**Original Research Article**

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ANTIOXIDANT ACTIVITY OF NOVAL COMPLEXES OF SCHIFF BASE DERIVED FROM (E)-2-((2-HYDROXY-1,2-DIPHENYLETHYLIDENE)AMINO)PHENOLV. Balamurugan^{1*}, L. Muruganadam¹, K. Radhakrishnan²

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ABSTRACT: In this study a new metal complexes of Co(II), Ni(II), Cu (II) and Zn(II) with (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol has been synthesized and characterized by elemental analysis, FT-IR, ¹H-NMR, ¹³C-NMR and molar conductance. The antioxidant activity of these complexes are being studied and compared with the standard ascorbic acid. Antioxidant study is carried out against the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH), which shows the metal complexes found to be a good antioxidant, as comparable to ascorbic acid.

KEYWORDS: Schiff base, novel metal complex, antioxidant, DPPH, NMR.

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1. INTRODUCTION

Reactive oxygen species (ROSs) play an important role in degenerative condition such as aging cancer, cardiovascular diseases, cataracts, neuron degenerative disorders, liver diseases and inflammations [1]. These free radicals occur in the body during an imbalance between ROSs (Reactive oxygen species) and anti oxidants. Hence, the dietary intake of antioxidant is necessary and important to balance the anti oxidant states that would reduce pathological conditions to that induced free radicals [2]. A metal complex plays an essential role in agriculture, pharmaceutical and industrial chemistry. The biological study of these complexes highlights the potential of metal (II) complex with bioactive ligand as anti-oxidant activity. The synthetic metal complexes are act as antioxidants, which strengthen the endogenous antioxidant defenses from ROS ravage and restore the optimal balance by neutralizing the reactive species. They are gaining immense importance by

virtue of their critical role in disease prevention. In the chosen copper (II) complex, its therapeutic efficacy in the state of oxidative stress has not been evaluated. In our previous study the synthesized schiff base ligand N, N'-bis(benzoin)-1,4 butane diimine is being tested against the bacterial and fungal species, which showed a remarkable zone of inhibition with standards and have a good antibacterial and antifungal activities [3]. Hence, the present study, an attempt has been made to evaluate an antioxidant potential of the (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol metal complexes. This research is focused on the antioxidant activity of metal complexes, in order to find out an increased activity with the presence of the metallic center.

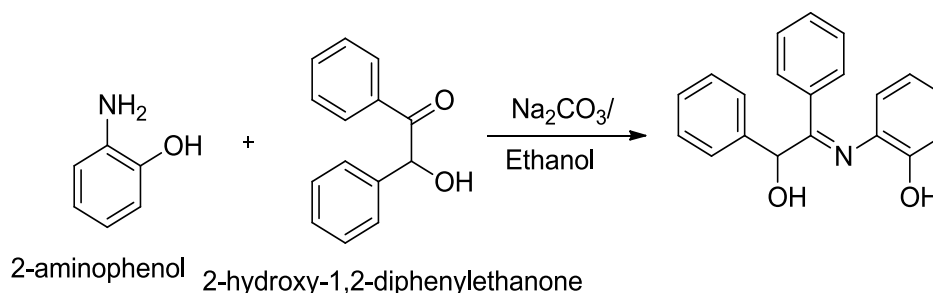
2. MATERIALS AND METHODS

Chemicals

The chemicals and solvents used in this work have been purchased from sigma chemicals, (Sigma Aldrich chemical Pvt. Ltd., Bangalore, Karnataka, India). All other reagents and chemicals used in this study are of analytical grade with high purity. All the glass wares used are washed thoroughly with distilled water and dried in an oven. An infrared spectrum has recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer in wave number region $400-4000\text{ cm}^{-1}$. The ^1H NMR spectrum of the complex is recorded in DMSO- d_6 solution on a Bruker-3410NM, 300 MHz spectrometer with chemical shifts which reported in ppm relative to TMS as internal standard.

