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## Synthesis, Sectral Characterization, Thermal and Anti-microbial Studies of New Binuclear Metal Complexes Containing Tetradentate Schiff Base Ligand

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#### **ABSTRACT**

A novel binuclear Schiff base ligand was prepared by the reaction between 3,3'diaminobenzidine with o-hydroxyacetophenone. The ligand and metal complexes have been characterized by elemental analysis,UV,IR, H, magnetic succeptibility, conductivity measurements and EPR. The molar conductance studies of Cu(II),Co(II) and Mn(II) complexes showed non-electrolyte in nature where as Ni(II) complex showed electrolytic in nature. The spectroscopic data of metal complexes indicated that the metal ions are complexed with azomethine nitrogen and phenolic oxygen atoms. The binuclear metal complexes exhibit different geometrical arrangements such as square planar and octahedral arrangements. The microbial activities and thermal studies have also been studied. In microbial activity all complexes showed good microbial activity higher than ligand against gram positive, gram negative bacteria and fungus.

Keywords: Schiff base, epr (electron spin resonance), o-hydroxyacetophenone, microbial activity

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## INTRODUCTION

Schiff base complexes have been extensively investigated in recent and past years and have been employed in areas of catalysis[6], material chemistry[11], and magneto chemistry[9]. Binuclear Schiff base complexes have been of continuing interest because of their roles as biological models, catalyst for organic reaction as components in the formation of new materials[12]. Copper complexes are considerably interesting due to their variety in coordination chemistry, technical application, catalysis, spectroscopic properties, anion selectivity, and their biological significance. [2,19]. A wide variety of cobalt(II) complexes are known to bind dioxygen more or less reversibly and are therefore frequently studied as model compounds for natural oxygen carriers and for their use in O<sub>2</sub> storage, as well as in organic synthesis due to their catalytic properties under mild conditions [14]. For these applications, we are extending this field in synthesis of novel binuclear Schiff base complexes.

In this paper the novel complexes derived from o-hydraxyacetophenone with 3,3' diaminobenzidine were synthesized and characterized by elemental analysis, UV, IR, NMR, EPR and molar conductance. Thermal study has also been studied. The Schiff base ligand and its complexes were investigated for their anti-bacterial and anti-fungal properties. One gram-positive bacteria (Staphylococcus aureus), one gram-negative bacteria (Escherichia coli) and one fungus (Aspergillus fumigatus) were used in this study to assess their antimicrobial properties.

## MATERIALS AND METHODS

## **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 [23]. O-hydroxyacetophenone and 3,3'-diaminobenzidine were purchased from Aldrich and were used as received..

## Physical measurements (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<sup>-1</sup> to 100 cm<sup>-1</sup> with a Bruker IFS66V in KBr and polyethylene medium for manganese complex and other complexes recorded in the range 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The molar conductance of the complexes in DMF (10<sup>-3</sup> M) solution was measured at 27±3 °C with an Elico model conductivity meter. UV-visible spectra were recorded in DMF with Elico spectrophotometer 164 in the range of 200-800 nm. H<sup>1</sup>NMR spectra was recorded on Bruker 300 spectrophotometer using DMSOd<sub>6</sub> as solvent. Chemical shifts are reported in ppm relative

to tetramethylsilane, using the solvent signal as internal reference. 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 1mW. 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°K/min with the range of 50 °C to 900 °C.

## **Anti-Microbial activity**

The Schiff base ligand and its complexes were investigated for anti-bacterial and anti-fungal properties. One Grampositive bacteria (Staphylococcus aureus), one Gram-negative bacteria (Escherichia coli) and one fungus (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 [1] was followed to determine the activity of he synthesized compounds against the sensitive organism S.sureus as gram positive bacteria and E.coli as Gram-negative and the fungus 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  $50,100,150\,\mu\text{g/mL}$ . The test was performed on medium potato dextrose agar contains infusion of  $200\,\text{g}$  potatoes,  $6\,\text{g}$  dextrose and  $15\,\text{g}$  agar [7]. 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  $36\,\text{h}$  at  $27\,\text{°C}$  in the case of bacteria and for  $48\,\text{h}$  at  $24\,\text{°C}$  in the case of fungus, inhibition of the organism which evidenced by clear zone surround each disk was measured and used to calculate mean of inhibition zones.

