# Available online at <u>www.pelagiaresearchlibrary.com</u>



**Pelagia Research Library** 

Der Chemica Sinica, 2014, 5(3):38-46



# Synthesis of heterocyclic metal complexes, structural design and their anti-microbial potentials

Basavaraj M. Kalshetty<sup>a\*</sup>, Ramesh S. Gani<sup>b</sup> and Mallikarjun B. Kalashetti<sup>c</sup>

<sup>a</sup>Department of Chemistry, B.L.D.E.A's Science College, Jamkhandi, Karnataka, India. <sup>b</sup>Department of Chemistry Bharathiar University, Coimbatore, Tamil Nadu, India. <sup>c</sup>Department of Chemistry, Karnataka University, Dharwad, Karanataka, India

# ABSTRACT

New Schiff bases were derived by the condensation of 3–Aldehydosalicylic acid with p-Toludine and p-anisidine in alcoholic medium, forming 2-hydroxy-3-[(p-tolylimino) methyl] benzoic acid (Scheme 1) and 2-hydroxy-3-[(4-methoxy phenylimino) methyl] benzoic acid (Scheme 2). The coordination complexes of bivalent metal ions such as Cu (II), Zn (II), Co (II), Cd (II) and Ni (II) with these ligands were synthesized at various pH ranges. Hence, the structural design of synthesized metal complexes reveals the different coordination at different pH-ranges. These complexes have been characterized on the basis of elemental analysis, FTIR spectra and <sup>1</sup>HNMR spectra. The complexes were colored and stable in air, the ligands act as monobasic bidantate, dibasic tridentate and dibasic tetradentate in nature at different pH ranges and forms 1:1 and 1:2 complexes with metal ions. The ligands and their metal complexes have also been tasted for their antimicrobial behavior against various microorganisms and all the complexes have shown good antimicrobial activity.

Keywords: Schiff base complexes, FTIR Spectra, structural design, nature of ligands, antimicrobial activity.

# INTRODUCTION

Schiff base ligands and their metal complexes have been an active area of research due to the active sites in biologically important molecules and rich coordination Chemistry. Such ligand systems are used in drug design and in herbicides [1-3]. And fungicides. Derivatives of Coumarin, Thiazolidinone and Triazoles so far reported as anti-inflammatory [4], anti-oxidant[5], Vasorelant [6], Cytotoxic [7], anti-HIV [8], anti-tubercular [9], anti-microbial [10] and other effective therapies [11]. The organometallic complexes are their versatile potential applications in pharmaceutical and in Chemical industries.

The metal complexes approach to develop new drugs, the development of Penicillin showed the presence of Thiozolidine ring. Next, the development of Coumarin and its derivatives like Amino-methyl Coumarin metal complexes are useful in the area of Medical Chemistry. The metal complexes with Nitrogen containing heterocyclic ligands have Potential applications in the areas of catalysis, luminescent materials [12-14] and are used as drug [15]. We were interested to isolate and characterize new heterocyclic metal complexes with p-Toludine, p-anisidine based ligands in combination with 3-Aldehydosalicyclic acid. Herein, we report on the synthesis, characterization and structures of metal complexes in different pH - ranges. Successfully, we have isolated a series of complexes and characterized using the spectroscopic and other Physico-chemical results. The Schiff base ligands (Scheme 1 and

Pelagia Research Library

# Basavaraj M. Kalshetty et al

Scheme 2) synthesized by standard methods. It is predicted that the coordination behavior of ligand would be developed on pH using different from these reported so far [16].

#### MATERIALS AND METHODS

All the chemicals used were of AR grade obtained from the commercial sources. The anhydrous metal chlorides were procured from Merck and Qualigens and used as such. The Schiff bases and metal complexes were synthesized by the known methods.

