Research Article

Studies on Synthesis and Spectral Characterization of Some Transition Metal Complexes of Azo-Azomethine Derivative of Diaminomaleonitrile

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New complexes of 2,3-bis(5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)maleonitrile (CDHBDMN) with VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) were synthesized and characterized by analytical and physicochemical techniques, that is, elemental analyses, molar conductivity, UV, IR, EPR, ¹H-NMR spectra, magnetic susceptibility and also by aid of scanning electron microscopy (SEM), nonlinear optical study (NLO), fluorescence spectral studies, and solvatochromic behaviors. Electronic and magnetic susceptibility measurements of the complexes indicate square pyramidal geometry for VO(II), octahedral for Ni(II), and square planar geometry for all the other complexes. The EPR spectral data provide information about their structures on the basis of Hamiltonian parameters and the degree of covalency. These metal complexes were also tested for their antibacterial and antifungal activities to assess their inhibiting potential. Metal-mediated fluorescence enhancement is observed on complexation of the azo Schiff base ligand. The synthesized compounds were investigated for nonlinear optical properties, and the surface morphology of the Cu(II) complex was studied by scanning electron microscopy.

1. Introduction

Schiff base ligands derived from the condensation of salicylaldehyde with diamines and their complexes [1, 2] played an important part in the development of inorganic chemistry, as widely studied coordination compounds are increasingly important as biochemical, analytical, and antimicrobial reagents [3, 4]. Also they have been used as antibacterial, antifungal, anticancer, antitubercular, hypertensive, and hypothermic reagents [5, 6]. Tetrameric HCN (diaminomaleonitrile, DAMN), a diamine, is one of the most versatile reagents in organic chemistry, used as a precursor for producing nucleotides and for synthesizing a wide variety of heterocyclic compounds [7, 8].

Their great potential has recently been demonstrated in the synthesis of conjugated linear polymers [9], in the thermostable optical material industry [10], and widely employed in the fluorescent dye industry [11].

Interestingly, coordination chemistry of azo Schiff bases derived from DAMN is not well explored. Only a few well-characterized complexes of DAMN-based ligands are known to us. Maclachlan et al. [12] for the first time reported the crystal structures of Schiff base derived from DAMN and salicylaldehyde with some metal complexes. A novel bisazomethine Schiff base formed by the condensation of 3-hydroxyquinoxaline-2-carboxaldehyde and 2,3-diaminomaleonitrile has been carried out by Arun et al. [13]. The studies revealed that the compound exists in two major tautomeric forms and the Schiff base exhibits positive absorption and fluorescent solvatochromism and displays dual fluorescence with large stoke shifts. Rajasekar et al. [14] have investigated Ni(II) and Cu(II) metal complexes derived from salicylaldehyde/5-methylsalicylaldehyde and diaminomaleonitrile (DAMN). In their work antibacterial activity was investigated and square planar geometry was proposed for Ni(II) and Cu(II) complexes.

Azo compounds are very important molecules and have attracted much attention in both academic and applied research [15–20]. Our interest in this molecule stems from its ability to act as a diamine and also from the fact that the electron-withdrawing CN groups affect the coordinating capacity of DAMN itself and have the potential to modulate the electronic properties of resulting coordination complexes and also their chemical reactivity. Hence the present work deals with the synthesis and characterization of the azo Schiff base ligand 2,3-bis(5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)maleonitrile (CDHBDMN) and its VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes. Photoluminescence, nonlinear optical properties, biological activity, electrochemical behavior, and solvatochromic behaviors of the azo compound and its complexes are also examined.

