



Synthesis and characterization of Mn (II), Cu (II) and Cd (II) complexes of bis-Schiff bases derived from diamionaphthalene and salicylaldehyde derivatives

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ABSTRACT

The present study deals with the preparation of Schiff bases and their complexes with some transition metal ions Mn (II), Cu (II) and Cd (II). The ligand (H_2L^1) was obtained by condensation of 2,3-diamionaphthalene with salicylaldehyde. The other ligand (H_2L^2) was obtained by condensation of 1,8-diamionaphthalene with 2-hydroxy-3-methoxybenzaldehyde. The ligands and their complexes have been characterized by elemental analysis, IR, 1H NMR, TGA, UV-VIS, ESR, magnetic susceptibility and fluorescence spectroscopy. The analytical spectra and magnetic data support the mononuclear formations of these complexes with square planar structures. Biological activities of the complexes were studied.

Introduction

The Schiff bases are important class of ligands in coordination chemistry and find extensive applications in different fields ^[1-3]. A large number of the metal complexes with different electronic structures have been synthesized using Schiff base ligands ^[4-7]. In recent years, metal complexes of Schiff bases have attracted considerable attention due to their remarkable antibacterial, antifungal and antitumor activities ^[8-12]. For example, Schiff bases complexes derived from 4-hydroxy salicylaldehyde and amines have strong anticancer activities ^[13]. Earlier work reported that some drugs showed increased activity, when administered as metal complexes rather than as organic compounds ^[14, 15]. It has been suggested that the azomethine linkage is responsible for the biological activities of Schiff bases such as, antitumor, antibacterial, antifungal and herbicidal activities ^[16-21].

A large number of Salen derivatives Schiff base (N_2O_2) complexes have been reported so far, and their catalytic ^[22-24] and biological properties ^[25-28] have been studied intensively. Little is known on the use of diamionaphthalene to form Schiff base with salicylaldehyde. Tetradentate N_2S_2 Schiff base L, obtained by the condensation of thiophene-2-carboxaldehyde and 1,8-diamionaphthalene reacted with Cu (II) to form a complex of the type, $[CuL](NO_3)_2$ ^[29].

The Schiff base ligand, N,N' -bis-(2-pyridinecarboxaldimine)-1,8-diamionaphthalene (L), obtained by the condensation of 2-pyridinecarboxaldehyde and 1,8-diamionaphthalene, has been used to synthesize the mononuclear complexes of the type $[MLCl_2]$ [$M = Co(II), Ni(II), Cu(II)$ and $Zn(II)$] and binding study of its Cu(II) complex with calf thymus DNA ^[30]. Also, antibacterial, antifungal, and DNA cleavage studies have performed using coumarin Schiff bases derived from 1,8-diamionaphthalene and 8-formyl-7-hydroxy-4-methylcoumarin/8-acetyl-7-hydroxy-4-methylcoumarin ^[31]. In the present work, we synthesized two Schiff bases by condensation reactions of 2,3-diamionaphthalene with salicylaldehyde and 1,8-diamionaphthalene with 2-hydroxy-3-methoxy benzaldehyde. Synthesis, characterization and biological studies of the two Schiff bases and their Mn (II), Cu (II) and Cd (II) complexes are reported.

Materials and Methods

Reagents

Salicylaldehyde, 2,3-diamionaphthalene, 1,8-diamionaphthalene, 2-hydroxy-3-methoxy benzaldehyde, salts of Mn (II), Cu (II) and Cd (II) acetate, were purchased from Aldrich and used without further purification.

Instruments

Elemental analysis for C, H and N were performed on a Perkin-Elmer 2400 elemental analyzer. Infrared measurements (KBr-pellets) were carried out on a Unicam-Mattson 1000 FT-IR spectrophotometer.

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¹H NMR measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Sample was dissolved in deuterated DMSO using TMS as internal reference. Thermo gravimetric analysis with a heating rate of 10°C using a Perkin-Elmer 7 series thermal analyzer thermal analyzer. UV-Vis spectra were measured on a Unicam UV2-300 spectrophotometer. ESR spectra of the complexes were recorded using a Bruker ESR-spectrometer model EMX. The magnetic susceptibilities of the paramagnetic complexes in the solid state (Gouy method) were measured on a Sherwood scientific magnetic susceptibility balance. Photoluminescence spectra were recorded on a Perkin Elmer LS 50B luminescence spectrophotometer.