#### Synthesis of Ligands (LH<sub>2</sub>)

3-Aldehydosalicylic acid and p-Toludine, p-anisidine separately dissolved in ethanol (25ml) with stirring. The reaction mixture was heated under reflux on a sand bath (heating mental) for 4 hours. On cooling to room temperature, the yellow coloured solid obtained was filtered, washed with methanol and dried in desiccators over silica gel. Yields 75% - 80%, M.P. of synthesized Schiff bases were found to be 242°C and 268oC respectively. 1HNMR:  $\delta$  6.8 to  $\delta$  8.1 (Aromatic H),  $\delta$ 2.3(s) (CH3)  $\delta$ 3.4(s) (-OCH<sub>3</sub>),  $\delta$ 9.3(s) to  $\delta$ 9.46(s) (-CH=N),  $\delta$ 10.5 (s) (-COOH) and  $\delta$ 13.34 (s) (-OH phenolic).

#### Synthesis of metal complexes

An equimolar quantity of Schiff bases and appropriate metal salt were dissolved separately in alcohol on continuous stirring. The resulting mixture was refluxed for 4 hours. On cooling to room temperature, the cooled complexes precipitated out was filtered, washed with hot water and finally dried under vacuum at room temperature. Yield 70 - 75%. M.P. of each organometallic complex were determined and recorded in the Table 2. The structures of the organometallic complexes were confirmed by spectral studies.

#### **Physical measurements**

Elemental analysis of C, H and Nitrogen were obtained using Erba 1108 analyzer and Nitrogen analyzer instruments. IR spectra were recorded on a Perkin Elmer 597 spectrometer using KBr pallets; <sup>1</sup>HNMR spectra of ligands were obtained using NMR spectrometer in DMSO solvent.

#### Anti-microbial activity

The anti-microbial activity of the ligand and the complexes was carried out against *Escherichia Coli* and *Staphylococcus aureus* by agar diffusion method. DMSO was taken as control. In order to check the potency of compounds, the solutions were prepared with 500 and 1000 ppm concentration in DMSO. The solutions prepared were soaked in Whitman filter paper No.1 (diameter 10mm), these paper discs were kept on the previously seeded Petri plates for incubation at 25°C to 30°C for 24 hours. The diameters of the zones of inhibition were measured in millimeter.

#### **RESULTS AND DISCUSSION**

#### **General Characterization**

Schiff base ligands  $(LH_2)$  scheme 1 and scheme 2 were dark yellow in color, possessing sharp melting points 236°C and 242°C respectively. Both were easily soluble in alcohol, owing to the possession of the phenolic (-OH) and carboxylic (-COOH) groups.



Scheme 1. [2-hydroxy-3-[(p-tolylimino) methyl] benzoic acid]

Pelagia Research Library



[2-hydroxy-3-[(4-methoxy phenylimino) methyl] benzoic acid

### Synthesis of metal complexes at various reaction conditions:

a. At pH- 3-4 (Acidic conditions): An aqueous solution of the ligands  $(LH_2)$  [Scheme 1 and Scheme 2] react with metal ions in (2:1) molar ratio forming metal complexes of the type [ML<sub>2</sub>], where M= Cu(II), Zn(II), Cd(II) [Scheme 3 and Scheme 4], indicating monomeric nature of metal complexes with OO-donor at this pH- range.

 $\begin{array}{ll} MCl_2 + 2LH_2 \ (aq) & \twoheadrightarrow & [M \ L_2] + 2HCl. \\ M = Cu \ (II), \ Zn \ (II), \ Cd \ (II). \end{array}$ 

b. At pH- 7-8 (Neutral conditions): 50% (v/v) water- alcohol solution of ligand (LH<sub>2</sub>) [Scheme 1 and Scheme 2] refluxed with alcoholic solution of metal ions in equimolar quantities, forming the metal complexes of the type  $[ML_2]$ , where M= Cu (II), Zn (II), Cd (II) [Scheme 5 and Scheme 6] suggesting monomeric nature of metal complexes with OON- donor at this pH ranges.

