

Research Article

Synthesis, Characterization, and Biological Activity of Some Transition Metal Complexes Derived from Novel Hydrazone Azo Schiff Base Ligand

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A series of metal(II) complexes ML where M = VO(II), Co(II), Ni(II), Cu(II), and Zn(II) have been synthesized from azo Schiff base ligand (N'E)-N'-5-((4-chlorophenyl)diazanyl)-2-hydroxybenzylidene)-2-hydroxybenzohydrazide and characterized on the basis of elemental analyses, electronic, IR, and ¹H NMR spectra, magnetic susceptibility and also by aid of scanning electron microscopy (SEM), X-ray powder diffraction, fluorescence spectral studies, and molar conductivity measurements. Conductivity measurements reveal that the complexes are nonelectrolytes. Spectroscopy and other analytical studies reveal distorted square planar geometry for copper, square-pyramidal geometry for oxovanadium, and tetrahedral geometry for other complexes. Redox behavior of the copper(II) complex has been studied with cyclic voltammetry, and the biological activities of the ligand and metal complexes have been studied against several microorganisms by the well diffusion method. All synthesized compounds can serve as potential photoactive materials as indicated from their characteristic fluorescence properties. The second harmonic generation (SHG) efficiency of the ligand was measured and found to be higher than that of urea and KDP. The SEM image of the copper(II) complex implies that the size of the particles is 50 nm.

1. Introduction

Azo Schiff base metal complexes have been studied extensively for years due to the synthetic flexibilities of these Schiff base ligands and their selectivity as well as sensitivity towards the transition metal ions [1]. Among the ligand systems, hydrazide and hydrazones occupy special place because transition metal complexes of these ligands developed due to their chelating capability, structural flexibility, interesting electrical as well as magnetic properties [2, 3], and, nowadays, they are extensively being used for their promising applications in the treatment of several diseases and also been used as synthetic and analytical reagents [4], as polymer-coating pigment and fluorescent materials [5–9].

Moreover, these ligands exhibit keto-enol tautomerism [10–14] bearing unusual coordination numbers. In the present paper, we report the synthesis and characterization of VO(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of

azo Schiff base derived from the condensation of 5-(4-chloro-phenylazo)-2-hydroxy benzaldehyde with 2-hydroxybenzohydrazide in a mole ratio of (1 : 1), respectively, and, due to the rich chemistry of vanadium metal [15, 16], we also aimed to prepare and characterize the vanadyl complex of hydrazone derivative.

2. Experimental

The chemicals and solvents were purchased from Aldrich Chemical & Co., and the 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 mark1 Gouy balance. Infrared spectral studies were carried out on a Shimadzu FT IR 8000 spectrophotometer using

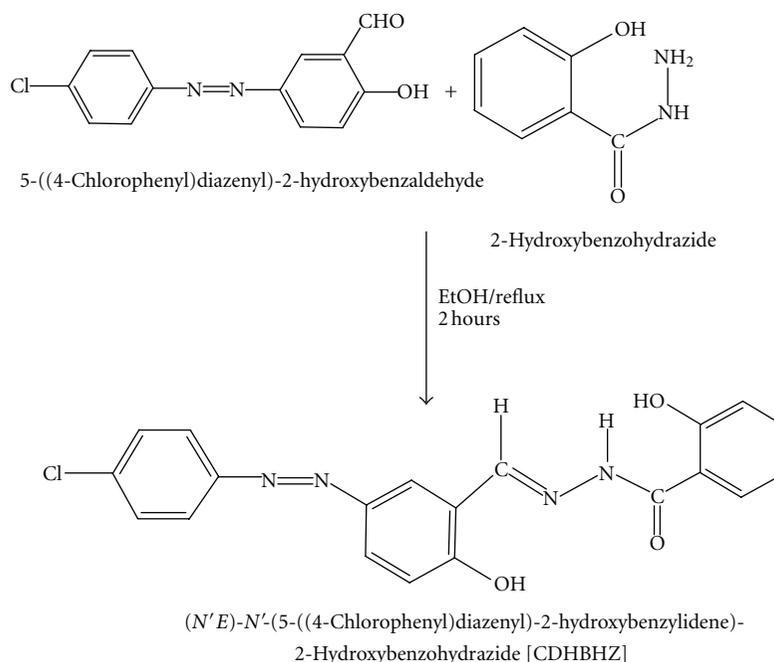


FIGURE 1: Synthesis of ligand (CDHBHZ).