Synthesis of the Schiff base (H₂L¹)

2,3-diaminonaphthalene (0.5 gm, 3.16 mmol) in 20 ml hot ethanolic solution was added drop wise into a solution of salicylaldehyde (0.77 gm, 6.32 mmol), the mixture was refluxed for 6 hours. The resulting deep orange colored precipitate was filtered and washed with ethanol followed by petroleum ether, then dried at room temperature, the purity of H₂L¹ was checked by TLC.

Synthesis of the Schiff base (H₂L²)

1,8-diaminonaphthalene (0.5 gm, 3.16mmol) in 20 ml hot ethanolic solution was added slowly dropwise to a solution of 2-hydroxy-3-methoxy benzaldehyde (0.96 gm, 6.32 mmol). The reaction mixture was refluxed for 6 hours. After cooling the obtained precipitate was filtered and recrystallized from ethanol. The resulting solid washed with petroleum ether, then dried to obtain dark brown precipitate, the purity of H₂L² was checked by TLC.

Synthesis of Mn (II), Cu (II) and Cd (II) complexes of Schiff base (H₂L¹)

To accurately weighted M (OAc)₂.nH₂O [M = Mn (II), n = 4; M = Cu(II), n = 1 ; M = Cd(II), n = 2] (1.4 mmol) in 20 ml ethanol, a solution of (0.5gm, 1.4mmol) of ligand (H₂L¹) in 10 ml absolute hot ethanol was added drop wise with stirring. The reaction mixture was refluxed for 6 hours. The resulting precipitates were filtered off, and washed with ethanol. It was then dried at room temperature.

Synthesis of Mn (II), Cu (II) and Cd (II) complexes of Schiff base (H₂L²)

A similar procedure as used for reaction with H₂L¹ has been used for the reaction of the metals with H₂L².

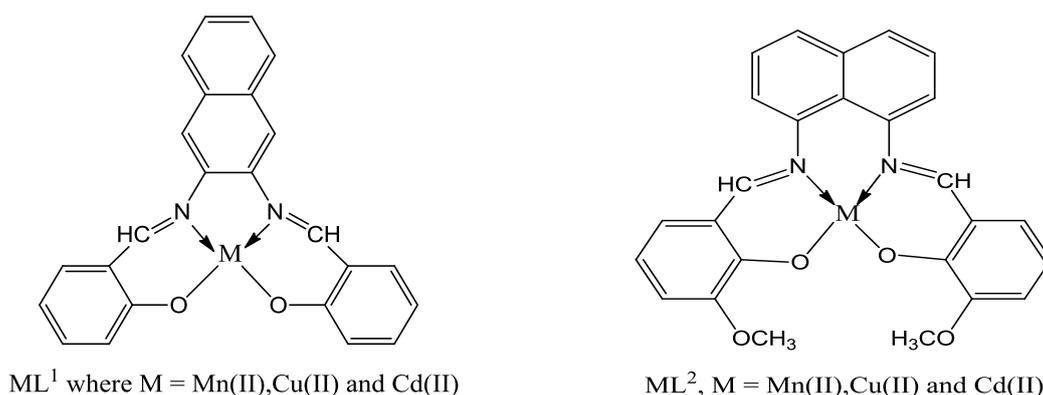
Results and discussion

The elemental analysis and some physical properties of the complexes are listed in Table 1. The resulting solid complexes are intensely colored and stable in air. They are soluble in polar solvent such as DMSO, DMF, slightly soluble in ethanol and methanol, but poorly soluble in water. The elemental analysis, Table 1, and the analytical data are in good agreement with the stoichiometry of the complexes as 1:1 M ratio.

The ligands (H₂L¹) and (H₂L²) upon reaction with Mn(II), Cu(II) and Cd(II) acetates yield complexes corresponding to the general formula [ML¹]and [ML²], as shown in Scheme 1. According to the molar conductivity measurements, Mn (II), Cu (II) and Cd (II) complexes of the two ligands did not show an important conductivity. This proves that complexes have non-electrolytic nature^[2].