 $MCl_2 (alc) + 2LH_2 (alc) \xrightarrow{\rightarrow} [M L_2] + HCl.$ Reflux EtOH

c. At pH- 10-11 (Alkaline conditions): An alcoholic solution of metal ions react with alcoholic solution of ligands [Scheme 1 and Scheme 2] in equimolar quantities in the presence of sodiumethoxide, forming the bimetallic complexes of the type [ML(EtOH)<sub>2</sub>] where M = Cu(II), Zn(II), Ni(II), Co(II), Cd(II) [Scheme 7 and scheme 8]. Suggesting dimeric nature of metal complexes with OONO- donor bimetallic complexes at this pH ranges.

 $\begin{array}{c} \text{Reflux EtOH} \\ 2\text{MCl}_2 + 2\text{LH}_2 & \xrightarrow{\phantom{aaaa}} 2 \left[\text{ML (EtOH)}_2\right] + 4 \text{ HCl} \\ \text{M} = \text{Cu (II), Zn (II), Ni (II), Co (II), Cd (II) .} \end{array}$ 

The physical characteristic and analytical data of the ligands and metal complexes were reported in Table 1. The molecular measurements indicting the nature of metal complexes at different pH ranges recorded in Table 2.



 $\label{eq:scheme 3} \begin{array}{c} Scheme \ 3\\ M \ (LH) \ 2]: M = Cu(II), Zn(II), Cd(II). \ OO\text{-donor at } pH = 3\text{-}4 \end{array}$ 



# Basavaraj M. Kalshetty et al



 $[M L(EtOH)_2]: M = Cu(II), Co(II) and Ni(II): OONO-donor at pH = 9$ 



Scheme 8 [ML (EtOH) 2]: M= Cu (II), Co (II), Ni (II): OONO-donor at pH=9

Table 1. The physical and analytical data of ligands and their metal complexes

Scheme	Molecular Formula	Molecular Weight	Color of complexes	Metal ions	Carbon (Obs)	Hydrogen (Obs)	Nitrogen (Obs)
1	C <sub>15</sub> H <sub>13</sub> O <sub>3</sub> N	255	Yellow		70.59	5.10	5.49
2	$C_{15}H_{13}O_4N$	271	Yellow		66.42	4.80	5.17
3	$CuC_{30}H_{22}O_6N_2$	569.5	Orange red	11.15	63.21	3.86	4.92
	$ZnC_{30}H_{22}O_6N_2$	571.4	Orange	11.45	63.00	3.85	4.90
	$CdC_{30}H_{22}O_6N_2$	618.4	Orange	18.18	58.22	3.56	4.53
4	$CuC_{30}H_{22}O_8N_2$	601.5	Orange red	10.87	59.85	3.66	4.66
	$ZnC_{30}H_{22}O_8N_2$	603.4	Orange	10.84	59.66	3.65	4.64
	$CdC_{30}H_{22}O_8N_2$	650.4	Orange	17.28	55.35	3.38	4.31
5	ZnC <sub>30</sub> H <sub>22</sub> O <sub>6</sub> N <sub>2</sub>	571.4	Orange	11.45	63.00	3.85	4.90
	$CdC_{30}H_{22}O_6N_2$	618.4	Orange yellow	18.18	58.22	3.56	4.53
6	$ZnC_{30}H_{22}O_8N_2$	603.4	Orange	10.84	59.66	3.65	4.64
	CdC30H22O8N2	650.4	Orange	17.28	55.35	3.38	4.31
7	$Cu_2C_{34}H_{34}O_8N_2$	725	Orange red	17.52	56.28	4.69	3.86
	$Zn_2C_{34}H_{34}O_8N_2$	728.8	Orange yellow	17.95	55.98	4.47	3.84
	Ni <sub>2</sub> C <sub>34</sub> H <sub>34</sub> O <sub>8</sub> N <sub>2</sub>	715.4	Brownish yellow	16.41	57.03	4.75	3.91
	$Co_2C_{34}H_{34}O_8N_2$	715.8	Golden yellow	16.46	56.99	4.75	3.91
	$Cd_2C_{34}H_{34}O_8N_2$	822.8	Dark red	27.32	49.59	4.13	3.40
8	$Cu_2C_{34}H_{34}O_{10}N_2$	757	Orange red	16.78	53.90	4.49	3.70
	$Zn_2C_{34}H_{34}O_{10}N_2$	760.8	Orange yellow	17.19	53.63	4.47	3.69
	$Ni_2C_{34}H_{34}O_{10}N_2$	747.4	Brownish yellow	15.71	54.59	4.55	3.75
	Co <sub>2</sub> C <sub>34</sub> H <sub>34</sub> O <sub>10</sub> N <sub>2</sub>	747.8	Golden yellow	15.75	54.56	4.55	3.74
	Cd <sub>2</sub> C <sub>34</sub> H <sub>34</sub> O <sub>10</sub> N <sub>2</sub>	854.8	Dark yellow	26.30	47.73	3.98	3.28

