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Synthesis, spectral characterization, electrochemical and anti-microbial activities of new binuclear Schiff base metal complexes derived from 3,3’ diaminobenzedine

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ABSTRACT

A novel oxime ligand has been synthesized by refluxing 3,3’-diaminobenzedine and phthalaldehyde monoxime. Copper (II), cobalt (II), nickel (II) and manganese (II) binuclear complexes of this ligand have been prepared and characterized by using elemental analysis, molar conductance studies, IR, UV, NMR, EPR and magnetic studies. The molar conductance measurements correspond to a non-electrolytic nature for all complexes which can be formulated as $[M_2(L)X_4]$ (Where M = Cu(II), Ni(II), Co(II) and Mn(II); X = Cl^-). The UV-visible spectra of all the complexes are well characterized by broad weak *d-d* band and a high intensity charge-transfer transition. Thermal studies supported the chemical formation of these complexes showed that they decomposed in three or four stages depending on the type of ligand. The far-IR spectrum confirms the presence of coordinate chloride ion in all the complexes as evidenced by one intense far IR bands around 310-330 cm^{-1}. In electrochemical studies the resulting cyclic voltammogram consists of single quasi-reversible one electron transfer. The ligand and complexes have been screened for their antimicrobial activity against two Gram-positive bacteria, two Gram-negative bacteria and fungi. The binuclear metal complexes were found to possess potent antimicrobial, antifungal activity better than ligand alone.

1. Introduction

The chemistry of oxime/oximato complexes have been broadly investigated [1], particularly in copper and nickel complexes with oxime ligands in recent years [2-3]. The co-ordination chemistry of the oxime ligands have been widely studied with the 3*d* metal ions [4-5]. The oxime-imines of ligands capable of withstand higher oxidation states of the central metal ion through strong ligand to metal [L-M] σ donation. The strength of the hydrogen bond in the two oxime groups depends on the size and chemical environment around the metal ion. Schiff base complexes can be utilized as catalysts for many organic reactions, optical materials, luminescence materials, DNA binding and cleavage reagents etc., [6,7]. Compounds containing oxime group was used as analytical reagent for the separation and determination of some transition metal ions [8]. Oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides [9]. The copper (II) complexes with oxime ligands are models of physical and chemical behaviour of biological copper system, considerably focused on these compounds [10-11]. The copper (II) complex of 1,10 phenopthroline was first synthetic metal complex showed DNA cleavage activity [12]. The ligands containing Nitrogen, Oxygen and sulphur can act as effective chelating agents for transition and non-transition metal ions [13].

In this paper, the novel complexes derived from phthalaldehyde monoxime with 3,3’-diaminobenzidine were synthesized and characterized by elemental analysis, molar conductance, IR, UV, NMR, EPR and magnetic studies. The redox behavior of the complexes, thermal study has been studied. The Schiff base ligand and its complexes were investigated for anti-microbial and anti-fungal properties. Two Gram-positive bacteria (*Staphylococcus aureus* and *Streptococcus pyogenes*), two Gram-negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*) and two fungi (*Fusarium oxysporum* and *Aspergillus fumigatus*) were used in this study to assess their antimicrobial properties.

2. Experimental

2.1. Chemicals and physical measurements

All the chemicals used were of analytical reagent grade and the solvents were dried and distilled before use according to standard procedure [14]. Hydroxylamine hydrochloride, *o*-phthalaldehyde, and 3,3’-diaminobenzidine were purchased from Aldrich and were used as received.

2.2. Apparatus and experimental condition

C, H and N contents were determined by Perkin Elmer CHN 2400 elemental analyzer, and IR Spectra was recorded in the range 4000 cm^{-1} to 100 cm^{-1} with a Bruker IFS66V in KBr and polyethylene medium.

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Table 1. Elemental analysis and physical parameters of the ligand and its complexes.