Table 1: The colors, formula weight, yields, melting points, magnetic moments and elemental analysis results of the (H₂L¹), (H₂L²) ligands and their complexes.

Compound	Color	FW (gm/mol)	M.P °C	Yield (%)	μ_{eff} (B.M)	Elemental analysis calculated (found) (%)		
						C	H	N
Ligand (H ₂ L ¹) C ₂₄ H ₁₈ N ₂ O ₂	Deep orange	366.42	195	75	–	78.69 (78.56)	4.92 (4.53)	7.68 (7.80)
Mn L ¹ MnC ₂₄ H ₁₆ N ₂ O ₂	Dark brown	419.40	333	65	1.75	68.67 (68.40)	3.81 (3.92)	6.68 (6.76)
Cu L ¹ CuC ₂₄ H ₁₆ N ₂ O ₂	Green	427.55	280	83	1.63	67.30 (67.70)	3.74 (3.84)	6.54 (6.40)
Cd L ¹ CdC ₂₄ H ₁₆ N ₂ O	Reddish brown	476.87	345	72	Dia	60.39 (60.61)	3.36 (3.73)	5.87 (5.61)
Ligand (H ₂ L ²) C ₂₆ H ₂₀ N ₂ O ₄	Dark brown	426.47	176	73	–	73.16 (73.0)	5.15 (5.42)	6.56 (6.76)
Mn L ² MnC ₂₆ H ₂₀ N ₂ O ₄	Black	479.40	338	79	1.62	65.10 (64.86)	4.17 (3.97)	5.84 (5.65)
Cu L ² Cu C ₂₆ H ₂₀ N ₂ O ₄	Dark green	488	290	81	1.58	63.93 (63.20)	4.09 (3.88)	5.74 (5.24)
Cd L ² Cd C ₂₆ H ₂₀ N ₂ O ₄	Dark green	536.90	350	75	Dia	58.11 (57.54)	3.73 (3.63)	5.22 (5.59)



Scheme 1

Infrared spectra

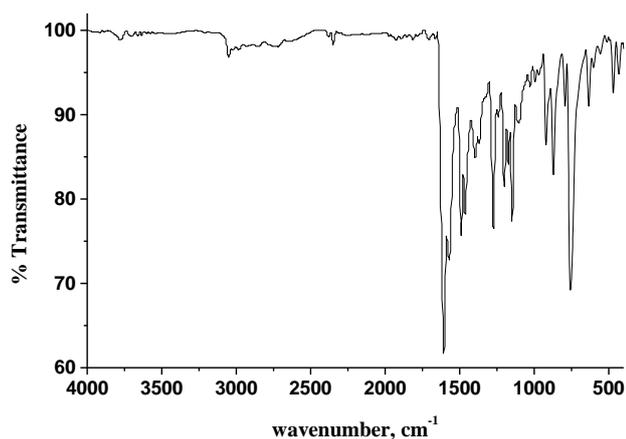
The most important IR-bands of the Schiff base ligands H₂L¹, H₂L² and their complexes are given in Table 2. The FT-IR spectra of the free ligands (H₂L¹) did not show band in the range of OH stretching frequency, Figure 1, while (H₂L²) exhibited the most characteristic bands are at 3339 cm⁻¹. The O–H stretching frequency of Salen-type ligand is expected in the 3300–3800 cm⁻¹ region, however, this frequency is generally displaced to ca. 3433 cm⁻¹ due to the internal hydrogen bond OH⋯N=C [32]. As the hydrogen bond becomes stronger, the bandwidth increases, and this band sometimes is not detected for ligand H₂L¹. Electron-donating groups on the phenolic ring increase the electron density on the hydroxyl oxygen making the H–O bond stronger, the absorption usually appears as a broad band in the FT-IR spectrum and this explain the appearance of OH band in H₂L². Also, the free ligands show bands at 1607, 1611 cm⁻¹ due to ν (–C=N) azomethine group, Table 2. The disappearance of ν(C=O) at 1735 cm⁻¹ and ν(NH₂) at 3405 cm⁻¹ bands in the spectra of the ligands indicate that the expected