## Fourier Transfer Infrared (FTIR) Spectroscopy

The FTIR spectra of the Schiff base ligands (Scheme 1 and 2) and the Metal complexes (Scheme 3 to 8) were recorded in Perkin-Elmer spectrum 100 FTIR spectrometer in KBr pellets in the range 400 - 4000 cm<sup>-1</sup>. The IR spectra of the Schiff base ligands display intense characteristics bands at 3429 cm<sup>-1</sup> and 3150 cm<sup>-1</sup> due to intra molecular H-bonded stretches of carboxylic (-COOH) and Phenolic (-OH) groups respectively. The IR spectra of Schiff base ligands the mono carboxylic acid have been assigned two characteristic frequency, one in C=O in plane

bending vibrations and another in OH in plane bending vibrations, the  $\gamma$ (C=O) carboxylic stretches at 1695 cm<sup>-1</sup>,  $\gamma$ (-OH) phenolic stretches at 1575 cm<sup>-1</sup>. The IR spectra of ligands in which the absence of bands due to NH<sub>2</sub> group clearly indicate the formation of –CH=N- linkage. However, a broad band at which its center of gravity  $\gamma$ (C=N) at about 1628 cm<sup>-1</sup> is observed. The presence of Aromatic rings have been identified by their characteristic ring vibrations at 1500 cm<sup>-1</sup> to 1400 cm<sup>-1</sup>, 1100 cm<sup>-1</sup> to 1050 cm<sup>-1</sup> and 900 cm<sup>-1</sup> to 700 cm<sup>-1</sup> at three different reaction conditions respectively. In order to give conclusive idea about the structure of free ligands and metal complexes, the main IR bands were compared with those of the ligand. The IR spectrum of the ligands showed a medium band at 2876 cm<sup>-1</sup> due to the intra molecularly hydrogen bonded hydroxyl group [17]. The absence of this band in the spectra of metal complexes indicates the breaking of the hydrogen bond and coordination of Oxygen atom to the metal after deprotonation [18]. A broad band with medium intensity at 906 cm<sup>-1</sup> due to out of plane bending of the ligands displayed a medium intensity band around 1556 cm<sup>-1</sup> due to V(C=N) shift to lower frequency region 1518 cm<sup>-1</sup> in metal complexes, indicating that N of azomethine is coordinated to metal ion at pH=7 neutral reaction conditions [20-21] as reported in Table 3.

Table 2. Phy	sical constants and	d nature of metal	complexes at	different pH-ranges
•			-	

Scheme	pH-range	Metal complex	Nature of complex	Stable up to Temperature	Donor atoms
1				242°C	
2				268°C	
3	3 – 4	$[ML_2]$	Monomeric	210°C	OO-donor
4	3 – 4	$[ML_2]$	Monomeric	208°C	OO-donor
5	7 - 8	$[Ml_2]$	Dibasic tridentate	232°C	OON-donor
6	7 - 8	$[ML_2]$	Dibasic tridentate	228°C	OON-donor
7	10-11	[ML(EtOH)] <sub>2</sub>	Dibasic tetra dentate	215°C	OONO-donor
8	10-11	[ML(EtOH)] <sub>2</sub>	Dibasic tetra dentate	218°C	OONO-donor