Synthesis of (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol

Hot ethanolic solutions of benzoin (2.12 g, 0.01mol) and 2-amino phenol (1.64 g, 0.01 mol) are being mixed and refluxed for 3 hours in a water bath. The resulting solution has been concentrated and cooled in an ice bath. The separated precipitate is collected through filtration by using a vacuum pump and washed with ethanol, dried over anhydrous CaCl_2 and recrystallised from ethanol. The percentage yield of the compound is 72 %. The compound is in white colour solid (Scheme). The melting point of BAP is determined and found to be 188°C . It is insoluble in water but completely soluble in methanol, ethanol, propanol, butanol, acetone, dimethyl formamide and DMSO [4-9].



Scheme: Synthesis of (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol

Preparation of (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol metal complexes

The metal complexes is being prepared by adding a solution of appropriate metal salts (5 mmol, in 30 mL methanol) into a hot 50 mL methanol solution in the Schiff base BAP (10 mmol, in 40 mL methanol) and refluxing between 3 to 4 hrs. The resulting solution has been allowed to evaporate at

room temperature. The separated complexes are collected and washed with methanol and ether. The product is dried over anhydrous calcium chloride in desiccators (~85 % yield) [10].

***In vitro* – Antioxidant Study**

DPPH free radical scavenging activity

DPPH radical-scavenging activity is determined by the method of Shimada, *et al.*, [11]. Briefly, a 2 ml aliquot of DPPH methanol solution (25µg/ml) was added to 0.5 ml sample solution at different concentrations. The mixture has been shaken vigorously and allowed to stand at room temperature in the dark for 30 min. Then the absorbance is being measured at 517nm in a spectrophotometer.

$$\text{Radical scavenging activity (\%)} = \left(\frac{A_C - A_S}{A_C} \right) \times 100$$

Where A_C = absorbance of the control and A_S = absorbance of reaction mixture (in the presence of sample).

All tests and analyses have been performed with three replicates and the results are averaged. An IC50 value that denotes the concentration of metal complexes required to scavenge 50% of the DPPH radicals and are obtained from a plot of scavenge activity vs. metal complex.

3. RESULTS AND DISCUSSION

The interaction between copper(II) ion and (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol, yielded the desired crystalline, metal complex compound. These compounds are insoluble in water and common organic solvents, but are readily soluble in acetone, chloroform and DMSO. IR spectra of Schiff base shown in Figure 1, showed the band region 1602 cm^{-1} , which indicate the presence of $\nu(\text{C}=\text{N})$ stretching vibration. The IR spectra of all complexes shows bands in the region $1658\text{-}1592\text{cm}^{-1}$ which shows the $\nu(\text{C}=\text{N})$ stretching vibration, a fundamental feature of azomethine group [12]. The coordination of water molecule is indicated by the appearance of broad band in the region of $3357, 3368, 3440, 3521\text{cm}^{-1}$. The coordination of the phenolic oxygen and azomethine further confirmed by the appearance of non-ligand bands at 511, 510, 515, 527 and 415, 411, 405, 423cm^{-1} due to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively [13-16]. Out-of-plane NH wagging is responsible for a broad band of medium intensity in the $900\text{-}600 \text{ cm}^{-1}$ region. These bands confirmed the coordination of the schiff base to the metal (II) ion. The IR data of the metal complexes summarized in table 1. The ^1H NMR spectrum of the Schiff base (scheme 1) exhibits a aliphatic C-H of -OH proton are found at 3.35ppm and a multiple at 8.1-7.8 (m, Ar-H) (table 2). The metal (II) complex compound revealed 1:1 metal to ligand ratio, resulting in a six coordinate complex compound and the proposed molecular structure showed in figure 4. The ^{13}C peaks observed between δ 133 to 126 ppm are due to aromatic carbons. The spectrum shows absorption at δ 72 ppm for hydroxyl carbon (Table 3). The peaks observed at δ 136 ppm are assigned due to the azomethine carbons. The observed and calculated percentage composition of C, H and N elements

of the synthesized Schiff base ligands and its metal complexes and molar conductance of the complexes are presented in Table 4[17-23]. The molar conductance of metal complexes of BAP lying in the range of $\mu_c = 27$ and $18 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, which indicates the non-electrolytic nature of the complexes [24].