imino compound was formed by condensation of 2, 3-diaminonaphthalene and salicylaldehyde for ligand (H₂L¹) or 1, 8-diaminonaphthalene with 2-hydroxy-3-methoxy benzaldehyde for ligand (H₂L²). It is also shown that there is no residual starting material left in the ligands as well. The bands of azomethine groups in the spectra of the free ligands (H₂L¹) and (H₂L²) displayed a shift in the spectra of their complexes indicating that the (C=N) coordinates to the metal ion through nitrogen atom. The free ligands H₂L¹ H₂L² exhibit Ar–O stretching bands at 1275 and 1242 cm⁻¹, respectively. These two bands are shifted to lower frequencies upon complexation, Table 2, confirming the involvement of the phenolic group in complex formation [33]. The mode of coordination is further supported by the presence of new bands in 457-474 cm⁻¹ and 516-588 cm⁻¹ ranges, for the two ligands that can be attributed to ν(M–O) and ν(M–N), respectively, Table 2, [34].

From the elemental analysis and IR results, it may be concluded that the Schiff base ligands (H₂L¹) and (H₂L²) are tetradentate and coordinated with metal ion through the phenolic oxygen and azomethine nitrogen atoms [35].

Table 2: characteristic IR bands (cm⁻¹) of the ligands (H₂L¹) and (H₂L²) and their complexes in KBr-pellets.

Compound	ν(O–H)	ν(C–H)	ν(C=N)	ν(C=C)	ν(C–O)	ν(M–N)	ν(M–O)
H ₂ L ¹	-	3051(m)	1607(s)	1570(s)	1275(s)	-	-
H ₂ L ²	3339(m.b)	3045(m)	1611(s)	1500(s)	1242(s)	-	-
Mn L ¹	-	3053(m)	1603(s)	1577(s)	1255(s)	562(m)	468(m)
Cu L ¹	-	3052(m)	1605(s)	1583(s)	1250(s)	588(m)	467(m)
Cd L ¹	-	3048(m)	1604(s)	1577(s)	1248(s)	565(m)	469(m)
Mn L ²	-	3054(m)	1607	1556(s)	1247(s)	522(m)	467(m)
Cu L ²	-	3055(m)	1601	1574(s)	1243(s)	516(m)	457(m)
Cd L ²	-	3052(m)	1606	1553(s)	1240(s)	517(m)	474(m)

Fig. 1: FT-IR spectrum of H_2L^1 .

The 1H NMR spectra

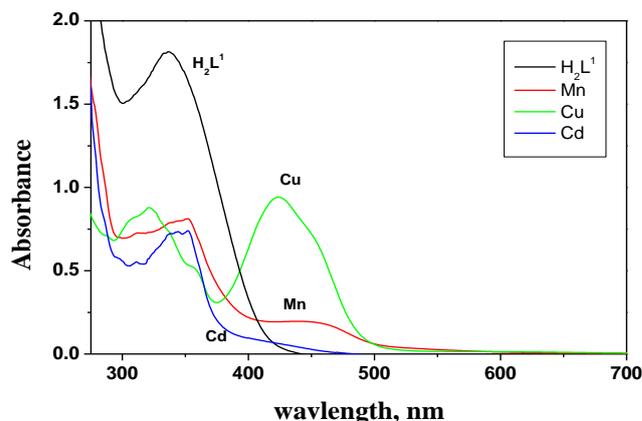
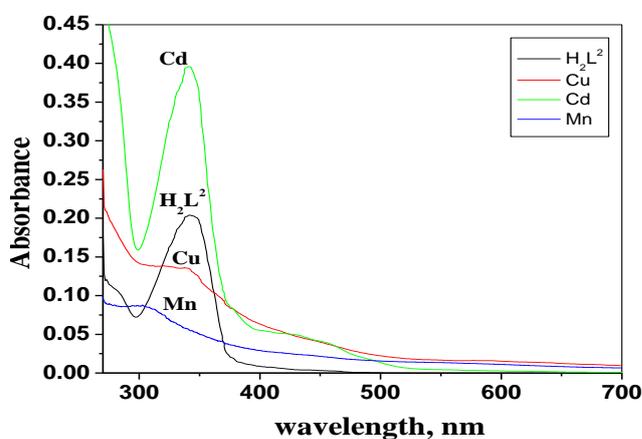
The 1H NMR spectra of the two Schiff bases and their Cd (II) complexes were recorded in DMSO- d_6 solution using (TMS) tetramethylsilane as internal standard. The 1H NMR spectra of the free ligands showed wide singlet at 12.87, 12.65ppm, respectively, for the H_2L^1 and H_2L^2 due to phenolic protons. The spectra also exhibited a singlet signal at 9.1 ppm for (H_2L^1) and 8.92 ppm for ligand H_2L^2 due to imine protons in addition to multiplets at 6.97-7.51 ppm for H_2L^1 and at 6.47-6.93 ppm for H_2L^2 are described to naphthalene and benzene protons. On the other hand, the free ligand H_2L^2 showed a singlet at 3.34 ppm due to the methoxy proton.