Fable 3.	FTIR	spectrosco	oic data	a of the	ligands	and tl	heir meta	l comple	xes

Scheme	Functional group	IR-values in cm <sup>-1</sup>	Scheme	Functional group	IR-values in cm <sup>-1</sup>
1	V(COOH)	3429 cm <sup>-1</sup>	2	V(COOH)	3429 cm <sup>-1</sup>
"	V(OH)	3150 cm <sup>-1</sup>	"	V(OH)	3150 cm <sup>-1</sup>
۰,	V(C=N)	1628 cm <sup>-1</sup>	"	V(C=N)	1628 cm <sup>-1</sup>
۰,	V(C-H)	3000 cm <sup>-1</sup>	.,	V(C-H)	3000 cm <sup>-1</sup>
۰,	V(C=O)	1695 cm <sup>-1</sup>	"	V(C=O)	1695 cm <sup>-1</sup>
"	V(OH) in plane bending	1377 cm <sup>-1</sup>	"	V(OH) in plane bending	1377 cm <sup>-1</sup>
۰,	V(OH) in out of plane bending	906 cm <sup>-1</sup>	"	V(OH) in out of plane bending	906 cm <sup>-1</sup>
۰,	V(C=O) in plane bending	1070 cm <sup>-1</sup>	"	V(C=O) in plane bending	1070 cm <sup>-1</sup>
3	V(-COO-)	1745 cm <sup>-1</sup>	4	V(-COO-)	1745 cm <sup>-1</sup>
۰,	V(C=N)	1628 cm <sup>-1</sup>	.,	V(C=N)	1628 cm <sup>-1</sup>
۰,	V(C-H)	3000 cm <sup>-1</sup>	"	V(C-H)	3000 cm <sup>-1</sup>
۰,	V(C=O)	1695 cm <sup>-1</sup>	"	V(C=O)	1695 cm <sup>-1</sup>
۰,	V(M-O)	440 cm <sup>-1</sup>	.,	V(M-O)	440 cm <sup>-1</sup>
5	V(-COO-)	1745 cm <sup>-1</sup>	6	V(-COO-)	1745 cm <sup>-1</sup>
"	V(C=N)	1628 cm <sup>-1</sup>	"	V(C=N)	1628 cm <sup>-1</sup>
۰,	V(C-H)	3000 cm <sup>-1</sup>	"	V(C-H)	3000 cm <sup>-1</sup>
"	V(M-N)	458 cm <sup>-1</sup>	"	V(M-N)	458 cm <sup>-1</sup>
"	V(M-O)	440 cm <sup>-1</sup>	"	V(M-O)	440 cm <sup>-1</sup>
7	V(-COO-)	1745 cm <sup>-1</sup>	8	V(-COO-)	1745 cm <sup>-1</sup>
"	V(C=N)	1628 cm <sup>-1</sup>	"	V(C=N)	1628 cm <sup>-1</sup>
••	V(C-H)	3000 cm <sup>-1</sup>	••	V(C-H)	3000 cm <sup>-1</sup>
"	V(M-N)	458 cm <sup>-1</sup>	"	V(M-N)	458 cm <sup>-1</sup>
•,	V(M-O)	440 cm <sup>-1</sup>	.,	V(M-O)	440 cm <sup>-1</sup>

## <sup>1</sup>H NMR Spectroscopy

The <sup>1</sup>HNMR spectra of ligands and their metal complexes were recorded by using Bruker Avance 300 spectrometer (300 MHz for <sup>1</sup>H NMR). Chemical shifts were recorded in  $\delta$  ppm in DMSO –d6 using tetra methyl silence (TMS) as internal standards. The <sup>1</sup>H NMR-spectra of p-Toludine and p-Anisidine Schiff bases derived with 3-Aldehydosalicylic acid, signals of NH<sub>2</sub> protons appear at  $\delta$ 10.5 ppm and  $\delta$ 9.4 ppm these signals shifted to high field in the spectra of the metal complexes and appear at  $\delta$ 9.4 ppm to  $\delta$ 9.6 ppm for organometallic complexes with ligand molecules, this indicates the bonding through the Nitrogen atom of the Schiff base ligands to the central metal ion

(Scheme 5, 6, 7, and 8). The <sup>1</sup>H NMR spectra of ligands and their metal complexes the signals of –CH3 and –OCH3 appear at  $\delta 2.3$  (s) and  $\delta 3.4$  (s). The 1HNMR spectra of Schiff bases showed the (-CH=N-) proton signals at  $\delta 9.3$  ppm –  $\delta 9.46$  ppm similarly the carboxylic proton signals appeared at  $\delta 10.5$  ppm.