2. Experimental

The chemical used for the synthesis purpose is used as such, and the common solvents used at various stages of this work are purified according to the standard procedures described in Weissenburg series [21]. 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 KBr discs. UV-Vis spectra were obtained using a THERMO SPECTRONIC 6 HEXIOS α and fluorescence spectra were determined with an ELICO SL174 spectrofluorometer. $^1\text{H-NMR}$ spectra were recorded on Bruker DRX-300, 300 MHz NMR spectrometer using TMS as reference. EPR spectrum of Cu(II) complex was recorded in Varian E-112 machine at 300 and 77 K using TCNE (tetracyanoethylene) as the g-marker. Cyclic voltammetric measurement for VO(II) and Cu(II) complexes 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, and the SEM images were recorded using JEOL-JSM-840 a scanning electron microscopy at Karunya Deemed University, Coimbatore.

2.1. Synthesis of 2,3-Bis(5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)maleonitrile (CDHBDMN)s. An ethanolic solution (20 mL) of 5-((4-chlorophenyl)diazenyl)-2-hydroxybenzaldehyde (CPDAHB) [22] (2.6 g, 10 mmol) was added to an ethanolic solution of diaminomaleonitrile (DAMN) (0.54 g, 5 mmol). The solution mixture was refluxed with a few drops of glacial acetic acid as catalyst for 8 h. The

resulting brown solution was cooled in ice to give brown precipitate, which was collected by filtration and dried under vacuum. Recrystallization from absolute ethanol gave brown solid. The overall yield varied between 60% and 70%. The scheme of the ligand is depicted in (Figure 1).

2.2. Synthesis of Metal(II) Complexes. To a solution of (1.48 g, 10 mmol) 2,3-bis(5-(4-chlorophenyl)diazenyl)-2-hydroxybenzylideneamino)maleonitrile (CDHBDMN) in 20 mL ethanol, (10 mmol) of metal chlorides/sulphates ($\text{M} = \text{VO}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and ZnCl_2) were added. The solution was refluxed at 40–50°C with constant stirring for 1 h, and the resulting solution was refrigerated for one day. The complexes were precipitated by adding petroleum ether. The colored complexes were filtered and washed with hot water and with ethanol and dried under vacuum. The yield obtained was 60–77% (Figure 2).

3. Results and Discussion

The complexes have been characterized by IR, UV-visible, $^1\text{H-NMR}$, EI-mass, EPR spectra, magnetic susceptibility measurements, and molar conductance. The analytical data of the ligand and the complexes together with their physical properties are given in Table 1. Based on the physicochemical characteristics, it was found that the air stable, moisture insensitive metal(II) complexes are soluble in chloroform and other common organic solvents. Analytical data are in good agreement with calculated values, as expected for the assigned formula, $[\text{ML}]$, where $\text{M} = \text{VO}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Cu}(\text{II})$, and $\text{Zn}(\text{II})$ and $[\text{ML}(\text{H}_2\text{O})_2]$ for Ni(II) complex; $\text{L} =$ azo Schiff base. All the complexes show 1 : 1 metal-ligand stoichiometry and are nonhygroscopic in nature. The ligand behaves as tetradentate, and the metals are coordinated through oxygen and nitrogen donor atoms. The molar conductance values of mononuclear complexes in DMSO ($1 \times 10^{-3} \text{ M}$) suggest the absence of ionic character.

3.1. Mass Spectral Studies. The mass spectra of azo Schiff base 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 592 m/z . The molecular ion peak for the copper(II) complex observed at 653 m/z confirms the stoichiometry of metal chelates as $[\text{ML}]$ type. It is also supported by the mass spectra of the other complexes, whereas nickel(II) complex shows molecular ion peak at 684 m/z confirming $[\text{MLCl}_2]$ type. The mass spectral data support the structures of mononuclear transition metal complexes. The isotopic peaks from chlorine atom are identified at the mass spectra of the all compounds. The mass spectra of the ligand and its copper(II) complex are shown in Figure S1 (See Supplementary Material available online at doi:<http://dx.doi.org/10.1155/2013/436275>).

3.2. IR Spectral Studies. The IR spectra provide valuable information regarding the nature of functional group attached to the metal atom. In order to study the binding

FIGURE 1: Synthesis of azo Schiff base ligand (CDHBDMN).