The 1H NMR spectrum of Cd (II) complexes showed approximately the same signals similar to those of the free ligands H_2L^1 and H_2L^2 with the exception of phenolic group. The phenolic O-H signal in the two ligands disappeared in the spectra of their complexes indicating that the OH-protons are removed by coordination with Cd (II) ion. Also, the spectra of Schiff bases protons of the azomethine group undergo downfield shift in the spectra of their complexes with Cd (II) indicating participation of this group in coordination with the metal ion. Therefore, from the elemental analysis and spectroscopic data it can be concluded that the Schiff bases (H_2L^1) and (H_2L^2) are known to be planar tetradentate with two active center (-OH) and two donor sites (C=N). They are capable of coordination to the metal ion occupying four coordination sites preferably with cis-nitrogen atoms. Hence, one can postulate that the structure of the complexes is square planar or tetrahedral.

Electronic spectra and magnetic susceptibility

The complexes of Mn (II) and Cu (II) are paramagnetic. The magnetic susceptibility values of Mn(II) and Cu(II) complexes are 1.75, 1.63 BM for ligand (H_2L^1) and are 1.62, 1.58 BM for the complexes with ligand (H_2L^2), respectively, which was consistent with presence of a single unpaired electron^[36]. The UV-Vis spectra were recorded in DMF solution with a concentration (1.0×10^{-5} M) for the two Schiff bases and their complexes in the wavelength range from 200 to 700nm and the spectra are shown in Figures 2 and 3. The Schiff

base H_2L^1 showed a strong broad peak centered at 338 nm, the ligand H_2L^2 showed a peak at 343 nm. These bands assigned due to $\pi-\pi^*$ transitions involving molecular orbitals essentially localized on the azomethine chromophore and benzene ring. In addition, the H_2L^2 ligand exhibit a low intense band in the 360–500nm region, involving $n \rightarrow \pi^*$ excitation. The bands at higher energies 263nm and 265 nm for H_2L^1 and H_2L^2 are associated with the benzene $\pi-\pi^*$ transition. For ML^1 complexes, the spectra of the complexes, showed that the azomethine chromophore $\pi-\pi^*$ transitions shifted to 351 nm for MnL^1 and CdL^1 complexes while CuL^1 splitted to two peaks at 325 and 361 nm indicating that the imino nitrogen is involved in coordination to the metal ion. The [MnL^1] complex showed a broad band with maximum at 450 nm due to metal to ligand charge transfer. The [CuL^1] complex exhibit band at 423 nm with a shoulder at 453 nm could be assigned due to MLCT transirions (Cu (II)-phenolate (π^*) transition; CT band from the filled d ($3d_{xz}$, $3d_{yz}$) orbitals of copper (II) to the antibonding orbitals of the phenolic residue)^[37], and $d-\pi^*$ transitions, respectively. On the other hand, complexes of H_2L^2 showed spectra similar to that of the ligand with appropriate shift due to complexation. The disappearance of the weak band around 685 nm for all complexes suggests that the chelate for metal ions have square planar geometry.

Fig. 2: Uv-visible spectra of H_2L^1 and its complexes in DMF.Fig. 3: Uv-visible spectra of H_2L^2 and its complexes in DMF.