The aromatic protons gave signals at  $\delta 6.8$  ppm to  $\delta 8.1$  ppm. Hence, the 1H NMR spectroscopic data of the ligands and their metal complexes are given in Table 4. [Standard= Gentamicin; Diameter of inhibition zone in mm; concentration in ppm].

Compound	Aromatic H	-CH3	-OCH3	-CH=N-	-COOH
Scheme 1	δ6.8 - δ8.1 ppm (m)	δ2.3 (s)		δ 9.3 (s)	δ 10.5 (s)
Scheme 2	δ6.8 - δ8.1 ppm (m)	δ2.3 (s)	δ 3.4 (s)	δ 9.46 (s)	δ 10.5 (s)
Scheme 3	δ7.1 - δ8.0 ppm (m)	δ2.2 (s)	δ 3.4 (s)	δ 9.3 (s)	δ 10.5 (s)
Scheme 4	δ7.1 - δ8.0 ppm (m)	δ2.2 (s)	δ 3.4 (s)	δ 9.3 (s)	δ 10.5 (s)
Scheme 5	δ7.1 - δ8.0 ppm (m)	δ2.3 (s)	δ 3.4 (s)	δ 9.46 (s)	δ 10.5 (s)
Scheme 6	δ7.1 - δ8.0 ppm (m)	δ2.3 (s)	δ 3.4 (s)	δ 9.46 (s)	δ 10.5 (s)
Scheme 7	δ6.7 - δ8.0 ppm (m)	δ2.4 (s)	δ 3.4 (s)	δ 9.3 (s)	δ 10.5 (s)
Scheme 8	δ6.7 - δ8.0 ppm (m)	δ2.4 (s)	δ 3.4 (s)	δ 9.3 (s)	δ 10.5 (s)

Table 4. <sup>1</sup>H NMR chemical shifts of the ligands and their metal complexes

Table 5. Anti-bacterial screening data of Schiff base and their metal complexes

Escherichia Coli Staphylococcus aureus								
Scheme	25	50	100	25	50	100		
1	12	13	16		10	12		
2	12	13	16	10	12	14		
3 with Cu	26	28	32	14	15	16		
3 with Zn	18	17	18	12	11	12		
4 with Cu	24	28	31	15	16	18		
4 with Zn	18	19	20	13	13	13		
5 with Cu	26	27	29	16	18	18		
5 with Zn	18	20	22	12	14	14		
6 with Cu	28	30	33	18	19	20		
6 with Zn	20	21	22	12	12	14		
7 with Cu	24	28	32	20	21	22		
7 with Zn	18	18	19	14	14	16		
Standard	20	23	20	12	12	14		
DMSO (-)								

Table 6. Biological evaluation (Antioxidant Capacity)