Compound	Color	Molecular Weight, g	Yield, %	M.p., °C	C, % Found (Calcd.)	H, % Found (Calcd.)	N, % Found (Calcd.)	Metal, % Found (Calcd.)
Ligand	Dark brown	738	85	220	71.0(71.5)	4.5(4.6)	15.1(15.2)	-
$[Cu_2(L)Cl_4]$	Dark green	1007	80	>275	52.2(52.4)	3.5(3.3)	11.5(11.1)	12.7(12.6)
$[Ni_2(L)Cl_4]$	Dark green	997	75	>275	52.8(52.9)	3.6(3.4)	12.0(11.2)	12.2(11.7)
$[Co_2(L)Cl_4]$	Dark pink	998	85	>275	52.9(52.9)	3.5(3.4)	11.8(11.2)	12.0(11.8)
$[Mn_2(L)Cl_4]$	Pink	990	80	>275	54.0(53.3)	3.4(3.4)	11.0(11.3)	11.2(11.0)

The molar conductance of the complexes in DMF (10^{-3} M) solution was measured at 27±3 °C with a systronic model 303 digital conductivity meter. UV-visible spectra were recorded in DMF with Shimadzu UV-160A spectrophotometer in the range of 200-800 nm. ^{1}H NMR spectra was recorded on Bruker 300 spectrophotometer using DMSO-d_6 as solvent. Chemical shifts are reported in ppm relative to tetramethylsilane, using the solvent signal as internal reference. Cyclic voltammograms were recorded on a fully computer controlled system (CHI 760 Model), using 3 electrode cell assembly with platinum electrode as working electrode, standard calomel as reference electrode and platinum as the auxiliary electrode. EPR spectra were recorded at room temperature on JEOL JESTE100 ESR spectrometer. The spectrometer was operated at X-band (8-12 GHz) with microwave power of 1 mW. The room temperature magnetic moments were measured on a PAR vibrating sample magnetometer (Model-155). The TGA and DTA curves of the complexes were recorded on NETZSCH-STA 409PC thermal analyzer in heating rate of 10 °C/min with the range of 50 to 900 °C.

2.3. Antimicrobial activity

The Schiff base ligand and its complexes were investigated for anti-bacterial and anti-fungal properties. Two Gram-positive bacteria (*Staphylococcus aureus* and *streptococcus pyogenes*), two Gram-negative bacteria (*Escherichia coli* and *Klebsiella pneumoniae*) and two fungi (*Fusarium oxysporum* and *Aspergillus fumigatus*) were used in this study to assess their antimicrobial properties. All complexes exhibit antibacterial and antifungal activities against these organisms and are found to be more effective than the free ligand.

The antimicrobial activity was carried out at Progen Lab. at Salem, Tamilnadu (India). The standard disc-agar diffusion method [15] was followed to determine the activity of the synthesized compounds against the sensitive organism *S. aureus* and *S. pyogenes* as Gram positive bacteria and *E. coli* and *K. pneumoniae* as Gram-negative bacteria and the fungi *F. oxysporum* and *A. fumigatus*. The antibiotic chloramphenicol was used as standard reference in the case of Gram-negative bacteria, tetracycline was used as standard reference in case of Gram-positive bacteria and clotrimazole was used as standard anti-fungal reference. The tested compounds were dissolved in DMF (Which have no inhibition activity), to get concentration of 100 µg/mL. The test was performed on medium potato dextrose agar contains infusion of 200 g potatoes, 6 g dextrose and 15 g agar [16]. Uniform size filter paper disks (3 disks per compound) were impregnated by equal volume from the specific concentration of dissolved tested compounds and carefully placed on incubated agar surface. After incubation for 36 h at 27 °C in the case of bacteria and for 48 h at 24 °C in the case of fungi, inhibition of the organism which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