## **Synthesis of Ligand**

O-hydroxyacetophenone 4mmol was dissolved in methanol, and 3,3'diaminobenzedine 1mmol dissolved in methanol. Both were mixed together and reflux for 2 h at 90 °C. The resulting dark brown color solution was allowed to cool. The dark brown color product was obtained. This product was filtered and dried in air.Yield-85 %. M.p 220 °C

## **Synthesis of complexes**

The metal complexes were prepared by reacting Copper(II)nitrate, Cobalt(II)nitrate, Nickel(II) acetate and manganese(II) chloride (2 mmol) and ligand (1 mmol) in acetonitrile were mixed separately and refluxed for about 2 h at 90 °C. The resulting product was filtered and dried over anhydrous  $P_2O_5$ . Color, yield, melting point were shown in the Table1.

#### RESULT AND DISCUSSION

The color, melting point, elemental analysis and empirical formulae of the prepared complexes are listed in Table1. 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 [3]. 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 is measured in DMF at  $10^{-3}$ M. The conductivity  $\Lambda$ m lies between 13 to 8  $\Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup> for copper, cobalt and manganese complexes. This result shows that the complexes were non-electrolyte in nature, and anions were coordinated inside the coordination sphere [16]. For nickel complex the conductivity lies in  $100 \ \Omega^{-1}$  cm<sup>2</sup> mol<sup>-1</sup>. This is due to the presence of anion which is present in the outside of coordination sphere.

The IR spectra of metal complexes and ligand were recorded in the range of 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> and for the manganese complex in the range of 100 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>. The azomethine group (C=N) stretching frequency of free ligand appears around 1604 cm<sup>-1</sup>. The frequency have been shifted to lower number in the range of 1590 to 1575 cm<sup>-1</sup> is accordance with the coordination of the azomethine function to the metal ion for all the complexes. The lowering wave number is due to decrease in electron density of the azomethine group. In IR spectra of ligand OH was band observed at 3370 cm<sup>-1</sup>. A band observed at 1300 cm<sup>-1</sup> was assigned at phenolic oxygen for free ligand. On complexation this band is shifted to higher frequency in the range 1308 to 1315 cm<sup>-1</sup> and it is further supported by the disappearance of OH frequency at 3370 cm<sup>-1</sup> in all complexes. The absorption of the co-ordinated

ions at 1460-1450, 1300-1310 and 1040-1455 cm<sup>-1</sup> suggest the presence of the co-ordinated nitrate groups[20]. The bands in the region 500 to 550 cm<sup>-1</sup> and 400 to 480 cm<sup>-1</sup> were due to the formation of M-O and M-N bands[4]. The absorption at 1350 cm<sup>-1</sup> was assigned to uncoordinated acetate ion. The bands at 315 cm<sup>-1</sup> are due to the M-Cl[13]. Electronic spectra of all the complexes were recorded in DMF medium. The data are listed in the Table 3.The bands observed in 240 to 260 nm are due to  $\pi \rightarrow \pi^*$  transition of benzene ring and azomethine group [18]. The bands were shifted to higher range, which is due nitrogen and oxygen that involved in coordination with metal ion. The absorption bands are observed in the range of 320 to 370 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 642 nm and arises due to the d-d transition  $2Eg \rightarrow 2T_{2g}$ , of Cu(II) ion suggest that the copper ion exhibits a octahedral geometry [8]. Electronic spectra of the nickel(II) binuclear complex shows bands at 520, 635 nm which are assigned to  ${}^{1}A_{g} \rightarrow {}^{1}B_{1g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$  transitions, respectively suggesting an square planner arrangement around the nickel(II) complex [8]. The electronic spectra of binuclear cobalt(II) complexes exhibit absorption at 520, 616 nm are assigned to  $4T_{1g}\left(F\right)\rightarrow 4T_{1g}(P),\, 4T_{1g}\rightarrow 4A_{2g}\,$  transitions, respectively corresponding to cobalt(II) octahedral complex [8]. The Mn(II) binuclear complex shows bands at 540,584 nm, respectively are corresponding to  ${}^{6}A_{1g} \rightarrow$  $^{4}\text{E}_{g}(4\text{D}), ^{6}\text{A}_{1g} \rightarrow ^{4}\text{T}_{2g}(4\text{G})$  transitions which are compatible to an octahedral geometry around manganese(II) ion [8]. The structure of ligand was confirmed by H<sup>1</sup> NMR. The triplet observed at 2.44 to 2.43 ppm was attributed to methyl group. The multiplet observed 6.61 to 7.83 ppm were due to aromatic system. The singlet at 14.95 ppm was assigned to proton of Ar-OH.