FIGURE 2: Structure of the metal(II) complexes of CDHBDMN.

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

Compound	FW g/mol ⁻¹	M	Found (Calcd) (%)			m.p. (°C)	Λ_M ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
			C	H	N		
C ₃₀ H ₁₈ Cl ₂ N ₈ O ₂ (CDHBDMN)	592	—	60.74 (60.72)	3.05 (3.06)	18.87 (18.88)	229–231	—
[VO(CDHBDMN)]	657	7.76 (7.74)	54.74 (54.73)	2.44 (2.45)	17.01 (17.02)	276–278	9.0
[Mn(CDHBDMN)]	645	8.52 (8.50)	55.73 (55.75)	2.53 (2.50)	17.33 (17.34)	289–291	10.3
[Co(CDHBDMN)]	649	9.08 (9.06)	55.43 (55.41)	2.47 (2.48)	17.24 (17.23)	301–303	9.5
[Ni(CDHBDMN)·2H ₂ O]	684	8.52 (8.55)	52.52 (52.51)	2.95 (2.94)	16.31 (16.33)	298–300	7.9
[Cu(CDHBDMN)]	653	9.72 (9.70)	55.03 (55.01)	2.44 (2.46)	17.12 (17.11)	311–313	7.4
[Zn(CDHBDMN)]	654	9.95 (9.96)	54.87 (54.86)	2.47 (2.46)	17.04 (17.06)	302–304	6.2

mode of the ligand to metal in the complexes, the IR spectrum of the free ligand was compared with the corresponding metal complexes. Selected vibrational bands of the ligand and its metal complexes are listed in Table 2, and the IR spectra of the ligand and Ni(II) complex are given in Figures S2a and S2b. The band at 1631 cm⁻¹ is characteristic of the azomethine nitrogen in the free ligand. The lowering in this frequency to 1602–1620 cm⁻¹ in all the complexes indicates involvement of the azomethine nitrogen in coordination with metal [23]. The ligand shows ν (O–H) at 3289 cm⁻¹, and the disappearance of this peak in spectra of all complexes indicates that chelation takes place via the phenolic OH and for nickel complex a broad variable band at 3981 cm⁻¹ is attributed to OH of the coordinated water molecules.

For the complexes bands at 515–542 cm⁻¹ could be assigned ν (M–O). Other weak bands around lower frequency 473–495 cm⁻¹ could be assigned to ν (M–N) [24]. A strong band at 1282 cm⁻¹ in the free azo Schiff base has been assigned to phenolic C–O stretch. Upon complexation, this band displaces to higher frequency (1303–1330 cm⁻¹) indicating coordination through phenolic oxygen [25]. In ligand and all the complexes bands at 2233–2242 cm⁻¹ are assigned to ν (–C≡N) [26]. The sharp band at 1492 cm⁻¹ is assigned to the stretching vibration of the diazo group of the ligand and the infrared spectra of the complexes did not show any frequency shift of the –N=N– band, which may be explained by nonparticipation in complex formation [27]. In addition to other bands, the vanadyl complex shows the characteristic V=O asymmetric stretching frequency at 940 cm⁻¹. These data are well in accordance with those of reported complexes.

3.3. ¹H-NMR Spectral Studies. The ¹H NMR spectra of the azo Schiff base and its zinc(II) complex in DMSO-d₆ were recorded. The two hydroxyl groups and azomethine groups

are in equivalent environment in the present ligand and its complexes. The ¹H NMR spectrum of the Schiff base ligand shows the following signals: phenyl as multiplets at 6.8 to 7.9 δ , the peak at 10.0 δ is attributable to the phenolic –OH group present in the salicylaldehyde moiety, and the azomethine proton (C–CH=N–) appears at 8.2 δ . Zinc complex shows that the phenolic –OH is involved in complexation due to the disappearance of the signal at 10.0 δ . The azomethine proton signal in the spectrum of the zinc complex is shifted downfield compared to the free ligand, suggesting deshielding of the azomethine group due to the coordination with metal ion. There is no appreciable change in all of the other signals of this complex.