2.4. Synthesis of ligand

Phthalaldehyde monoxime was prepared by the reaction of hydroxylamine hydrochloride with *o*-phthaldehyde. Hydroxylamine hydrochloride (6 mmol) in 10 mL of ethanol and *o*-phthaldehyde (6 mmol) in 10 mL of ethanol were mixed. After mixing acidified with few drops of sodium acetate and heated at reflux for 2 h at 80 °C. The precipitated compound (oxime) was filtered and dried in desiccator using silica gel as drying agent. Phthalaldehyde monoxime (4 mmol) was dissolved in 10 mL of methanol, and 3,3'-diaminobenzedine (1 mmol) dissolved in 10 mL of methanol. Both were mixed together and heated at reflux for 3 h at 90 °C. The resulting dark brown color solution was allowed to cool, and then the dark brown color product was obtained. This product was dried in air. Yield: 85 %. M.p.: 220 °C (Figure 1).

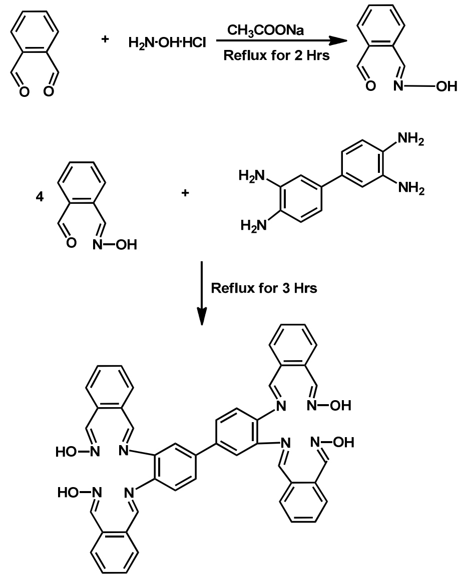


Figure 1. Synthesis of binucleating Schiff base ligand.

2.5. Synthesis of complexes

The metal complexes were prepared by reacting metal chlorides (2 mmol) in 10 mL of acetonitrile and ligand (1 mmol) in 15 mL of acetonitrile were mixed and heated at reflux for about 2 h at 90 °C. The resulting product was filtered and dried desiccator using silica gel as drying agent (Figure 2). Color, yield, melting point was shown in the Table 1.

3. Result and discussion

The color, melting point, elemental analysis and empirical formulae of the prepared complexes are listed in Table 1. The results of the elemental analysis are in good agreement with the calculated values. The metal contents of the complexes were determined according to literature methods [17]. The binuclear complexes are stable in air, non-hygroscopic, insoluble in water and most organic solvents, but are easily soluble in DMF & DMSO. The electrolytic nature of the complexes was measured in DMF at 10^{-3} M. The conductivity Λ_m lies between 13 to 7 Ω^{-1} cm^2 mol^{-1}. This result shows that the complexes were non-electrolyte in nature, and anions were coordinated inside the coordination sphere [18].

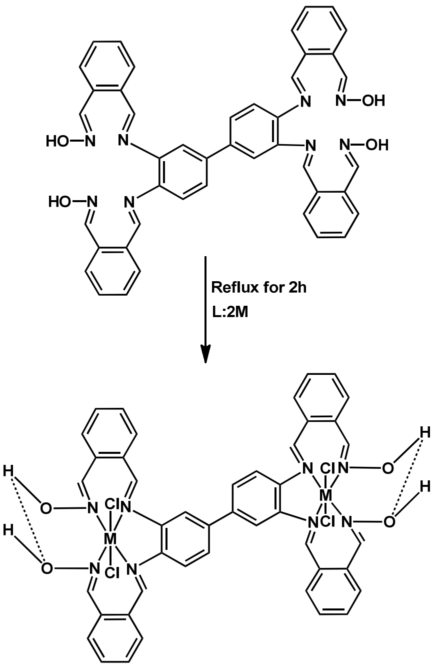
Table 2. IR spectral data of the ligand and its complexes (ν in cm^{-1}).