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. ESR spectra of the Cu(II) complex were recorded in Varian E112 machine at 300 and 77 K using tetracyanoethylene (TCNE) as the g marker. Cyclic voltammetric measurement for Cu(II) complex in DMSO was carried out on an 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. The second-harmonic generation (SHG) conversion efficiency of the Schiff base ligand was determined by the modified version of powder technique in IISc, Bangalore. XRD of copper complex was recorded using OCPL/ARD/26. SEM images were recorded in a Hitachi SEM analyzer.

2.1. Preparation of Ligand (CDHBHZ). Azo Schiff base ligand (N'E)-N'-(5-((4-chlorophenyl)diazenyl)-2-hydroxybenzylidene)-2-hydroxybenzohydrazide (CDHBHZ) was prepared by adding equimolar amount of 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde [17] (1 mmol in 10 mL of ethanol) to 2-hydroxybenzohydrazide (1 mmol in 10 mL of ethanol). The mixture was refluxed while stirring for 2 hours. The formed solid product was filtered off, washed with ethanol several times followed by recrystallization from ethanol, and finally dried under vacuum (Figure 1).

2.2. Preparation of Metal Complexes. The metal complexes were prepared by adding equimolar amounts of salts of

VO(II), Co(II), Ni(II), Cu(II), and Zn(II) (1 mmol in 20 mL of ethanol) to the azo Schiff base ligand CDHBHZ (1 mmol in 25 mL of ethanol) in the presence of 1 mmol of NaOH. The mixture was refluxed while stirring for one hour, and the resulting solid complexes were filtered off, washed several times with ethanol, followed by drying under vacuum (Figure 2).

2.3. Antimicrobial Study. The biological activities of synthesized azo Schiff base and their metal complexes have been studied for their antibacterial and antifungal activities by well diffusion method, and the stock solution (0.001 mol) was prepared by dissolving the compounds in DMSO, and the solutions were serially diluted to find the minimum inhibitory concentration (MIC) values ($\mu\text{g mL}^{-1}$). Four bacterial stains (*Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, and *Bacillus subtilis*) were incubated for 24 h at 37°C, and fungal stains (*Aspergillus niger*, *Candida albicans*, and *Rhizoctonia bataticola*) were incubated for 48 h at 37°C. Standard antibacterial Streptomycin and antifungal drug nystatin were used for comparison under similar conditions. Antimicrobial activity studies were performed in triplicate, and the average was taken as the final reading.

2.4. NLO Study. The second-harmonic generation (SHG) conversion efficiency of the Schiff base was determined by modified version of powder technique developed by Sumathi et al. [18]. The compound was ground into powder and packed between two transparent glass slides. An Nd:YAG laser beam of wavelength 1064 nm was made to fall normally on the sample cell. The transmitted fundamental wave was absorbed by a CuSO₄ solution, which removes the incident 1064 nm light and Filter BG-38 also removes any residual 1064 nm light. Interference filter band width is 4 nm and