3.4. Electronic Spectral and Magnetic Susceptibility Studies. The electronic absorption spectra of the ligand and its complexes were recorded in DMSO at 300 K. The absorption spectra of the ligand show strong peaks at 25125 and 29069 cm⁻¹ which were assigned to the –N=N– azo group and –CH=N– groups of the azo Schiff base ligand, respectively. The spectral data of the ligand and its complexes are given in Table 3.

The absorption spectrum of vanadyl(II) complex shows absorption at 12345 and 20120 cm⁻¹ due to ²B₂ → ²E and ²B₂ → ²B₁ transitions consistent with that of square pyramidal geometry, and the same is further confirmed from its magnetic moment value of 1.76 B.M. [28]. The electronic absorption spectrum of cobalt(II) complex shows absorption at 15748 cm⁻¹, which may be tentatively assigned to ²A_{1g} → ²B_{2g} transition. The spectrum resembles those reported for square planar cobalt(II) complexes [29], and the effective magnetic moment of the cobalt(II) complex is 2.51 B.M. corresponding to the square-planar stereochemistry around d⁷ cobalt(II) ion [30].

Nickel(II) complex exhibited three absorption bands at 10989, 17636, and 23041 cm⁻¹ and may be tentatively

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

Compound	ν (C $\equiv$ N)	ν (CH=N)	ν (C–O)	ν (N=N)	ν (M–O)	ν (M–N)
(CDHBDMN)	2242	1631	1282	1402	—	—
[VO(CDHBDMN)]	2233	1611	1317	1401	530	485
[Mn(CDHBDMN)]	2240	1620	1315	1403	510	473
[Co(CDHBDMN)]	2237	1602	1303	1400	542	493
[Ni(CDHBDMN)·2H ₂ O]	2239	1610	1320	1402	516	480
[Cu(CDHBDMN)]	2241	1606	1309	1401	515	478
[Zn(CDHBDMN)]	2240	1604	1330	1400	540	495

TABLE 3: Electronic spectral data of CDHBDMN and its metal(II) complexes.

Compound	λ_{max} (cm^{-1}) ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	Transition	Geometry	μ_{eff} (B.M.)
(CDHBDMN)	25125 (2002) 29069 (4490)	ILCT* ILCT	—	—
[VO(CDHBDMN)]	12345 (152) 20120 (280)	${}^2\text{B}_2 \rightarrow {}^2\text{E}$ ${}^2\text{B}_2 \rightarrow {}^2\text{B}_1$	Square pyramidal	1.76
[Co(CDHBDMN)]	15748 (182)	${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{2g}$	Square planar	2.51
[Ni(CDHBDMN)·(H ₂ O) ₂]	10989 (216)	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$	Octahedral	3.15
	17636 (210)	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$		
	23041 (279)	${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$		
[Cu(CDHBDMN)]	18903 (240)	${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$	Square planar	1.87

* Intraligand charge transfer.

assigned as ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions indicating the octahedral geometry of the complex.

The value of the various ligand field parameters 10Dq , B , β , β' , and ν_2/ν_1 was calculated to be 10989 cm^{-1} , 314 cm^{-1} , 0.30, 69, and 1.6. The covalent factor β equal to B/B' for the complex is less than one suggesting considerable amount of covalent character of the metal-ligand bonds. The energy separation between ${}^3\text{A}_{2g}(\text{F})$ and ${}^3\text{T}_{2g}(\text{F})$ is equal to 10Dq and the values of 10Dq in octahedral Ni(II) complexes vary between 6400 and 12700 cm^{-1} , depending on the position of the ligand in the spectrochemical series. The 10Dq value of the present nickel(II) complex is 10989 cm^{-1} which is the characteristic of octahedral geometry. The magnetic moment value 3.15 B.M. for Ni(II) complex supports the suggested geometry around the Ni(II) ion [31]. The molar intensity of nickel complexes is in the range of 210 – $279\text{ L mol}^{-1} \text{cm}^{-1}$.