Compound	O-H	C=N	N-O	M-N	O-H....O	M-Cl
Ligand	3200	1608	1470	-	1726	-
$[Cu_2(L)Cl_4]$	3330	1589	1420	464	1720	311
$[Ni_2(L)Cl_4]$	3358	1595	1475	460	1710	324
$[Co_2(L)Cl_4]$	3355	1594	1473	423	1722	315
$[Mn_2(L)Cl_4]$	3341	1590	1479	447	1716	329

Table 3. Electronic spectral data and magnetic values of the ligand and its complexes.

Compound	μ_{eff}, B.M.	Λm, Ω^{-1} cm^2 mol^{-1}	λ_{max}, nm		
			$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	*d - d*
Ligand	-	-	246	325	-
$[Cu_2(L)Cl_4]$	1.84	12.9	269	390	664
$[Ni_2(L)Cl_4]$	2.80	8.2	268	393	555, 600
$[Co_2(L)Cl_4]$	4.82	12.4	270	398	604, 666
$[Mn_2(L)Cl_4]$	5.85	7.7	257	385	552, 597

IR spectra is very much useful to give information to predict the nature of bonding of ligand to metal and nature of complexes. The IR spectra of metal complexes and ligand were recorded in the range of 100 to 4000 cm^{-1} (Table 2). In IR spectra of ligand OH was band observed at 3200 cm^{-1}, C=N band at 1608, and N-O at 1470 cm^{-1}. In metal complexes the broad band were observed at 1720, 1710, 1722, and 1716 cm^{-1} for Cu(II), Ni(II), Co(II) and Mn(II) complexes, respectively. A broad band was obtained due to O-H....O intra molecular hydrogen bond [19-20]. The shift in C=N and O-H in complexes predict the concept of co-ordination of ligand through nitrogen atoms. A shift in N-O frequency of complexes proved the oxime group of nitrogen is coordinated. The bands at 470-420 cm^{-1} are due to coordination of metal and the oximino or imino nitrogen of complexes (M-N) [21]. The bands at 310-330 cm^{-1} are due to the M-Cl [22].



L: Ligand
M: Cu(II), Ni(II), Co(II), Mn(II) chlorides

Figure 2. Synthesis of metal complexes.

Electronic spectra of all the complexes were recorded in DMF medium. The data were summarized in Table 3. In electronic spectra of metal complexes the wide range of bands are due to transition of -CH=N-, charge transfer results from electrons interaction between the metal and the ligand which involves either a metal to ligand or ligand to metal electron transfer [23]. The bands observed in 240 to 280 nm are due to $\pi \rightarrow \pi^*$ transition of C=N group [24]. The band was shifted to higher range, which is due nitrogen that involved in coordination with metal ion. The absorption bands are observed in the range of 320 to 400 nm due to $n \rightarrow \pi^*$ transition from imine group corresponding to the ligand or metal complexes. The copper (II) binuclear complex shows a broad absorption peak at 664 nm and arises due to the d-d transition $^2Eg \rightarrow {}^2T_{2g}$ of Cu(II) ion suggest that the copper ion exhibits an octahedral geometry [25-26]. Electronic spectra of the nickel (II) binuclear complex shows bands at 555 and 600 nm which are assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transitions, respectively, suggesting an octahedral arrangement around the nickel(II) complex [25-26]. The electronic spectra of binuclear cobalt (II) complexes exhibit absorption at 604 and 666 nm are assigned to $4T_{1g}(F) \rightarrow 4T_{1g}(P)$, $4T_{1g} \rightarrow 4A_{2g}$ transitions, respectively corresponding to cobalt (II) octahedral complex [25-26]. The Mn(II) binuclear complex shows bands at 552 and 597 nm, respectively, are corresponding to $^6A_{1g} \rightarrow {}^4E_g(4D)$, $^6A_{1g} \rightarrow {}^4T_{2g}(4G)$ transitions which are compatible to an octahedral geometry around manganese (II) ion [25-26].