Electron spin resonance spectra

The ESR spectra of the complexes provide information on the metal environment. ESR spectra of the polycrystalline Mn (II) and Cu (II) complexes at room temperature exhibited an isotropic signal, without any hyperfine splitting. ESR spectra of $[\text{MnL}^1]$, $[\text{CuL}^1]$, $[\text{MnL}^2]$ and $[\text{CuL}^2]$ complexes are given in Fig. 4. The g tensor values of the copper (II) complexes could be used to obtain the ground state ^[38]. The values of g_{\parallel} and g_{\perp} for Mn (II) and Cu (II) complexes of ligand H_2L^1 have been found to be 2.0094, 2.0063 and 2.0683, 2.0276, respectively. On the other hand, the values of g_{\parallel} and g_{\perp} for Mn (II) and Cu (II) complexes of the ligand H_2L^2 have been found to be 2.0026, 2.0013 and 2.1185, 2.1064, respectively. Since the $g_{\parallel} < 2.3$ value it confirms the covalent character of the metal-ligand bond. In square planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $g_{\parallel} > g_{\perp} > 2$ while the unpaired electron lies in the d_{z^2} orbital giving $g_{\parallel} > 2$. This provides an evidence that the unpaired electron is localized in the $d_{x^2-y^2}$ orbital and the ground state is $^2\text{B}_{1g}$ ^[39, 40].

Fluorescence spectra

Complexes containing the Schiff-base ligand bis-salicylidene- ethylenediamino (salen) are particularly interesting for luminescence studies, since they show good chemical stability, intense absorption coefficients and high photoluminescence quantum yields ^[41, 42]. Aluminum salen complexes, in particular, display higher ϕ_{em} than salen complexes containing metals such as

cobalt, chromium and manganese ^[41] and the wavelength maximum for emission can be tuned from 438 to 599 nm ^[42].

In this work steady-state fluorescence studies have been employed as independent evidence of complexation between the ligands and the metal ions. Figures 5 and 6 represent the luminescence spectra of the ligands and their corresponding complexes. Photoluminescence study of the Schiff base ligands and the reported complexes were carried out at room temperature in dimethyl formamide solution. The emission spectra have been obtained by excitation at 350 nm.

The emission spectra of H_2L^1 and its complexes in 1×10^{-5} mol L^{-1} DMF solution at room temperature, Figure 5, show that the emission spectral shape of complexes are closely resemble that of the ligand with weak emission at 420 nm. As can be seen in Fig 5, the emission of H_2L^1 is enhanced upon complexation with Cd^{2+} while quenched with Mn^{2+} and Cu^{2+} complexes. Factors like a simple binding of ligand to the d^{10} metal ions ^[43], an increased rigidity in structure of the complexes ^[44], a restriction in the photoinduced electron transfer (PET) ^[45], etc. are assigned to the increase in the photoluminescence.

H_2L^1 shows a strong fluorescence emission at 488 nm while H_2L^2 exhibits fluorescence peak at 398 nm. It is clear that H_2L^1 has lower energy emission than H_2L^2 ligand due to difference in attachment structure of naphthalene moiety. The enhancement of the fluorescence of the cadmium complexes compared to their respective ligands is due to CHEF (chelation enhancement of fluorescence emission) ^[46].