## EPR and magnetic studies

EPR 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 g parallel and g perpendicular values. The  $g_{iso}$  value of the complex is 2.095. The value of  $g_{iso}$  shows that the copper (II) complex is in octahedral environment. The magnetic moments of copper(II), Cobalt(II) and Manganese(II) are 1.81, 4.14, 5.85 B.M respectively which are almost equal to the total spin only value. This indicates that the two paramagnetic centers are equivalent and there is no interaction between the metal centers. The pairing of electron is prevented by greater distance between two metal centers [21].

## Thermal study

In copper(II) binuclear complex one endothermic peak was observed at 120 °C which is assigned to the elimination of 4NO<sub>3</sub><sup>-</sup> molecule at 30-210°C 23(23.46) %. Two exothermic peak and two endothermic peak were observed at 240,515 °C and 315,670 °C respectively which is attributed to loss of aromatic ligand group from 211 to 760°C 29.00(28.76) %. After 760 °C the decomposition was not completed. In nickel(II) binuclear complex one endothermic peak at 70 °C and another exothermic peak observed at 105 °C were assigned to the loss of four acetate ions at 30 to 200°C 22.00(22.80) %. One exothermic peak at 315 °C and another exothermic peak at 435 °C were due to loss of aromatic ligand groups from 201 to 615°C 30.00(29.37) %. One endothermic peak at 670 °C and one exothermic peak at 825 °C were assigned to loss of four CH<sub>3</sub>CN at 616-900°C 16.5(15.84) %. After 900 °C the decomposition was not completed (Table 4).

## Anti-microbial 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 as gram positive bacteria and E.coli as Gram-negative and the fungi A.fumigatus by using broth micro dilution procedures. From table(5), 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 Aspergillus fumigatus and metal complexes show activity in the following order Cu > Co > Ni > Mn. It is known that chelation tends to make the ligand to act as more powerful and potent bacterial agent. A possible explanation for this increase in the activity upon chelation is that, in chelated complex, positive charge of the metal is partially shared with donor atoms present on ligands and there is an electron delocalization over the whole chelating ring. This, in turn, increases the lipid layers of the bacterial membranes. Generally, it is suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms [5,10,15,17,22].

## **CONCLUSION**

The ligand and its metal complexes were prepared and characterized by physio-chemical methods. In molar conductance of binuclear copper(II), cobalt(II) and manganese(II)complexes were non-electrolytic in nature whereas nickel(II) binuclear complex showed electrolyte in nature. The spectroscopic data of metal complex indicated that the metal ions are complexed with nitrogen of the imine and phenolic oxygen atoms. In magnetic moments studies complexes showed that there is no interaction between two metal centers. The TGA showed that in nickel complex anion coordinated outside the coordination sphere. Hence the copper(II),cobalt(II) and manganese(II) complexes have been octahedral structures. Nickel(II) binuclear complex has been in square planar structure. In antibacterial studies cobalt(II) binuclear complex showed good activity and in antifungal studies of copper(II) binuclear complex showed good activity.

Table-1: Physical data and elemental analysis.