The structure of ligand was confirmed by ^1H NMR. The singlet at 8.13 ppm was attributed to CH=N proton. The multiplet observed 7.4 to 8.0 ppm were due to aromatic system. The singlet at 11.37 ppm was due to proton of N-OH.

3.1. Electrochemical study

Electrochemical properties mainly depend up the chelating ring/size, distribution of unsaturation and substitution pattern in the chelating ring. The electrochemical properties were studied by using cyclic voltammetry in DMF solution containing TBAP as supporting electrolyte in the potential range of 1.2 to -2.0 V. The data were shown in the Table 4. The quasi-reversibility of reduction process is confirmed with the corresponding peak separation value between the cathodic peak potential and anodic peak potential, the anodic peak current to cathodic peak current ratio is almost unity. In copper complex the first redox potential appears at 487 mV and 295 mV. The ΔEp_1 was 192 mV and the second redox potential appears at -674 mV, -500 mV. The ΔEp_2 was -174 mV. From the ΔEp values copper complexes followed quasi-irreversibility. The ratio between anodic peak current to cathodic peak current was almost unity this also confirmed the reaction followed quasi-irreversibility. Based on above redox potential the copper complex may involve step wise reduction process as follows,

$$Cu(II)\,Cu(II) \leftrightarrows Cu(II)\,Cu(I) \leftrightarrows Cu(I)\,Cu(I) \qquad (1)$$

In nickel complex, ΔEp_1 of first redox potential was 105 mV and ΔEp_2 of second redox potential was -125 mV these two value are confirmed that the nickel complex followed quasi-irreversibility.

Table 4. Electrochemical data of the metal complexes.

Compound	Epa	Epc	ΔEp_1	Epa	Epc	ΔEp_2
$[Cu_2(L)Cl_4]$	487	295	192	-674	-500	-174
$[Ni_2(L)Cl_4]$	370	475	105	-600	-475	-125
$[Co_2(L)Cl_4]$	325	200	125	-1300	-1200	-100
$[Mn_2(L)Cl_4]$	85	185	100	-850	-725	-125

Supporting electrolyte: Tetra butyl ammonium perchlorate (0.05 M). Complex concentration: 0.01 M. Solvent: DMF. Scan rate: 100 mV.s^{-1}. ΔEp = Epa-Epc (Epa and Epc are anodic and cathodic potentials, respectively).

Table 5. Thermal analysis data of the metal complexes.

Compound	Range °C	DTA °C	Estimated Loss (Calcd.) %		Assignments
			Mass loss %	Total loss %	
$[Cu_2(L)Cl_4]$	50-160 °C 161-760 °C >760 °C	Endo-125 °C Exo-540 °C	7.48 (6.75) 60.55 (60.18)	68.03 (66.93)	1. Loss of four hydroxyl ions. 2. Loss of four chloride ions and aromatic ligand groups. 3. Decomposition in progress.
$[Co_2(L)Cl_4]$	50-120 °C 121-190 °C 191-750 °C >750 °C	Endo-100 °C Endo-155 °C Exo-525 °C	7.98 (6.81) 12.47 (14.23) 48.50 (46.49)	68.95 (67.53)	1. Loss of four hydroxyl ion 2. Loss of four chloride ions 3. Loss of aromatic ligand groups. 4. Decomposition in progress.

Table 6. Antimicrobial activities of ligand and its metal complexes*.

Sample	Bacteria				Fungi	
	Gram-positive		Gram-negative			
	S. aureus	*S. pyogenes*	*E. coli*	*K. pneumoniae*	*F. oxysporum*	*A. fumigatus*
Tetracycline	25	27	--	--	--	--
Chloramphenicol	--	--	29	30	--	--
Clotrimazole	--	--	--	--	21	23
Ligand	12	11	14	13	09	08
$[Cu_2(L)Cl_2]$	14	18	20	18	16	17
$[Ni_2(L)Cl_2]$	18	21	21	22	15	15
$[Co_2(L)Cl_2]$	19	22	24	23	15	15
$[Mn_2(L)Cl_2]$	13	15	19	17	12	09

* Inhibition zone in mm, concentration 100 μg/mL.