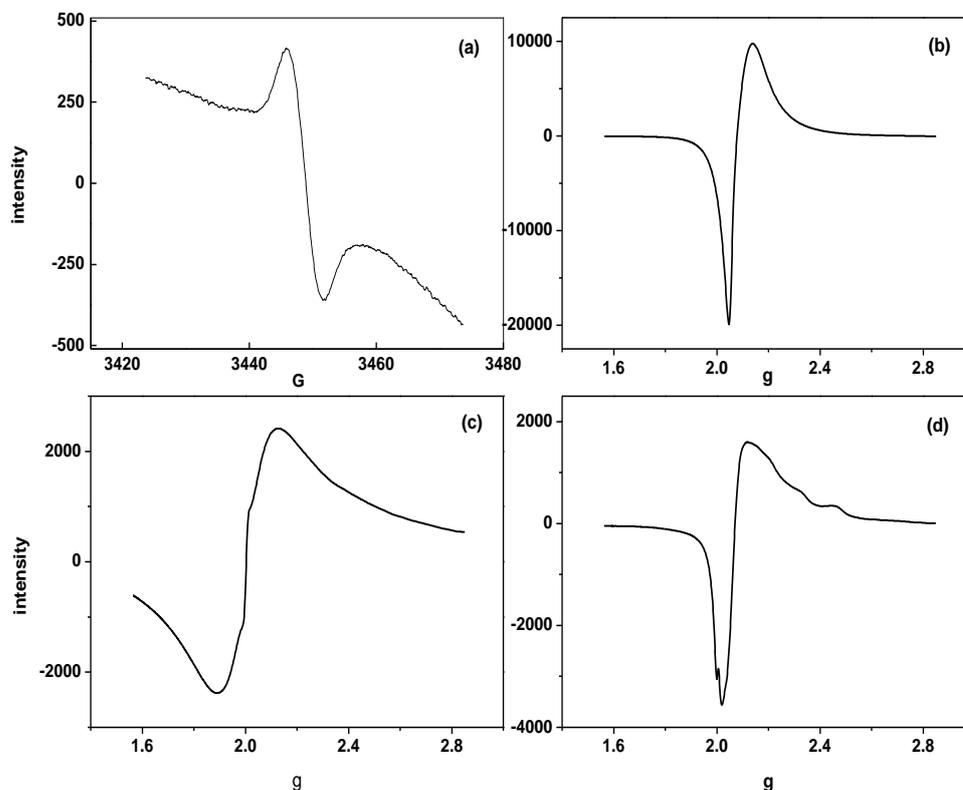
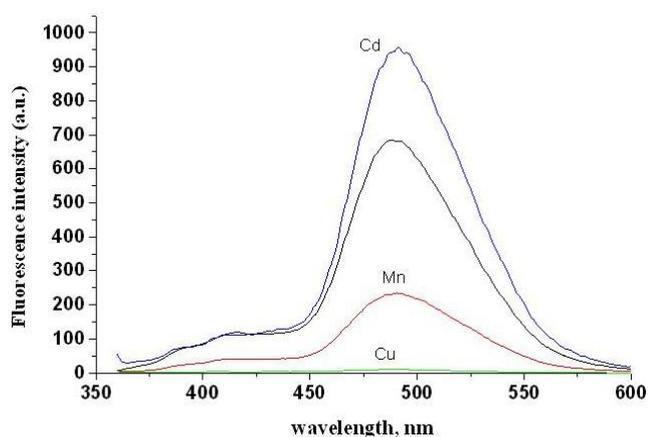
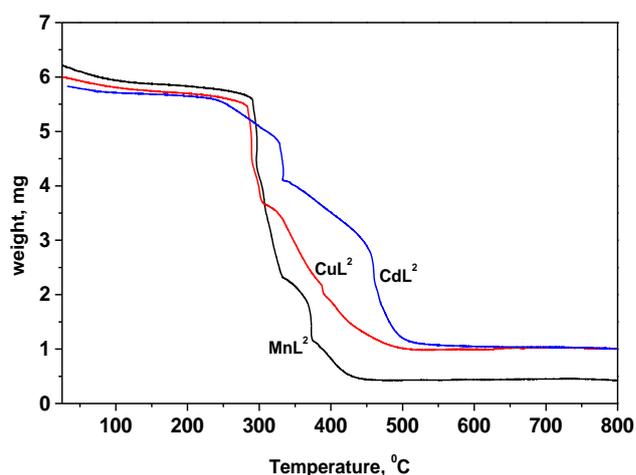
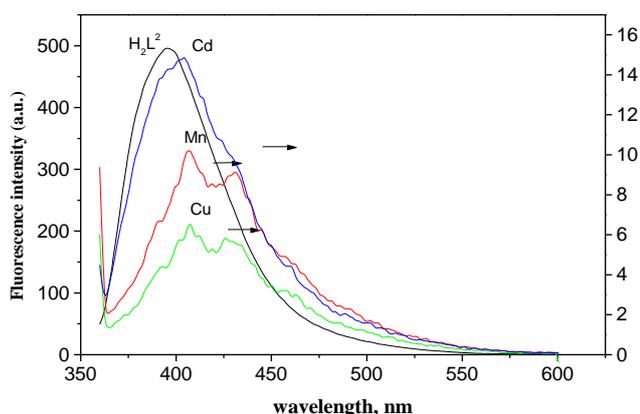
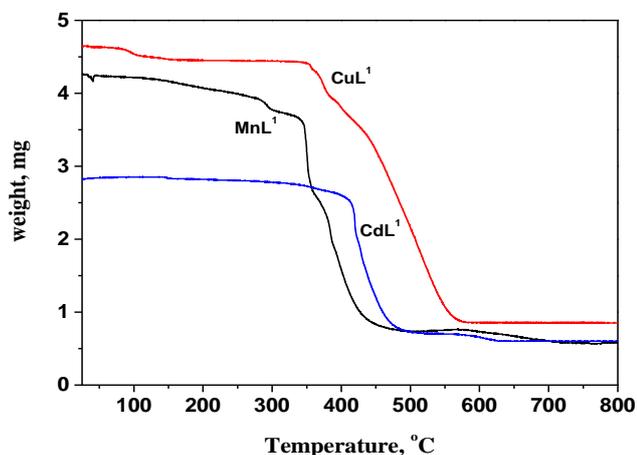