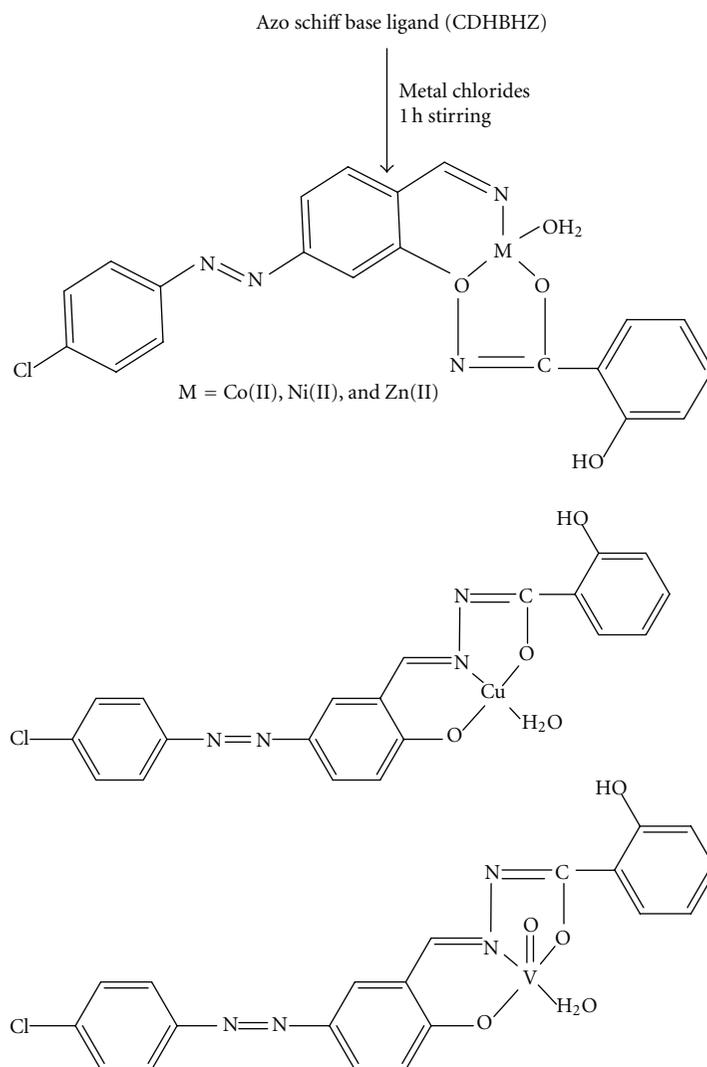


FIGURE 2: Proposed structure of metal(II) complexes.

for central wavelength of 532 nm. The 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 and urea. The input energy used in this particular setup is 2.2 mJ/pulse.

3. Results and Discussion

The azo Schiff base ligand was prepared by reacting equimolar amounts of 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde with 2-hydroxybenzohydrazide in ethanol medium. The structures of the ligand and the complexes were established from their IR, ¹H-NMR spectra, elemental analyses, and magnetic susceptibility measurements. The complexes are intensely coloured stable solids, and the low molar conductance values of the complexes reveal their nonelectrolytic nature. The results of the elemental analysis (Table 1) of the Schiff base are in good agreement with those calculated

for the suggested formula and agree with a 1 : 1 metal to ligand stoichiometry for all the complexes.

3.1. Infrared Spectra. The structurally significant IR bands for free ligand and its complexes have been reported in Table 2. The free ligand exhibits IR bands at 3207 cm⁻¹ (N-H), 1693 cm⁻¹ (C=O), and 1620 cm⁻¹ (C=N). The bands at 3451 and 2923 cm⁻¹ in the free ligand are attributed to the free OH stretching of the diazonium moiety and phenolic moiety [19]. In the complexes, the band due to phenolic OH vibrations remained unaltered, suggesting the noninvolvement of the phenolic proton in the complex formation, whereas the band at 3451 cm⁻¹ due to diazonium moiety disappeared, indicating deprotonation of the OH group and subsequent coordination of the oxygen to the metal ion. This fact was further confirmed by the ¹H NMR study, and this is not appropriate for all the reported complexes as most of the metal ions are paramagnetic. The band at 1620 cm⁻¹ due to the azomethine group of the ligand [20] underwent a shift to lower frequency (by 1610–1589 cm⁻¹)