In cobalt complex, ΔEp_1 was 125 mV and ΔEp_2 was -100 mV, and manganese complex ΔEp_1 was 100 mV and ΔEp_2 was -125 mV. Based on the above results cobalt and manganese complex also followed quasi-irreversibility reactions [27-29].

3.2. ESR and magnetic moments studies

ESR measurement has been made for copper complex using powder sample at room temperature, which could provide only value of g_{iso} and does not give hint about the individual g perpendicular and g parallel. The g_{iso} value of the complex is 2.157. The value of g_{iso} shows that the copper (II) complex is in octahedral environment. The magnetic moments of Cu(II), Ni(II), Co(II), Mn(II) are 1.84, 2.80, 4.82 and 5.85 B.M., respectively. The values are almost equal spin only value. This indicates that the two metal centers are equivalent and there is no interaction between two metal centers. The pairing of electron is prevented by greater distance between two metal centers [30].

3.3. Thermal study

Thermal analysis such as thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was widely applied in studying the thermal behavior of metal complexes [31-32]. The data (Table 5) provides information concerning thermal stability and thermal decomposition of these compounds in solid state. In copper complex one endothermic peak was observed at 125 °C is assigned to loss of four hydroxyl ions from 50 to 160 °C 7.48 (6.75)%. One exothermic peak observed at 540 °C which is due to loss of four chloride ions and aromatic ring in the ligands from 161-760 °C, 60.55 (60.18)%. After 760 °C the decomposition not completed. In cobalt complex one endothermic peak was observed at 100 °C which is the elimination four hydroxyl ions at 50-120 °C, 7.98 (6.81)%. Another endothermic peak was observed at 155 °C is assigned to the loss of four chloride ions 12.47 (14.23) % at 121 °C to 190 °C. One exothermic peak at 525 °C is attributed to the loss of aromatic ring in the ligands from 191 °C to 750 °C 48.50 (46.49) %. The decomposition is not completed after 750 °C.

3.4. Antimicrobial assay

Biological activity of the ligand and a series of its metal complexes [Cu(II), Ni(II), Co(II) and Mn(II)] were screened for antibacterial activity against *S. sureus* and *S. pyogenes* as Gram positive bacteria and *E. coli* and *K. pneumoniae* as Gram-negative and the fungi *F. oxysporum* and *A. fumigatus* by using disc-agar diffusion method. From Table 6, the Gram positive bacteria on all metal complexes were found to inhibit all tested bacteria at different rates and the activity as following order Co > Ni > Cu > Mn. In Gram negative bacteria also follows the same order and all complexes have higher bacterial activity than ligand. In fungal activity, the ligand showed activity against *Fusarium oxysporum* and *Aspergillus fumigatus* and metal complexes showing activity in the following order Cu > Co = Ni >Mn. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or on differences in ribosome of microbial cells [33-37]. The complexes show more activity and the ligands have less activity against same microorganisms under identical experimental conditions. This would suggest that, the chelation could facilitate the ability of a complex to cross a cell membrane and can be explained by Tweedy's chelation theory [38]. Chelation considerably reduces the polarity of the metal ion because of partial sharing of its positive charge with donor groups and possible electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layer of the cell membrane.

4. Conclusion

The potential binucleating tetradentate Schiff base has been prepared and employed to synthesize a novel binuclear Schiff base metal complexes. The spectroscopic data of metal complex indicated that the metal ions were complexed with nitrogen of the oxime and imine groups and presence of octahedral geometry around metal ions. Further, these complexes were tested for anti-bacterial and antifungal activity. The synthesized complexes are less active than the standards.

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