spectral parameters for this compound are $g_{\perp} = 2.07$, $g_{\parallel} = 2.15$, and $g_{iso} = 2.09$ which are evident that the unpaired electron lies predominantly

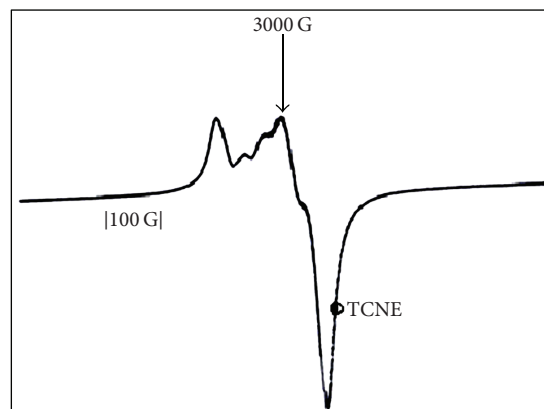
TABLE 5: Electronic parameters of Ni(II) and Co(II) complexes.

Compound	ν_2/ν_1	B (cm ⁻¹)	β	β°	10Dq (cm ⁻¹)
[Co(CDTMP) ₂ ·2H ₂ O] (L ₁ 3)	1.25	717	0.74	26	10335
[Ni(CDTMP) ₂ ·2H ₂ O] (L ₁ 4)	1.52	567	0.55	45	10384

FIGURE 4: Cyclic voltammogram of [Cu(CDTMP)₂] in DMSO.

in the $d_{x^2-y^2}$ orbital as $g_{\parallel} > g_{\perp} > g_e$, and this shows the characteristic of square planar geometry [31]. The g_{iso} value is less than 2.3 indicating the covalent character of the metal-ligand bond [32]. In the axial spectra, the g -values are related with exchange interaction coupling constant (G) by the expression $G = g_{\parallel} - 2.0023/g_{\perp} - 2.0023$. According to Matsubayashi [33], if the value of G is larger than four, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or slightly misaligned. If its value is less than four, the exchange interaction is considerable, and the local tetragonal axes are misaligned. For present copper complex, the G value is 2.1, which suggests that the exchange interaction is considerable, and the local tetragonal axes are misaligned. The α^2 values fall in the range 0.72 indicating the presence of appreciable in-plane covalency [34]. The magnetic moment of the copper(II) complex calculated using the relation $\mu^2 = 3/4|g|^2$ is found to be 2.01 B.M., and the orbital reduction factors K_{\parallel} and K_{\perp} were estimated from the expression $K_{\parallel} = (g_{\parallel} - 2.0023)\Delta E/8\lambda$, $K_{\perp} = (g_{\perp} - 2.0023)\Delta E/2\lambda$, $\lambda = -828$ cm⁻¹ (spin-orbit coupling constant for the free ion). For this complex, the observed order K_{\parallel} (0.32) < K_{\perp} (0.46) implying the presence of in-plane π -bonding. The EPR spectrum is shown in Figure 5.

Based on the previous discussions such as elemental analysis, molar conductance, EI mass, IR, magnetic susceptibility measurements, and electronic and EPR spectral studies, the following structure may be proposed for the complexes. The synthesized azo-azomethine ligand was coordinated to the metal ion through the azomethine nitrogen and oxygen atom of the hydroxyl group in salicylaldehyde. The geometry around the Cu(II) complex is square planar, VO(II) is square

FIGURE 5: EPR spectrum of [Cu(CDTMP)₂].

pyramidal, and the other metal(II) ion is in octahedral geometry and depicted in Scheme 2.

3.7. Biological Activities. The antimicrobial activity of the azo Schiff base compound CDTMP and its complexes were tested *in vitro* by the well diffusion method [35] against the bacterial strains (*Pseudomonas aeruginosa*, *Escherichia coli*, and *Staphylococcus aureus*) and the fungal strains (*Candida albicans* and *Aspergillus niger*). Amikacin and Ketoconazole were used as reference compounds for antibacterial and antifungal activities, respectively. Stock solution (10⁻³ M) was prepared by dissolving the compounds in DMSO. The diameter of the inhibition zones was measured in millimeters. Antimicrobial activities were performed in triplicate, and the average was taken as the final reading. The growth of inhibition zones after incubation is shown in Table 8 and Figure 6.