The electronic spectrum of the copper(II) complex under study exhibits absorption band at 18903 cm^{-1} , tentatively assigned to ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$ transition which is the characteristic of square planar geometry. The magnetic moment of the copper(II) complex is 1.87 B.M. and is also supportive of square planar geometry [32]. The Mn(II) complex has a high spin magnetic moment of 5.29 B.M., expected for a d^5 system with five unpaired electrons [33]. The magnetic moment of the zinc(II) complexes does not show any vibrational peak in the visible region which indicates the diamagnetic behavior of the complexes.

3.5. Electrochemical Behavior. The electrochemical properties of VO(II) and Cu(II) complexes have been investigated by cyclic voltammetry. Tetrabutylammoniumperchlorate (TBAP) was used as supporting electrolyte. The cyclic voltammogram (Figure S3) of Cu(II) complex ($1 \times 10^{-3}\text{ M}$) in DMSO at the 100 mVs^{-1} scan rate shows a well-defined redox process corresponding to the formation of the Cu(II)/Cu(I) couple at $E_{\text{pa}} = 0.562\text{ V}$ and the associated cathodic peak at $E_{\text{pc}} = 0.145\text{ V}$. This couple is found to be irreversible with ΔE_p ($E_{\text{pa}} - E_{\text{pc}}$) = 417 V . The result was verified by varying the scan rates with peak potentials. Table S1 infers that the E_{pc} and E_{pa} values with different scan rates and the difference in the value of $E_{\text{pa}} - E_{\text{pc}}$ are larger than the value required for a reversible process (59 mV) which indicates that the electron transfer process is irreversible [34]. The oxovanadium [35] complex exhibited two-step oxidation peaks at 0.223 V and 0.661 V and one reduction peak at -0.702 V . The redox process involves $\text{V(IV)} \rightarrow \text{V(III)} \rightarrow \text{V(II)} \rightarrow \text{V(IV)}$.

3.6. EPR Spectral Studies. The spin Hamiltonian parameters of the Cu(II) complex are listed in Table 4. The observed spectral parameters show anisotropic EPR spectra with $g_{\parallel}(2.10) > g_{\perp}(2.06) > g_e(2.0023)$ is a characteristic of square-planar geometry [36], and the g_{iso} (2.07) value less than 2.3 indicates the covalent character of the metal-ligand bond. The α^2 value for the present complex of 0.79 indicates appreciable the in-plane covalency. The magnetic moment

TABLE 4: EPR spectral parameters of [Cu(CDHBDM)].

Compound	$g_{\parallel}$	$g_{\perp}$	g_{iso}	α^2	β^2	$A_{\parallel}x$ 10^4 cm^{-1}	$A_{\perp}x$ 10^4 cm^{-1}	$A_{\text{iso}}x$ 10^4 cm^{-1}	$g_{\parallel}/A_{\parallel}$ cm	$K_{\parallel}$	$K_{\perp}$	μ (B.M.)
[Cu(CDHBDM)]	2.10	2.06	2.07	0.79	0.95	195	56	103	107.6	0.98	0.69	1.87

of the copper(II) complex calculated using the relation $\mu^2 = 3/4 |g|^2$ is 1.87 B.M., indicative of an unpaired electron. The orbital reduction factors $K_{\parallel}$ and $K_{\perp}$ are estimated and, for this complex, $K_{\parallel}(0.98) > K_{\perp}(0.69)$ indicates poor in-plane π -bonding which is also reflected in β^2 value [37]. The EPR spectrum of the copper complex is shown in Figure 3.