Complex	Color	Molecular	Yield	m.p.	C %	Н %	N %	Metal %
		weight g	in %	in	Found(Cal)	Found(Cal)	Found(Cal)	Found(Cal)
				°C				
Ligand	Dark	686	85	220	76.5(76.9)	5.4(5.5)	8.2(8.1)	-
	brown							
[Cu2(L)(NO3)4]	Deep	1057	80	>270	49.4(49.9)	3.1(3.2)	10.3(10.6)	12.2(12.0)
	green							
$[Ni_2(L)]^{4+}4Ac^{-}$	Yellowish	1035	75	>270	60.4(60.2)	4.5(4.4)	5.2(5.4)	11.1(11.3)
	green							
[Co <sub>2</sub> (L)	Brown	1048	83	>270	50.1(50.3)	3.2(3.2)	10.3(10.6)	11.4(11.2)
$(NO_3)_4]$								
$[Mn_2(L)Cl_4]$	Dark red	933	77	>270	56.9(56.5)	3.5(3.6)	6.1(6.0)	11.2(11.7)

Table-2: IR Spectral Studies of Ligand and Metal Complexes (in cm<sup>-1</sup>)

Complex	О–Н	C=N	М-О	M-N	No <sub>3</sub>	M-Cl	CH <sub>3</sub> COO	C-O
Ligand	3370	1604	-	-	-	-	-	1300
$[Cu_2(L)(NO_3)_4]$	-	1579	525	442	1450,1310 ,1040	-	-	1315
$[Ni_2(L)]^{4+}4Ac^{-}$	-	1575	533	450	-	-	1350	1308
[Co <sub>2</sub> (L) (NO <sub>3</sub> ) <sub>4</sub> ]	-	1585	543	448	1455,1302 1036	-	-	1311
$[Mn_2(L)Cl_4]$	-	1590	537	456	-	315	-	1309

Table-3: UV Spectral and Magnetic Studies

Complex	11	$\Lambda m$ $\Omega^{-1} cm^2$ $mol^{-1}$	$\lambda_{max}$ in nm				
	$\mu_{eff}$ (B.M)		π→π*	n→π*	d — d		
Ligand	-	=	240	320	-		
[Cu <sub>2</sub> (L)	1.81	13	255	353	642		

$(NO_3)_4]$					
[Ni2(L)]4+4Ac-	-	100	260	365	520,635
[Co <sub>2</sub> (L) (NO <sub>3</sub> ) <sub>4</sub> ]	4.41	11	258	350	520,616
$[Mn_2(L)Cl_4]$	5.85	08	252	370	540,584

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Fig.-1: Synthesis of Ligand and its metal complexes