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

Compound	Formula weight (g mol ⁻¹)	M	Experimental (Calcd.) (%)				Yield %	m.p. °C	Λ_M (S cm ² mol ⁻¹)
			C	H	N				
[C ₂₀ H ₁₅ N ₄ O ₃ Cl] (CDHBHZ)	394.82	—	60.82 (60.84)	3.84 (3.83)	14.20 (14.19)	92	286	—	
[VOL · H ₂ O]	492.79	10.33 (10.34)	51.19 (51.18)	3.69 (3.68)	11.35 (11.37)	86	>360	10.4	
[CoL · H ₂ O]	484.78	12.18 (12.16)	51.99 (52.03)	3.73 (3.74)	11.59 (11.56)	79	>360	10.9	
[NiL · H ₂ O]	484.54	12.09 (12.11)	52.01 (52.05)	3.75 (3.74)	11.55 (11.56)	90	>360	9.5	
[CuL · H ₂ O]	489.39	10.97 (12.98)	51.55 (51.54)	3.70 (3.71)	11.42 (11.45)	87	>360	8.9	
[ZnL · H ₂ O]	491.24	13.32 (13.31)	51.37 (51.35)	3.71 (3.69)	11.43 (11.41)	76	>360	10.2	

TABLE 2: Selected IR frequencies of CDHBHZ and its metal(II) complexes (cm⁻¹).

Compound	ν (N–H)	ν (CH=N)	ν (C=O)	ν (N=C–O)	ν (M–O)	ν (M–N)
CDHBHZ	3207	1620	1693	—	—	—
[VOL · H ₂ O]	—	1602	—	1526	516, 619	480
[CoL · H ₂ O]	—	1594	—	1506	526, 582	426
[NiL · H ₂ O]	—	1609	—	1517	511, 580	431
[CuL · H ₂ O]	—	1610	—	1525	520, 611	422
[ZnL · H ₂ O]	—	1589	—	1511	516, 584	425

after complexation, indicating the coordination of azomethine nitrogen to metal ion which was further confirmed by observation of the shift in the ν (N–N) stretching frequency from 1006 cm⁻¹ to 1021–1047 cm⁻¹ regions [20]. In all complexes, the disappearance of the band at 3207 cm⁻¹, due to ν (NH) and 1693 cm⁻¹, due to ν (C=O), supports the deprotonation of –NH proton and subsequent coordination of the oxygen of the amide carbonyl to the metal ion via enolization. This suggestion is supported by the appearance of a new band in the range 1506–1526 cm⁻¹, which may be assigned to ν (N=C–O) [21]. This finding may be due to bonding of the ligand with the metal ions through the enolic deprotonated oxygen. The appearance of the new bands in the ranges 511–526 cm⁻¹ and 422–480 cm⁻¹ was taken as an indication of coordination between the metal ions and the oxygen and nitrogen, respectively [5]. In addition to other bands, the vanadyl complex shows a band at 1017 cm⁻¹ attributed to the V=O vibration [22].

3.2. ¹H NMR Spectra. The ¹H NMR spectrum of the ligand showed two peaks for the hydroxyl group (13.1 and 12.5 ppm), the NH group (11.5 ppm), and the azomethine group, H–C=N (8.1 ppm). The peaks observed as multiplets 7–7.8 ppm can be assigned to aromatic protons. In the spectrum of the Zn(II) complex, the signal of –NH disappeared indicating that the ligand coordinated to the metal in its enolic form. The signal characteristic to the phenolic hydroxyl group appeared in the same position indicating that the hydroxyl group did not participate in coordination [23].

3.3. Mass Spectra. The mass spectrum of H₂L supported the suggested structure of the ligand, revealing a molecular ion [M+2] peak at m/z at 397, consistent with the molecular weight of the ligand (See Supplementary Material available

online at doi:10.1155/2011/493942), whereas the molecular ion [M+2] peak for VO(II) Co(II), Ni(II), Cu(II), and Zn(II) complexes observed at m/z = 495, 487, 486, 491, and 493 equivalent to its molecular weight confirms the stoichiometric composition of [ML(H₂O)] type (Figure S3).