3.7. Biological Studies. The ligands and their metal complexes were tested for their antibacterial and antifungal activities by well diffusion method [38]. Four bacterial stains (*Staphylococcus aureus*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Pseudomonas putida*, *Bacillus subtilis*) were incubated for 24 h at 37°C, and fungal stains (*Aspergillus niger*, *Aspergillus flavus*, and *Rhizoctonia bataicola*) were incubated for 48 h at 37°C. Standard antibacterial drug, Streptomycin, was also screened under similar conditions for comparison. The fungi were subcultured in potato dextrose agar medium, and the standard antifungal drug, Nystatin, was used for control. Stock solution (10^{-3} M) was prepared by dissolving the compounds in DMSO. Antimicrobial activity studies were performed in triplicate, and the average was taken as the final reading. The growth of inhibition zones after incubation is summarized in Table S2.

The result of the microbial data (Figures 4(a), 4(b), and 4(c)) indicates that some of the metal complexes exhibit higher antibacterial activity as compared to the free ligand. The increase in antimicrobial activity may be considered in light of Searl's concept and Tweedy's chelation theory [39]. The antimicrobial results evidently show that the activity of the Schiff base becomes more pronounced when it is coordinated to the metal ions. The structure of the tested compounds seems to be the principal factor influencing the antimicrobial activity. Co(II), Cu(II), and Zn(II) complexes were found to have better activity against all the microbial species, probably due the axial symmetry (square planar) in DMSO solution.

This enhancement in the activity may be rationalized on the basis of their structures, mainly possessing electron withdrawing groups chlorine and $-\text{C}\equiv\text{N}$. It has been suggested that the Schiff base with nitrogen and oxygen donor systems inhibits enzyme activity, since the enzymes which require these groups of their activity appear to be especially more susceptible to deactivation by metal ions on coordination. Tisseh and coworkers synthesized 5-substituted 1H-tetrazoles and observed the positive antimicrobial activity of its complexes against all species of Gram-positive and Gram-negative bacteria and fungi [40, 41].

3.8. Fluorescence Studies. The photoluminescence properties of azo Schiff base ligand and its metal complexes were studied at room temperature in DMSO. The emission spectrum

FIGURE 3: EPR spectrum of [Cu(CDHBDM)].

of the ligand excited at 361 nm shows an emission peak at 359 nm. The metal complexes show strong fluorescence with moderate quantum yield which is shown in Table S3; excitation at 480–546 nm gives an emission at 479–540 nm, assigned to π - π^* intraligand fluorescence. It is interesting that the complexes show a higher intensity than that of the free ligand. This is supported from their calculated quantum yield values with reference to quinine sulfate. Metal ions can enhance or quench the fluorescence emission of some Schiff base ligands containing an aromatic ring. Quenching of fluorescence of a ligand by transition metal ions during complexation is a rather common phenomenon which is explained by processes such as magnetic perturbation, redox activity, and electronic energy transfer.

Enhancement of fluorescence through complexation is, however, of much interest as it opens up the opportunity for photochemical applications of these complexes [42]. In the absence of metal ions the fluorescence of the ligand is probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to the presence of lone pairs of electrons of the donor atoms in the ligand. Such a PET process is prevented by the complexation of ligand with metal ions; thus the fluorescence intensity may be greatly enhanced by the coordination of metals. The chelation of the ligand to metals increases the rigidity of the ligand and thus reduces the loss of energy by thermal vibrational decay [43]. The emission and excitation spectra of the metal complexes are depicted in Figures 5(a) and 5(b).

3.9. Solvatochromic Behavior. Absorption properties of the ligand were further investigated by recording spectra in solvents of various polarities to elucidate any solvatochromic effect, as it has been accepted that the electronic transitions of azo-azomethine ligands strongly depend on the nature of media [44]. For this purpose organic solvents of a different polarity, namely, DMF, DMSO, THF, dichloromethane and chloroform at a concentration of approximately 10^{-3} M were

FIGURE 4: (a) Biospectrum of the ligand and its complexes for antibacterial activity. (b) Biospectrum of the ligand and its complexes for antifungal activity. (c) The inhibition zones formed for *Pseudomonas putida* and *Aspergillus niger*.