The observed result indicates that most of the complexes have higher activity than the free ligand. Such increased activity of the complexes can be explained on the basis of Overtone's concept [36] and Tweedy's Chelation theory [37]. Among the complexes, copper complex was found to be the most active and could inhibit the fungal growth at higher concentration. The greater activity of Cu(II) complex can be explained on the basis of their particle size [38]. From scanning electron microscopy it is clear that copper complex has nanoparticle size. This smaller size may be the reason for increased biological activity. It has been suggested that the mode of action of the compounds may involve the formation of hydrogen bond through azomethine group with the active center of cell constituents resulting in interference with normal cell process. These complexes also disturb the respiration process of the cell and thus block the synthesis of the proteins that restricts further growth of the organism.

TABLE 6: Redox potential of [Cu(CDTMP)₂] at different scan rates.

Compound	Scan rate (mV)	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)
[Cu(CDTMP) ₂] (L₁5)	100	0.122	0.812	0.690
			0.352	
	150	0.105	0.862	0.757
			0.409	
	200	0.092	0.871	0.779

TABLE 7: EPR spectral parameters of [Cu(CDTMP)₂].

Compound	g_{\parallel}	g_{\perp}	g_{iso}	α^2	β^2	$\frac{A_{\parallel}}{10^{-4} \text{ cm}^{-1}}$	$\frac{A_{\perp}}{10^{-4} \text{ cm}^{-1}}$	$\frac{A_{iso}}{10^{-4} \text{ cm}^{-1}}$	$g_{\parallel}/A_{\parallel} \text{ cm}$	K_{\parallel}	K_{\perp}	μ (B.M.)
[Cu(CDTMP) ₂] (L₁5)	2.15	2.07	2.09	0.72	0.28	175	98	124	122	0.32	0.46	2.01

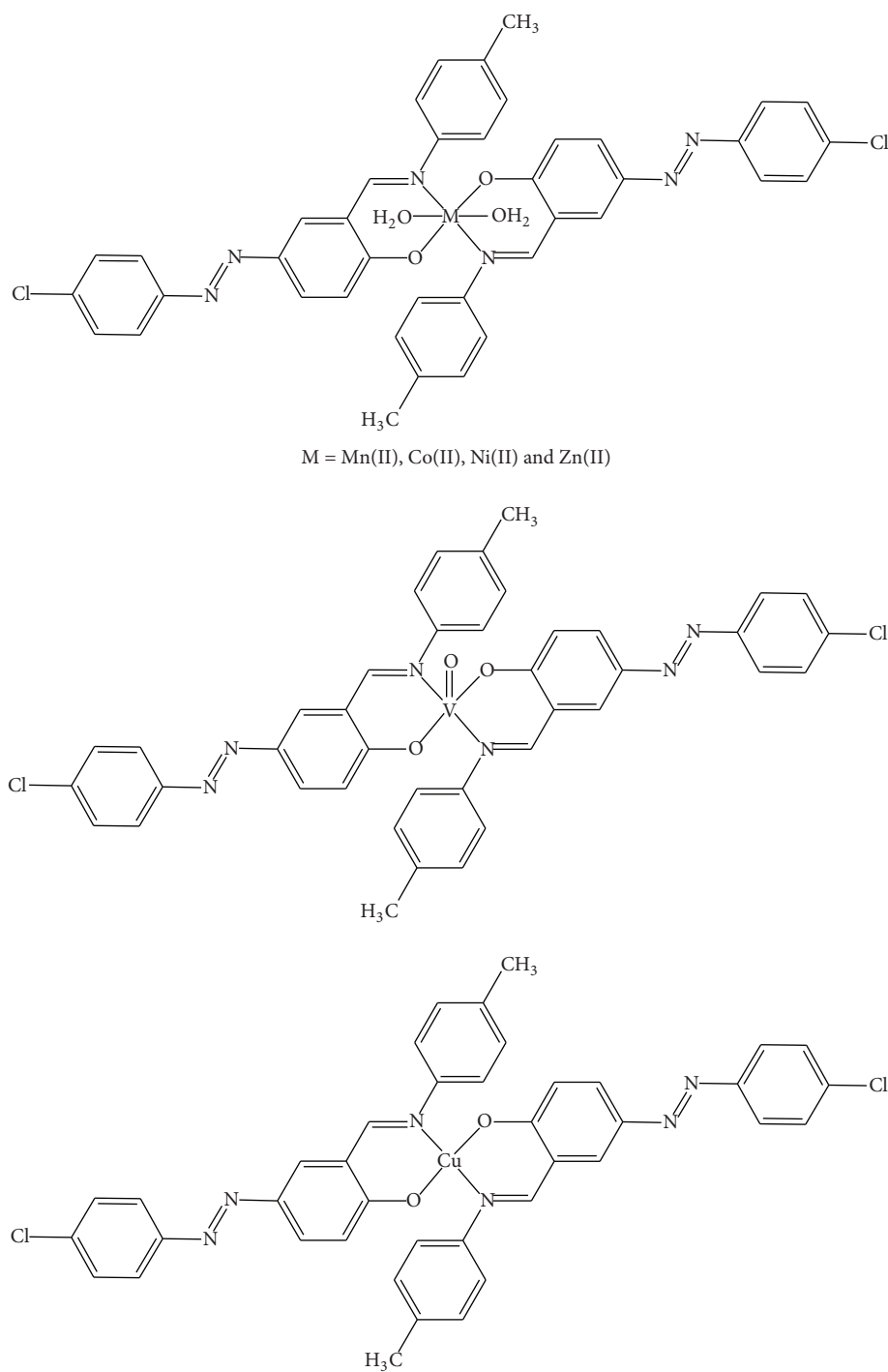
TABLE 8: The *in vitro* antimicrobial activity of [CDTMP] and its metal(II) complexes*.