3.4. Electronic Spectra and Magnetic Moment. The electronic spectra and magnetic moment of the ligand and its metal(II) complexes are listed in (Table 3). The absorption bands at 30,303 and 35,087 cm⁻¹ attributed to benzene $\pi \rightarrow \pi^*$ transitions are observed in the spectrum of the free ligand. The band at 38,167 cm⁻¹ is assigned to imino $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transition [24]. The UV-Vis spectrum of the vanadyl(II) complex exhibits three d-d bands observed at 782, 610, and 428 nm assignable to ²B₂ → ²E, ²B₂ → ²B₁, and ²B₂ → ²A₁ transitions which are characteristic of square-pyramidal geometry [25]. The spectra of [CoL · H₂O] and [NiL · H₂O] complexes showed absorption bands at 560 and 644 nm which could be attributed to the ⁴A₂(F) → ⁴T₁(P) and ³T₁(F) → ³T₁(P) transitions corresponding to the tetrahedral geometry [26] and confirmed by the measured magnetic moments values, 4.21 and 3.32 B.M., respectively [27]. The Cu(II) complex exhibits an intense band at 654 nm assignable to the ²B_{1g} → ²A_{1g} transition, indicating square planar geometry. Also the magnetic moment of 2.01 BM further supports the geometry [28]. The spectra of all the complexes show an intense band at 310–439 nm, which can be assigned to a charge transfer (CT) transition. In the Zn(II) complex, a tetrahedral structure is proposed, and the diamagnetic behavior was confirmed.

3.5. ESR Spectra. A powder ESR spectrum of copper(II) complex was recorded at room temperature using (TCNE) as reference, and the spin Hamiltonian parameters of the

TABLE 3: Electronic spectral data of the complexes.

Compound	Absorption (nm)	Band assignment	Geometry	Magnetic moment (BM)
CDHBHZ	262	INCT	—	—
	285	INCT		
	330	INCT		
[VOL · H ₂ O]	782	² B ₂ → ² E	Square pyramidal	1.74
	610	² B ₂ → ² B ₁		
	428	² B ₂ → ² A ₁		
[CoL · H ₂ O]	325	INCT	Tetrahedral	4.21
	425	INCT		
	560	⁴ A ₂ (F) → ⁴ T ₁ (P)		
[NiL · H ₂ O]	310	INCT	Tetrahedral	3.32
	364	INCT		
	644	³ T ₁ (F) → ³ T ₁ (P)		
[CuL · H ₂ O]	356	INCT	Distorted square planar	2.01
	439	INCT		
	654	² B _{1g} → ² A _{1g}		

TABLE 4: ESR spectral parameters of copper(II) complex.

Complex	g_{\parallel}	g_{\perp}	g_{iso}	α^2	β^2	$A_{\parallel} \times 10^4 \text{ cm}^{-1}$	$A^{\perp} \times 10^{-4} \text{ cm}^{-1}$	$A_{\text{iso}} \times 10^{-4} \text{ cm}^{-1}$	$g_{\parallel}/A_{\parallel} \text{ cm}$	K_{\perp}	$\mu \text{ (B.M.)}$
[CuL · H ₂ O]	2.22	2.04	2.10	0.77	0.82	181	76	111	122	0.54	2.01

Cu(II) complex are listed in (Table 4). The spectrum of the complex revealed axial features ($g_{\parallel} > g_{\perp} > 2.0023$) and suggests a dx^2-y^2 ground state orbital, characteristic of distorted square-planar geometry in Cu(II) complexes [29]. Sheela et al. showed that, for an ionic environment, g_{\parallel} is normally 2.3 or larger, but, for a covalent environment, g_{\parallel} is less than 2.3 [30]. The g_{\parallel} value for the Cu(II) complex is 2.22, consequently the environment is covalent. The observed $K_{\parallel}(0.62) > K_{\perp}(0.54)$ demonstrates the significant contribution from out-of-plane π bonding in metal-ligand bonding. The evaluated value of 0.77 for the bonding parameter α^2 also indicates that the Cu(II) complex has covalent character [31]. The empirical factor $f = g_{\parallel}/A_{\parallel} \text{ cm}^{-1}$ is an index of tetragonal distortion, and its value may vary from 105 to 135 for small to extreme distortions in square planar complexes [32], and it depends on the nature of the coordinated atoms [33]. The f value for the Cu(II) complex is found to be 122, indicating significant distortion from planarity (Figure S4).