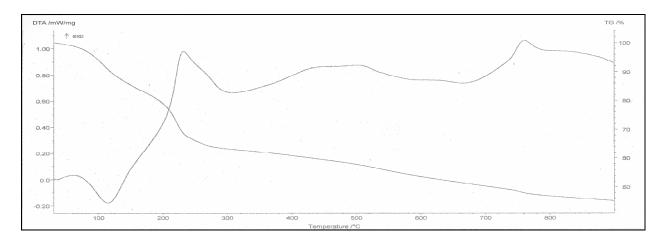


Fig.-2: TG/DTA of [Cu<sub>2</sub>(L) (NO<sub>3</sub>)<sub>4</sub>] complex

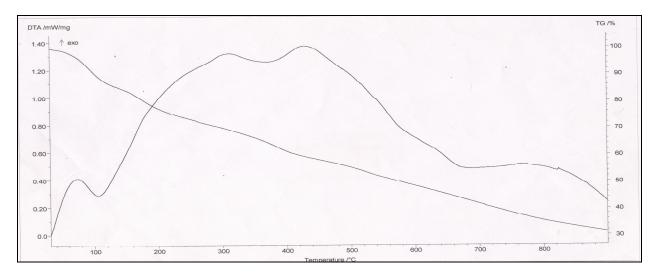


Fig.-3: TG/DTA of  $[Ni_2(L)]^{4+}4Ac^-$  complex

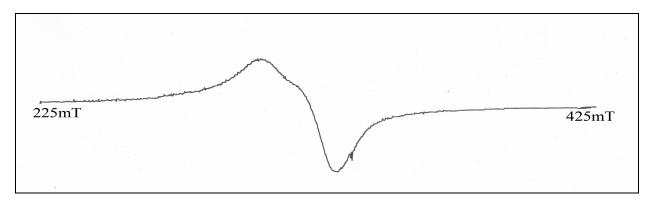


Fig.-4: EPR Spectrum of  $[Cu_2(L) (NO_3)_4]$  Complex

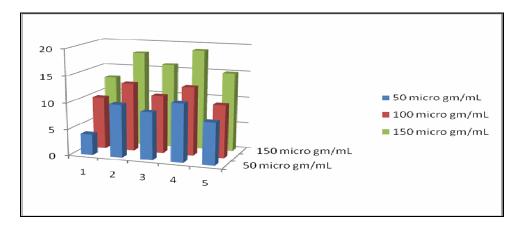


Fig.-5a: Anti-bacterial studies (S.aureus gram positive) of Schiff base ligand and its metal Complexes.

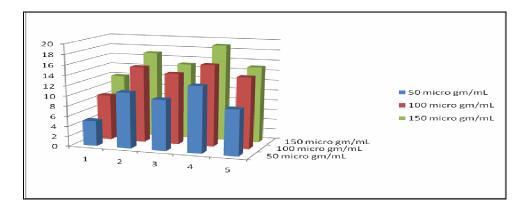


Fig.-5b: Anti-bacterial studies (E.coli gram negative)) of Schiff base ligand and its metal complexes

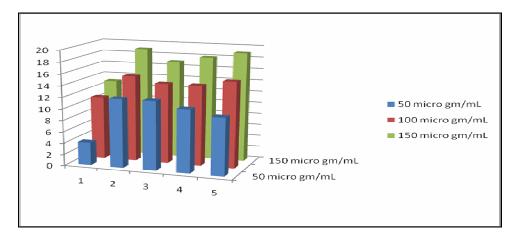


Fig.-5c: Anti-fungal studies of (A.fumigatus) Schiff base ligand and its metal complexes 1=Ligand 2=copper complex, 3=nickel complex, 4=cobalt complex and 4=manganese complex Inhibition zone in cm.

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Table-4: Thermal Studies

			Estimated loss(Cal)%		
Complex	Range °C	DTA°C	Mass loss %	Total loss %	Assignments
[Cu <sub>2</sub> (L)	30-210 °C	Endo-120 °C	23.00(23.46)	52.00(52.22)	1. Elimination of 4NO <sub>3</sub>
$(NO_3)_4$	211-760 °C	Endo-315,670 °C	29.00(28.76)		ions.
	>760 °C	Exo240,515 °C			2. Elimination of
					aromatic ligand
					groups.
					3. Decomposition in
			22 00 (22 00)	60.7(60.04)	progress.
53.7. (7.)34+44	30-200 °C	Endo-70 °C	22.00(22.80)	68.5(68.01)	1. Elimination of four
[Ni2(L)]4+4Ac-	201-615 °C	Exo-105 °C			acetate ions.
	616-900 °C	Exo-315,435 °C	30.00(29.37)		2. Elimination of
	>900 °C	Endo-670,Exo-	16.50(15.84)		aromatic ligand groups.
		825 °C			3. Elimination of
		023 C			4CH3CN groups.
					4. Decomposition in
					progress.

Table-5: Anti-microbial Activities of Ligand and Metal Complexes

	Bacteria								Fungi	
	Gı	Gram-positive			Gram-negative					
		S.aureus		E.Coli			A.Fumigatus			
	50	100	150	50	100	150	50	100	150	
Sample	μg/mL	μg/mL	μg/mL	μg/mL	μg/mL	μg/mL	μg/mL	μg/mL	μg/mL	
Ligand	4	10	13	5	9	12	4	11	13	
$[Cu_2(L)\ (NO_3)_4]$	10	13	18	11	15	17	12	15	19	
[Ni2(L)]4+4Ac-	9	11	16	10	14	15	12	14	17	
$[\operatorname{Co}_2(L) \ (\operatorname{NO}_3)_4]$	11	13	19	13	16	19	11	14	18	
$[Mn_2(L)Cl_4]$	8	10	15	9	14	15	10	15	19	

Inhibition zone in cms.

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