FIGURE 5: (a) Emission and (b) excitation spectra of metal(II) complexes.

used. The absorption curves of the ligand in various solvents are shown in Figure 6. We found that the absorption band at 295–398 nm generally shows strong bathochromic shift (positive solvatochromism) as the polarity of solvent was increased. The influence of solvents for the prepared azo

compound increases in the order DMSO (395 nm) > DMF (368 nm) > THF (322 nm) > CH₂Cl₂ (311 nm) > CHCl₃ (272 nm). This observed behavior is accounted as that the prepared azo compound in the ground state and in the excitation state indicate different polarities. This positive

FIGURE 6: Absorption spectra of CDHBDMN in various organic solvents.

solvatochromism exhibited by the compound may be due to the effect of dipole moment changes of the excited state, changes in the hydrogen bonding strength, and/or due to excited state protonation [45]. Furthermore, in the present case the presence of electron withdrawing $-\text{C}\equiv\text{N}$ group in addition to the Cl atom may influence the absorption characteristics of the azo compound.

3.10. Nonlinear Optical Properties. The SHG (second harmonic generation) efficiency of the azo Schiff base ligand CDHBDMN was determined by modified version of powder technique developed by Kurtz and Perry [46]. 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. The experimental data infers that the ligand shows one fourth of the activity of urea and 0.5 times more active than KDP. Though the present investigated azo Schiff base ligand CDHBDMN possesses a pathway of π -conjugated electrons, the NLO activity is low and this may be due to the absence of electron-pull and electron-push substituents on the benzene rings. The presence of electron acceptor group, that is, chlorine on both sides of the azo compound causes reduction in second-order nonlinearity. Hence, we can conclude that the substituents play an important role in charge transfer through the molecule, and therefore it seems that the substituents require a special attention in designing the azo Schiff base ligands for nonlinear optical properties.

3.11. Scanning Electron Microscopy (SEM). Scanning electron microscope is used here to investigate the surface morphology and particle size of the azo Schiff base CDHBDMN. SEM of CDHBDMN reveals a brittle, glassy, and crystalline structure. Layers in the micrograph reveal that the system contains atoms in a well-defined pattern; thus reactants have

FIGURE 7: SEM image of $[\text{Cu}(\text{CDHBDMN})]$.

reacted completely to form a clear homogenous compound. In general, the SEM photograph shows single phase formation with well-defined grain like shape and particle size in the range of 0.5 μm . The SEM image of the copper(II) complex is depicted in Figure 7.

4. Conclusions

The VO(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) azo Schiff base complexes were prepared and characterized using different analytical techniques. Electronic spectral data and magnetic susceptibility measurements support octahedral geometry for Ni(II), square pyramidal geometry for VO(II), and square planar geometry for other complexes. Cyclic voltammetry of Cu(II) complex exhibits irreversible electron transfer process. All the complexes show antimicrobial activity, and the presence of an electron-withdrawing group enhances the antimicrobial activities. The presence of electron acceptor group, that is, chlorine on both the sides of the azo compound causes reduction in second-order nonlinearity. Hence, the present study demonstrated that that the substituents require a special attention in designing the azo Schiff base ligands for nonlinear optical properties. The presence of the azo and azomethine moiety can give rise to photochromism, and this phenomenon will make the new complexes favorable to be used in the fluorescence switches and sensors. The surface morphology studied using SEM showed the well-defined crystallite size of 0.5 μm . The solvatochromic behaviors infer that, due to the presence of electron-accepting, $-\text{Cl}$ and $-\text{C}\equiv\text{N}$ groups, the λ_{max} was shifted bathochromic in all solvents used.

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