Absorb	% radi	cal scavenging					
Schiff base and Metal complex	1	2	3	1	2	3	% radical scavenging with standard deviation
P-Anisidine Schiff base compound.	0.393	0.344	0.265	44.63	52.89	61.70	53.07±8.53
P-Toludine Schiff base compound.	0.411	0.364	0.321	41.64	48.66	53.61	48.07±5.85
Cu - complex with PA at $pH=3$ to 4.	0.435	0.531	0.342	38.5	25.10	50.57	38.05±12.74
Cd -complex with PT at $pH=3$ to 4.	0.425	0.353	0.318	39.97	50.20	54.04	48.07±7.27
Cu -complex with PA at pH= 7 to 8.	0.668	0.639	0.618	5.64	9.87	7.4	7.63±2.12
Cd -complex with PA at pH= 7 to 8.	0.386	0.351	0.325	45.48	50.49	53.03	49.66±3.84
Cd - complex with PT at pH= 7 to8.	0.312	0.170	0.145	55.90	76.02	79.04	70.32±12.57
Ni - complex with PA at pH= 7 to 8.	0.169	0.079	0.138	76.12	88.85	80.05	81.67±6.51
Co - complex with PT at pH= 7 to 8.	0.417	0.375	0.348	41.10	47.10	49.70	45.96±4.41
Cu - complex with PT at pH= 9 to 10.	0.489	0.457	0.437	30.93	35.54	36.84	34.43±3.10
Cu - complex with PA at pH= 9 to 10.	0.550	0.324	0.334	22.31	54.30	51.73	42.78±17.77
Standard : Glutathione	0.370	0.265	0.371	47.77	62.62	46.38	52.25±9.00
Blank	0.708	0.709	0.692				

## **Anti-Microbial Activity**

The ligands and metal complexes were screened for their antibacterial activity against the bacteria Escherichia Coli and Staphylococcus aureus strains. The antibacterial activity was evaluated by the Disc diffusion method [22]. The compounds were dissolved in dimethyl sulfoxide (DMS) at 500 and 1000 ppm concentration. The activity was measured by measuring the diameter of the zone of inhibition in millimeter. The results showed that the ligands and all metal complexes exhibit bacteriostatic behavior towards the bacterial strains. The free ligands and metal

complexes like Cu (II) and Zn (II) were found to show good activity against Escherichia Coli and Staphylococcus aureus respectively.

The results reveal that, the activities of the free ligands were found to be enhanced on complexation with metal ions. It has been observed that the metal complexes showed enhanced antibacterial activity as compared to the free ligands against the same organism under identical experimental conditions as reported in the Table 5.

According to the Tweedy's chelation theory, the chelation reduces the polarity of the metal atom only due to the partial sharing of its positive charge with donor groups and possible  $\pi$  electron delocalization over the whole ring. This increases the lipophillic character of the metal chelate which favors its permeating through the lipid layer of bacterial membranes. The toxicity increases with the increasing in concentration of the complexes. Thus, chelation increases lipophillic character in the metal complexes and results in the enhancement of activity.

## **DPPH Radical Scavenging Assay**

A rapid, simple and inexpensive method to measure antioxidant capacity of the substance involves the use of the free radical, 2- 2-diphenyl-1-picrylhydrazyl (DPPH). DPPH is widely used to test the ability of the compounds to act as free radical scavengers or hydrogen donors. Antioxidants tested on DPPH were also found extremely effective in cell systems. This simple test further provides information on the ability of a compound to donate electrons during antioxidant action [23]. The radical scavenging mechanism is based on the transfer of acidic H atom from the compound to DPPH radical to form DPPH-H.

Among the tested compounds (scheme 1 and 2), and the synthesized organometallic complexes (scheme 3 to 8) exhibited very good radical scavenging capacity with concentration of 100  $\mu$ g/ Ml in comparison with standard Glutathione. Other compounds showed mode rate activity. The good radical scavenging of capacity of compounds scheme 5 to 8 is due to at pH-7 to 8 and pH- 10 to 11, the metal complexes behave as dibasic tridentate OON- donor and dibasic tetradentate OONO- donor suggesting that involvement of nitrogen with metal ion in the coordinate complex .The variation exhibited in DPPH scavenging capacity could be attributed to the effect of different substitution present in the compounds. All compounds were screened for antioxidant properties. But dibasic tetradentate complexes OONO – donor (scheme 7 and 8) showed significant DPPH activity reported in the table 6. Hence, this study has widened the scope of developing easy method to synthesize indole, Coumarin and triazoles metal complexes derivatives as promising antioxidants.