3.6. Antimicrobial Study. The antimicrobial activity results (Table 5) reveal that the Cu(II) and Co(II) complex shows fairly good activity against all the tested bacterial strains, and in general the activity order of the synthesized compounds can be represented as Cu(II) > Co(II) > Ni(II) > Zn(II) > VO(II) > L. The higher activity of the metal complexes may be owing to the effect of metal ions on the normal cell membrane [34]. Metal chelates bear polar and nonpolar properties together; this makes them suitable for permeation to the cells and tissues. In addition, chelation may enhance or suppress the biochemical potential of bioactive organic species. Further, lipophilicity, which controls the rate of entry

of molecules into the cell, is modified by coordination, so the metal complex can become more active than the free ligand. Therefore, the metal complexes show greater antimicrobial activities than the uncoordinated ligand and free metal ion which in fact is in agreement with the literature [35]. These mixed-ligand complexes have an advantage in that the respective bioactivities of the uncoordinated ligands and metal ions are combined which could make them more potent antimicrobial agents.

3.7. Redox Behavior. Cyclic voltammograms of the copper complex was recorded in DMSO solution, with 0.1 mol dm⁻³ TBAP as supporting electrolyte, and the results are summarized in (Table 6). It clearly reveals that the redox process of the copper(II) complex at the scan rate 200 mV involves one-step reduction cathodic peak for Cu(II) → Cu(0) at $E_{\text{pc}} = [0.7491 \text{ V}]$. In the anodic side, the direct oxidation of Cu(II) → Cu(0) is observed with a strong stripping peak at $E_{\text{pa}} = [-0.2652 \text{ V}]$ [36]. The reversibility of the copper(II)/copper(0) couple was checked by varying the scan rates with peak potentials. From the table, it is observed that E_{pc} and E_{pa} value changes with the scan rate, and ΔE_p values increase with increasing scan rate and is found to be more than 400 mV, and the ratio of anodic to cathodic peak currents ($I_{\text{pc}}/I_{\text{pa}} \approx 1$) corresponds to a simple one electron process. The difference in the value of $E_{\text{pc}} - E_{\text{pa}}$ is ΔE_p which is larger than the value required for a reversible process (59 mV) indicating that, reduction of Cu(II) at silver electrode is not only diffusion controlled but also by electron transfer kinetics. These observations indicate that the electron transfer process is irreversible (Figure S5).

TABLE 5: The in vitro antimicrobial activity of ligand, their metal(II) complexes, and free-metal cations evaluated by minimum (MIC inhibitory concentration, $\mu\text{g/mL}$).

Compound	Antibacterial activity				Antifungal activity		
	Metal complexes (free-metal cations)				Metal complexes (free-metal cations)		
	<i>S. aureus</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>B. subtilis</i>	<i>A. niger</i>	<i>C. albicans</i>	<i>R. bataicola</i>
CDHBHZ	200	100	350	400	300	200	300
[VOL · H ₂ O]	75 (175)	55 (—)	200 (300)	150 (—)	175 (370)	50 (275)	200 (250)
[CoL · H ₂ O]	10 (350)	15 (095)	25 (500)	20 (410)	55 (650)	10 (—)	75 (—)
[NiL · H ₂ O]	30 (215)	25 (150)	20 (550)	80 (—)	60 (400)	70 (350)	35 (450)
[CuL · H ₂ O]	10 (400)	25 (275)	20 (705)	15 (550)	10 (515)	10 (500)	30 (655)
[ZnL · H ₂ O]	90 (205)	45 (—)	100 (370)	200 (—)	50 (—)	50 (105)	75 (305)
Standard	5	5	10	5	5	10	5

TABLE 6: Redox potential for the copper(II) complex.