Compound	Concentration ($\mu\text{g mL}^{-1}$)	Zone of inhibition (in mm)				
		<i>E. coli</i>	<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>A. niger</i>	<i>C. albicans</i>
CDTMP (L₁)	5	9	9	10	R	8
	10	13	10	12	9	12
	15	10	12	R	11	9
[VO(CDTMP) ₂] (L₁1)	5	16	R	14	15	16
	10	19	20	19	20	19
	15	25	27	22	26	27
[Mn(CDTMP) ₂ ·2H ₂ O] (L₁2)	5	8	10	18	9	R
	10	14	21	R	11	R
	15	R	R	11	R	R
[Co(CDTMP) ₂ ·2H ₂ O] (L₁3)	5	R	18	16	10	11
	10	19	25	24	12	18
	15	24	29	27	21	23
[Ni(CDTMP) ₂ ·2H ₂ O] (L₁4)	5	R	12	R	14	11
	10	17	21	17	17	14
	15	10	24	24	25	20
[Cu(CDTMP) ₂] (L₁5)	5	21	20	21	20	23
	10	26	31	23	31	25
	15	27	33	26	32	29
[Zn(CDTMP) ₂ ·2H ₂ O] (L₁6)	5	7	5	7	7	5
	10	12	10	10	10	7
	15	15	20	15	12	15
Standard	5	5	5	5	2	2
	10	7	7	7	5	5
	15	9	9	9	7	7

Standard (Amikacin and Ketoconazole). * Zone of inhibition in mm. Each value observed is within the error limits of ± 2 . R: resistant.

TABLE 9: Fluorescence parameters of [CDTMP] and its metal(II) complexes.

Compound	Excitation wavelength λ_{\max} (nm)	Emission wavelength λ_{\max} (nm)	Quantum yield (ϕ_f)
CDTMP (L₁)	353	376	0.721
[VO(CDTMP) ₂] (L₁1)	799	804	0.880
[Co(CDTMP) ₂ ·2H ₂ O] (L₁3)	440	462	0.994
[Ni(CDTMP) ₂ ·2H ₂ O] (L₁4)	566	601	0.053
[Cu(CDTMP) ₂] (L₁5)	426	496	0.062



SCHEME 2: Geometry of the metal(II) complexes.