Table 1: The Infrared Spectral Data of the Metal Complex

Compound	ν (OH)	ν (C=N)	ν (M-O)	ν (M-N)
BAP	3346	1602	-	-
[Co(BAP)(H ₂ O)Cl ₂]	3357	1592	511	415
[Ni(BAP)(H ₂ O) ₃]2ClO ₄	3368	1596	510	411
[Cu(BAP)(H ₂ O) Cl ₂]	3440	1658	515	405
[Zn(BAP)(H ₂ O)Cl ₂]	3521	1613	527	423

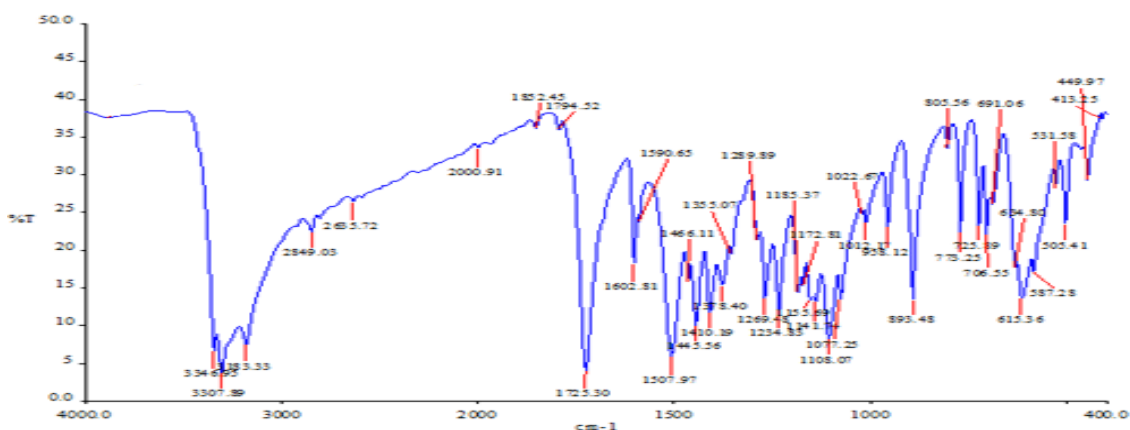


Figure 1: IR spectrum of Schiff base

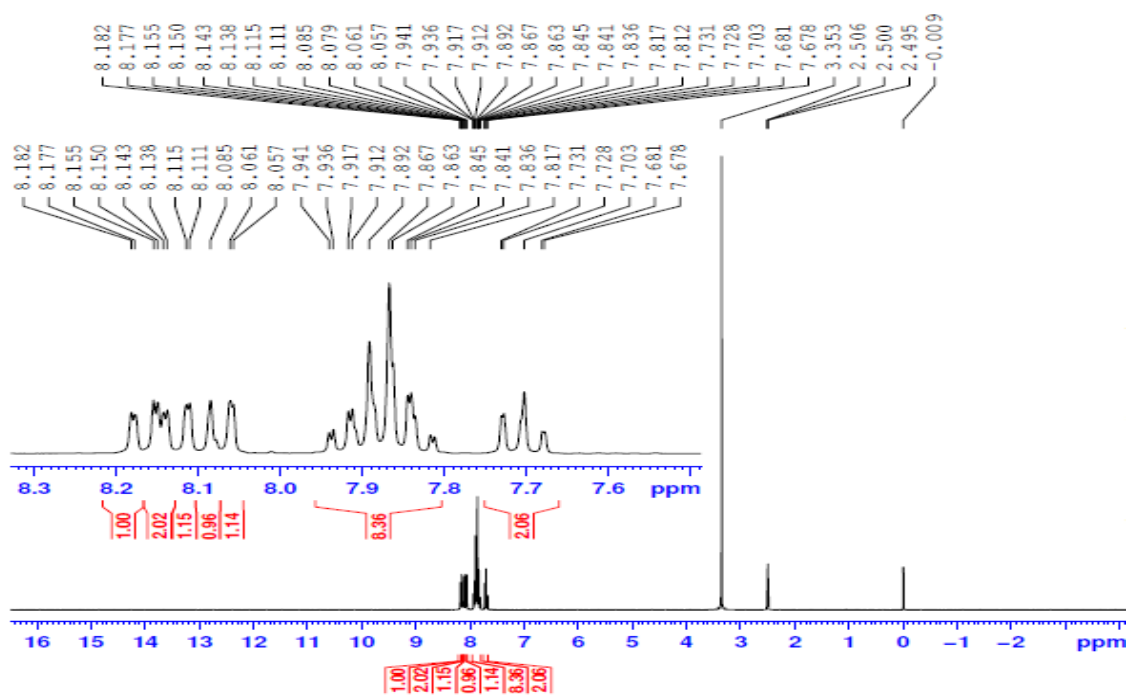


Figure 2: ¹H NMR spectrum of Schiff base