Complex	Scan rate (mV s^{-1})	E_{pc} (V)	E_{pa} (V)	ΔE_{p} (V)	$I_{\text{pc}}/I_{\text{pa}}$ (μA)
[CuL · H ₂ O]	100	0.523	-0.151	0.674	1.142
	150	0.612	-0.201	0.813	1.136
	200	0.749	-0.224	0.973	1.160

TABLE 7: Fluorescence characteristic of ligand and its complexes.

Compound	Excitation wavelength λ_{max} (nm)	Fluorescence wavelength λ_{max} (nm)	Quantum yield (ϕ_f)
CDHBHZ	331	342	0.90
[VOL · H ₂ O]	576	621	0.46
[CoL · H ₂ O]	405	456	0.86
[NiL · H ₂ O]	614	619	0.91
[CuL · H ₂ O]	566	572	0.92

3.8. Fluorescence Study. The photoluminescence properties of the azo Schiff base ligand and their complexes were studied at room temperature. All the complexes exhibit strong fluorescence with moderate quantum yield (Table 7) in comparison to the ligand. The excitation spectra of the ligand show a maximum at 331 nm and show an emission peak at 342 nm. Generally, azo Schiff base systems exhibit fluorescence due to intraligand $\pi-\pi^*$ transitions, and the emission is neither MLCT (metal-to-ligand charge transfer) nor LMCT in nature enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical applications of these complexes [37] (Figure S6).

3.9. NLO Property. Total first hyperpolarizability (β_{tot}) for azo Schiff base ligand is studied here and shows the better second harmonic efficiency than urea and KDP. (N'E)-N'-(5-((4-chlorophenyl)diazanyl)-2-hydroxybenzylidene)-2-hydroxybenzohydrazide show 1.8 times more activity than urea and KDP, respectively. Ligand has donor-acceptor property, and the electron-withdrawing atom of chlorine can prevent the lone pair electron of nitrogen atom in N=N group to be delocalized and causes a reduction in second-order nonlinearity [1]. We can conclude that substituent, chloro

group play a role in charge transfer through the molecule, and therefore it seems that the substituents require a special attention in designing the azo Schiff base ligand.

3.10. Powder XRD and SEM Studies. Powder XRD patterns of copper(II) complex show the sharp crystalline peaks indicating their crystalline phase. The crystallite size of the complex d_{XRD} could be estimated from XRD patterns by applying full-width half maximum of the characteristic peak to Scherrer's equation using the XRD line broadening method [38] which is as follows:

$$d_{\text{XRD}} = \frac{0.9\lambda}{\text{FWHM} \cos \theta}, \quad (1)$$

where λ is the wavelength used, FWHM is the full width at half maxima, and θ is the diffraction angle. The XRD shows that Cu(II) complex has the crystallite size of 60 nm, respectively. It represents the mean size of every nanocrystallite complexes. All the other complexes support similar crystallite size pattern. The Cu(II) complex has an average crystallite size of 50 nm. Scanning electron micrograph is used to evaluate morphology and particle size of the Schiff base metal complex. The SEM pictures of the samples are shown in. From the figure, an ice square-like shape is observed in the complex with the particle size of 50 nm (Figure S7).

4. Conclusion

The coordination ability of the newly synthesized azo Schiff base has been proved in complexation reaction with VO(II), Co(II), Ni(II), Cu(II), and Zn(II) ions. IR, UV-vis spectra, and magnetic measurements of the ligand and its metal complexes confirmed the suggested coordination of the ligand through phenolic carbonyl oxygen, oxygen of OH group, and nitrogen of the azomethine group as tridentate. The process of chelation dominantly affects the biological activity of the complexes that are potent against pathogens. In general, all the synthesized compounds can serve as potential photoactive materials, as indicated from their characteristic fluorescence properties. Based on these facts, it could be proposed that these novel materials can be better accommodated for optical applications.

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