3.8. Fluorescence Studies. The photoluminescence properties of CDTMP and their complexes were studied at room temperature, and the data are reported in Table 9. The excitation spectra of ligand show a maximum at 353 nm and an emission maximum at $\lambda_{\text{em}} = 376$ nm. The metal(II) complexes show strong fluorescence with high-quantum yield, and the

excitation at 426–799 nm gives an emission at 442–804 nm, assigned to $\pi-\pi^*$ intraligand fluorescence [39, 40]. Emission intensity of the metal(II) complexes is higher than that of free ligands, and the enhanced fluorescence efficiency of the complexes is attributed to coordination increasing the rigidity, thereby reducing energy loss by thermal vibration

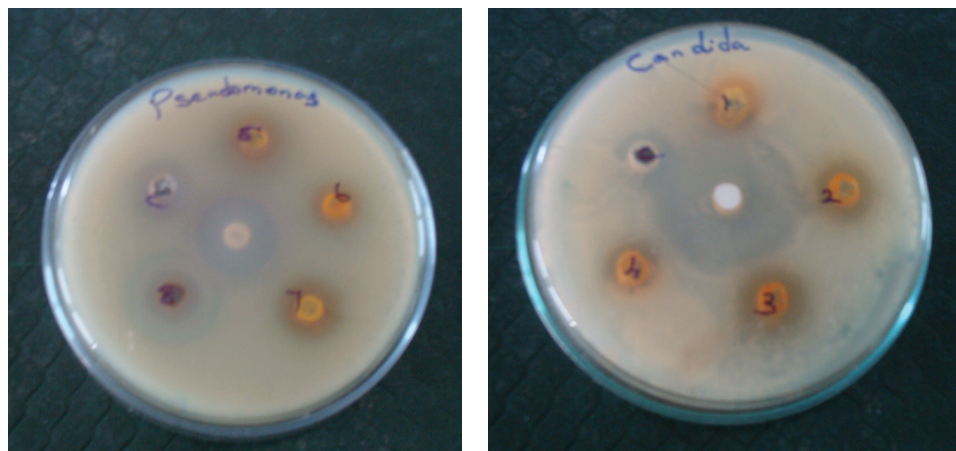


FIGURE 6: The inhibition zones formed for *Pseudomonas aeruginosa* and *Candida albicans*.

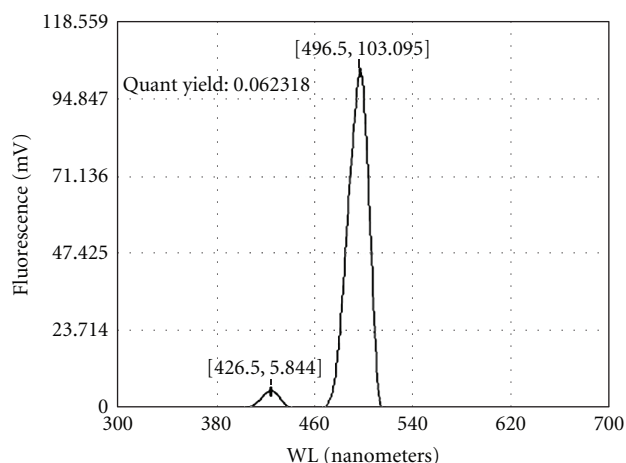


FIGURE 7: Fluorescence spectrum of $[\text{Cu}(\text{CDTMP})_2]$.

decay [41]. Introduction of the substituent on the azo ligand has an interesting effect on the intensity of emission spectra. The fluorescence quantum yields [42] of the ligand and its complexes were also obtained. From this fluorescence study it is evident that these azo compounds might possess potential molecular sensing or photoconductive applications. Fluorescence spectrum of copper(II) complex is depicted in Figure 7.