# CONCLUSION

At lower pH=3 to 4 ranges, the ligands behave as monobasic bidantate, due to non-involvement of Nitrogen atom. At moderate pH =7 to 8 (neutral pH) ranges, the ligands behave as dibasic tridentate due to the involvement of nitrogen atom. Finally at higher pH range (pH= 10 to 11), the behavior of ligands with metal ions as a dibasic tetra dentate for the involvement of nitrogen and oxygen atoms.

### Acknowledgement

Authors are thankful to the Chairman, Department of Chemistry, Karnatak University, Dharwad for providing the facilities in getting the physical and analytical data of ligands and their metal complexes. We take this opportunity to thank Bharat Ratna C N R Rao for providing financial support through VGST group to carryout Major project under CESEM Programme. We are also very thankful to the Principal of our College for their encouragement and Laboratory facility to carry out this research work.

### REFERENCES

[1]Belaid S, Landreau A, Djebbar S, Benali-Baitich O, Bouet G, Bouchara JP. J. Inorg Biochem. 2008 Jan; 102: 63-69.

[2]Rabie UM, Assran ASA, Abou-El-Wafa MHM. J. Mol. Struct.2008; 872: 113-122.

[3]Yilmaz I, Temel H, Alp H. Synthesis, *Polyhedron*. 2008;27:125-132.

[4]Salavati M, e Niasari, Sobbani A. J Mol Catal (A). 2008;285:58-67.

[5]Juan CL, Jie B, Ming MF, Xing LG. Catal Commun.2008;9:658.

[6]Ziyadanogullari B, Cevizic D, Temel H, Gullari RZ. J Hazard Mater. 2008;150:285e289.

[7]Sutar AK, Gupta KC. Reactive Funct Polym. 2008;68:12e26.

Pelagia Research Library

## Basavaraj M. Kalshetty et al

[8]Kalshetty BM, Gani RS, Karabasannavar SS, Kalashetti MB. *Glob J Sci.Frontier Res Chem.* 2013;13:29e37. Version 1.0.

[9]Rudnicka W, Foks H, Jano M, Wiec, Zwolsk, Wiek K. Acta Pol. Pharm. 1986;43:523.

[10] Holla BS, Veerendra B, Shivanada MK, Poojary B. Eur J Med Chem. 2003;38:759-767.

[11] Mullican MD, Wilson MW, Connor DT, Kostlan CR, Schrier DJ, Dyer RD. J Med Chem. 1993 Apr 16;36:1090-1099.

[12]Berta Holló, Zoran D. Tomić, Péter Pogány, Attila Kovács, Vukadin M. Leovac, Katalin Mészáros Szécsényi. *Polyhedron*, **2009**, 28, 3881-3889.

[13] Hesham Habib, Anke Hoffmann, Henning A. Hoppe, Gunther Steinfeld, and Christoph Janiak A. J Inorg. Chem. 2009 48 (5),2166-2180.

[14] Hua-Ze Dong, Jian Zhao, Shao-Hua Gou, Hai-Bin Zhu Polyhedron, 2009, 28, 1040-1048.

[15] C. F. Mills, "Zinc in human body", Springer, New York, 1989.

[16]Nag NK, Pal S, Sing C. metal Chem. August 2005, 30: 523-526.

[17]M.R.Maurya, A.K.Chandrakar and S. Chand, J. Mol. Catal. A: Chem. 270, 225 (2007).

[18]K. Natarajan, S. Karvembu, S. Hemlatha and R. Prabhakaran, *Inorg. Chem. Commun* Volume 6, Issue 5, May **2003**, Pages 486–490

[19]V. V. Dhande, V. B. Badwaik and A. S. Aswar, Russ. J. Inorg. Chem., 2207, 52, 1206.

[20] A.P.Mishra and M.Khare Journal of the Indian Chemical Society. 2000;77(8):367-370.

[21]Basavaraj M. Kalshetty, Shambuling S, Karabasannavar, Ramesh S. Gani and Mallikarjun B. Kalashetti.

*Drug invention today* 5 (**2013**) 105-112.

[22] N.Raman, J.Indian Che.Soc.2009,86,1143.

[23]Tiwari AK. Current science.2004; 86(8);1092-1102