Fig. 4: ESR spectra of the polycrystalline a) MnL^1 , b) CuL^1 c) MnL^2 and d) CuL^2 complexes at room temperature.

Fig. 5: Fluorescence spectra of H_2L^1 and its complexes.Fig. 8: TGA of ML^2 .Fig. 6: Fluorescence spectra of H_2L^2 and its complexes.

Thermo gravimetric analysis

In order to give more insight into the structure of the complexes, the thermal studies of the complexes were carried out using thermogravimetry (TG) technique. Figures 7 and 8 shows the weight loss of the ML^1 and ML^2 complexes in the range of 40-800 C^0 . The complexes of HL^1 were thermally stable up to 300 C^0 , the organic ligand in complexes decomposed to give metal oxide residue as MnO_2 , CuO and CdO . The stability of ML^1 complexes follow the order $MnL^1 < CuL^1 < CdL^1$. On the other hand, the complexes ML^2 were less stable than ML^1 complexes, they are stable up to 270 C^0 .

Fig. 7: TGA of ML^1 .

Biological activity

The antibacterial activity of the ligands and their Mn (II) and Cu (II) complexes was tested against 5 microbial strains, Gram-positive like *Staphylococcus aureus*, *Micrococcus luteus* and *Bacillus subtilis*, Gram-negative bacteria like *E. coli* and *Pseudomonas*-sp. The sensitivity of a microorganism to the standard antibiotics (SAM (20) and CN (10)) and the complexes was performed using the diffusion agar technique. The results showed that the ligands have no biological activity for any of the strains and Mn (II) complexes of the Schiff base H_2L^1 exhibited antibacterial activity for all strains used. The Inhibition zone in case of the Mn (II) complexes were in the range 11-14 mm compared to 22 in case of the standard drugs. On the other hand, CuL^1 showed only inhibition zone of 10 mm with *Bacillus subtilis*.

Conclusion

Novel mononuclear Mn (II), Cu (II) and Cd (II) complexes have been synthesized from the reactions of the corresponding metal acetate salt with neutral N_2O_2 donor tetradentate Schiff bases namely: N,N' -bis (salicylaldehyde) 2, 3-diaminonaphthalene (H_2L^1) and N,N' -bis(2-hydroxy-3-methoxybenzaldehyde)-1,8-diaminonaphthalene (H_2L^2). All the complexes are colored, stable in air and insoluble in water and common solvents but soluble in polar solvent like DMF and DMSO. The analytical data obtained suggested 1:1 (M:L) stoichiometry for all complexes. The prepared complexes have non-electrolytic nature. Furthermore, the reported ligands exhibit strong fluorescence at room temperature and this fluorescence is enhanced or quenched depending on the metal and the ligand. Interestingly the prepared complexes have been tested for construction of anion selective polymeric membrane electrodes which could be used successfully as ion-selective electrodes in analytical applications and the results obtained will be published in approximate time.

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