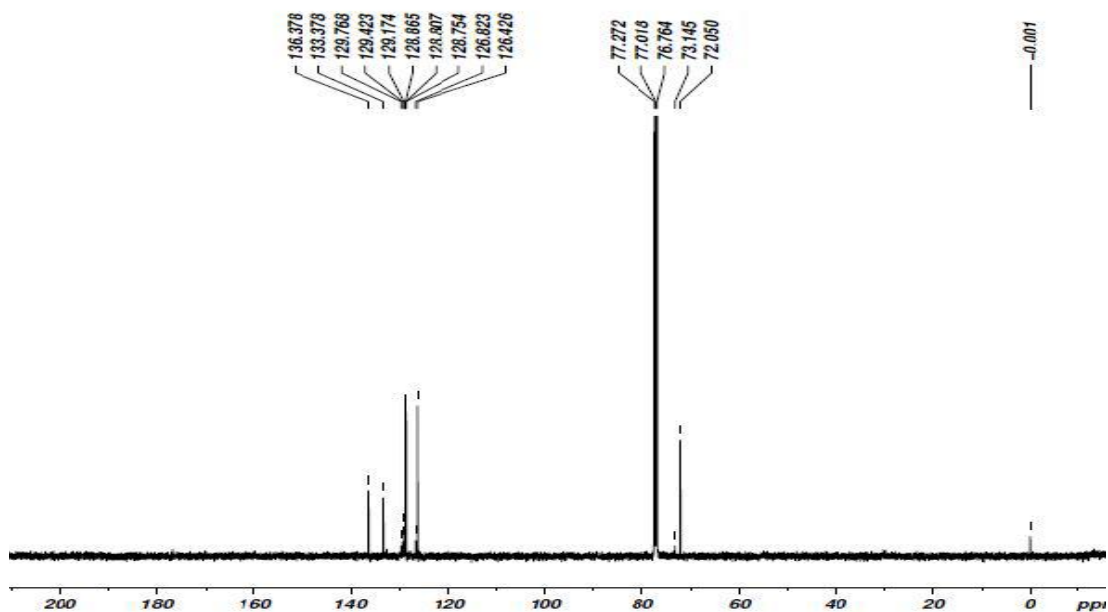


Figure 3: ¹³C NMR spectrum of BAP

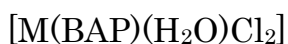
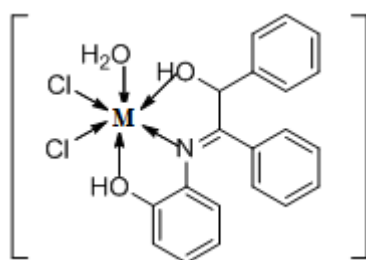


Figure 4: Shows the molecular structure of metal (II) complexes of (E)-2-((2-hydroxy-1,2-diphenylethylidene)amino)phenol compound

Table 2: ¹H NMR spectral data of Schiff bases

Schiff base	Chemical shift	Assignment
BAP	3.35	C-H of –OH proton
	7.7-7.6	CH proton
	8.1-7.8	Aromatic CH protons