3.9. NLO Property. The recent recognition is that the organic materials with conjugated π -electron systems exhibit extremely large optical nonlinear responses, and this leads to rapid growth of interest in a field which is currently dominated by inorganic materials [43]. The SHG (second harmonic generation) efficiency of the azo compound (CDTMP) was determined by modified version of powder technique developed by Kurtz and Perry [44]. The efficiency of the sample was compared with microcrystalline powder of KDP and urea. The input energy used in this particular setup is 2.2 mJ/pulse. Azo Schiff base shows the better

second harmonic efficiency than urea and KDP. 4-((4-Chlorophenyl)diazanyl)-2-((*p*-tolylimino)methyl)phenol shows 1.6 and 3.9 times more activity than urea and KDP, respectively.

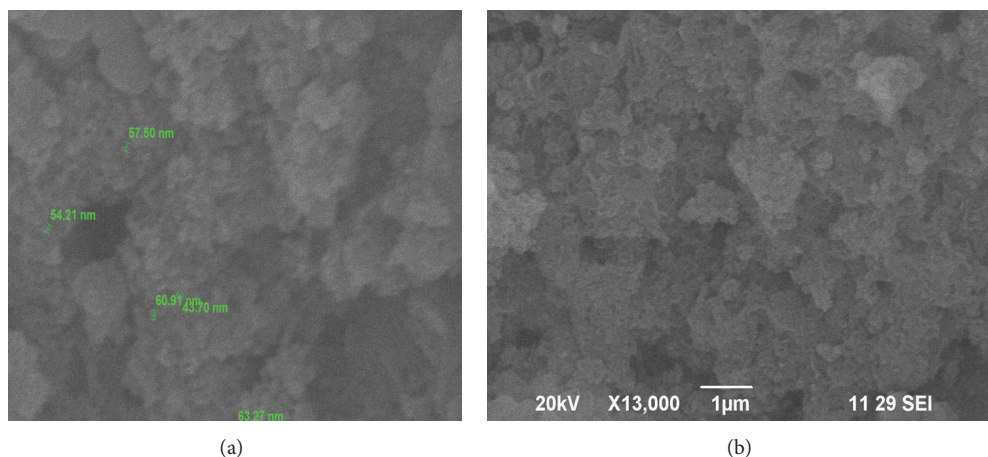
The electron-pull and electron-push substituents on the benzene rings have much influence on the electronic structure of azo compounds. The conjugative and induction effects of Cl atom as electron-pull groups and CH_3 as electron-push groups make electron density on the benzene rings change, and the band of $\text{N}=\text{N}$ become an effective electronic passage. The delocalized π -electron distribution of the azo dye makes it possible to possess a larger nonlinear optical susceptibility.

3.10. Scanning Electron Microscopy. The morphology and particle size of the Schiff base metal complex have been illustrated by the scanning electron micrograph (SEM). SEM uses a focused beam of high-energy electrons to generate a variety of signals from the surface of a solid specimen. The signals reveal information about the sample, including external morphology, topography, chemical composition, crystalline structure, and orientation of materials making up the sample.

Figure 8 depicts the SEM photograph of the synthesized Cu(II) complex. We noted that there is a uniform matrix of the synthesized complex in the pictograph and the image of copper complex shows a flower-like shape with 60 nm particle size, clearly indicating that the Cu(II) complex is amorphous in agreement with the powder XRD results. The smaller grain sizes found from XRD and SEM suggest that these complexes are polycrystalline with nanosized grains.

4. Conclusions

The azo Schiff base complexes of VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) obtained from 4-((4-chlorophenyl)diazanyl)-2-((*p*-tolylimino)methyl)phenol (CDTMP) were synthesized and characterized by spectral and analytical methods. Redox couple of the copper(II) complex was assigned as irreversible from their cyclic voltammetric data. CDTMP exhibits appreciable NLO

FIGURE 8: SEM images of $[\text{Cu}(\text{CDTMP})_2]$.

property in comparison with urea and KDP; hence the compound may be studied for optical sensing material. The ligand and all metal(II) complexes possess appreciable antibacterial and antifungal activities, and the copper(II) complex was found to be more potent than the other complexes due to the nanoparticle size. In general, all the synthesized compound can serve as potential photoactive materials, as indicated from their characteristic fluorescence properties. Based on these results, it could be proposed that these novel azo materials can be better accommodated for technological and pharmaceutical usage.

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