Table 3: ¹³C NMR spectral data of Schiff bases

¹³ C NMR Spectrum	Signal [ppm]	Group identification
BAP	72	Hydroxyl carbon atoms
	133-126	Aromatic carbon atoms
	136	Azomethine carbon atom

Table 4: Elemental analysis and molar conductance of metal complexes of Schiff base

Molecular formula	Compound	Molecular weight	Melting point °C	Elemental analysis % Found and (% Calculated)					Molar conductance ($\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$)
				(%) C	(%) H	(%) N	(%) O	(%) Cl	
C ₂₀ H ₁₉ Cl ₂ CoNO ₃	[Co(BAP)(H ₂ O)Cl ₂]	451	221	53.27 (53.24)	4.29 (4.24)	3.13 (3.10)	10.70 (10.64)	15.78 (15.71)	27
C ₂₀ H ₁₉ Cl ₂ NiNO ₃	[Ni(BAP)(H ₂ O) ₃]2ClO ₄	450	218	53.25 (53.22)	4.27 (4.25)	3.11 (3.10)	10.68 (10.60)	15.75 (15.70)	25
C ₂₀ H ₁₉ Cl ₂ CuNO ₃	[Cu(BAP)(H ₂ O)Cl ₂]	455	213	52.62 (52.60)	4.28 (4.20)	3.12 (3.07)	10.59 (10.53)	15.60 (15.56)	22
C ₂₀ H ₁₉ Cl ₂ NO ₃ Zn	[Zn(BAP)(H ₂ O)Cl ₂]	457	226	52.49 (52.45)	4.26 (4.18)	3.10 (3.06)	10.45 (10.49)	15.53 (15.49)	18

DPPH-scavenging activity

In the DPPH assay, the ability of the Cu(II) complex to effectively scavenge DPPH radical is displayed in Figure 5, where it is compared with that of ascorbic acid as standard. Lower absorbance of the reaction mixture indicated higher free radical scavenging activity [25]. The IC₅₀ value of the copper complex is found to be more than the standard of Ascorbic acid [26].

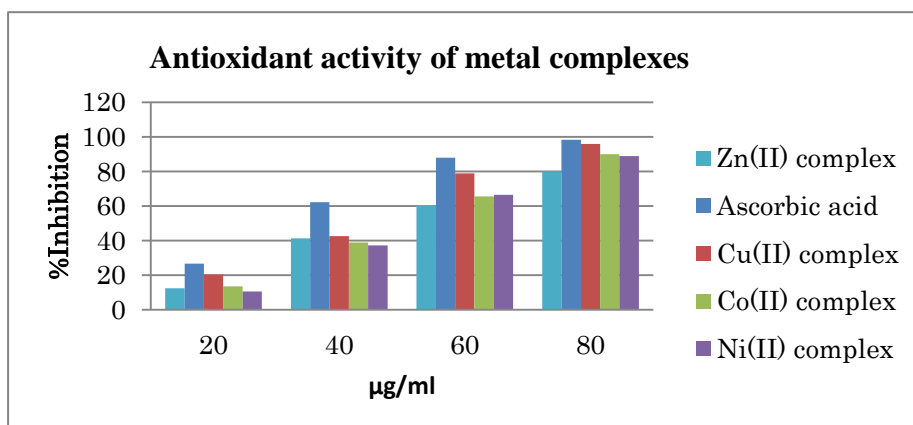


Figure 5: DPPH radicals scavenging capacity metal complexes at different concentrations.

Each value is the average of triplicates, representing \pm S.D.

4. CONCLUSION

The Schiff base ligand and its Co(II), Ni(II), Cu(II), and Zn(II) complex are being prepared. Metal complexes have been characterized by elemental analysis, IR, NMR spectra. The proposed structure of metal complex has been illustrated in Figure 4. The synthesized metal complex is screened for reduction of DPPH. Based on the results obtained, the metal complex found to be good antioxidant, as comparable with ascorbic acid.

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2018 Sept – Oct RJLBPCS 4(5) Page No.448

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