



# Journal of Applicable Chemistry

2013, 2 (5):1315-1323

(International Peer Reviewed Journal)



## Isatin Based Schiff Base And Its Complexes- Synthesis, Spectral Investigation And Antibacterial Studies

G. Anbarasu, C. Srividhya, P. Maheswaran and R. Rajavel\*

\*Department of Chemistry, Periyar University, Salem, Tamilnadu, **INDIA**

Email: [chemanbarasu@gmail.com](mailto:chemanbarasu@gmail.com)

Received on 16<sup>th</sup> September and finalized on 18<sup>th</sup> September 2013.

### ABSTRACT

A new Schiff base ligand 2-((E)-((Z)-2-(4-Chlorophenylimino)indole-3-ylidene)amino)phenol (L) was synthesized from isatin, 2-aminophenol and 4-chloroaniline. Then its Ni(II), Co(II), Mn(II) and Cu(II) complexes were synthesized by reacting 2:1 ratio of ligand and metal(II) acetate salts. The synthesized Schiff base ligand and its metal complexes have been characterized by elemental analysis, IR, UV-Vis spectra, <sup>1</sup>H-NMR and cyclic Voltammetry studies. The synthesized Schiff base and their transition metal complexes have been screened for their antibacterial activity against *E. coli*, *S. typhi*; the complexes show enhanced activity than their corresponding ligand. Furthermore, the antioxidant activity of the ligand and its M(II) complexes was determined by DPPH radical scavenging method, which indicates that the synthesized complexes exhibit more effective antioxidant activity than the ligand alone.

**Keywords:** Schiff bases, transition metal complexes, Spectral study and Antibacterial activity.

### INTRODUCTION

Schiff base form stable complexes with most of the transition metals and hence have played an important role in the development of coordination chemistry [1]. One of the most important achievements realized in the last century in the field of life-sciences was the finding of some bio metals that play important role in the regulation and control of essential biological and physiological processes. Most commonly the transition metals such as iron, copper, cobalt, nickel, etc act as bio metals [2]. The synthetic versatility of isatin has led to an extensive use of this compound in organic synthesis [3]. Many coordination compounds of transition metals with isatin derivatives show greater activity than the ligands alone. During the past decades, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors. This may be attributed to their stability, biological activity [4] and potential applications in many fields such as oxidation catalysis [5], electrochemistry [6]. Based on the above mentioned properties for Schiff bases, we reported herein the synthesis and spectroscopic studies of a Schiff base derived from isatin and their metal complexes.

## MATERIALS AND METHODS

The infrared spectrum of the ligands and its complexes were recorded with KBr-pellets on Bruker-Vector FT-IR Spectrometer operating between 400-4000  $\text{cm}^{-1}$ . The electronic spectra were recorded on a Perkin Elmer Lambda-25 UV/Vis spectrometer. Molar conductance of the complexes was measured in DMSO ( $10^{-3}$  M) solutions using a coronation digital conductivity meter. Magnetic susceptibility measurements were carried out by employing the Gouy method at room temperature.  $^1\text{H}$  NMR signals were obtained from Bruker Avance III, 400 MHz model spectrometer. CHI instrument model 680 was used for recording the cyclic voltametry of the ligand and its complexes, with DMF as solvent and 0.1 M TBAP as supporting electrolyte. A three-electrode configuration was used viz., platinum working and counter electrode and SCE reference electrode.

**Synthesis of Schiff base ligand:** The ligand (L) was prepared by the drop wise addition of a solution of isatin (1.4713 g) in methanol (20 ml), to a solution of a 2-aminophenol (1.0913 g) in methanol (20 ml). After this addition was completed, 4-chloroaniline was added slowly with constant stirring. Then the resulting mixture was refluxed for 4 hr. It is then allowed to cool for an hour. A brown coloured solid separated was filtered off, washed with ethanol, air dried and the purity of the ligand was checked by TLC.

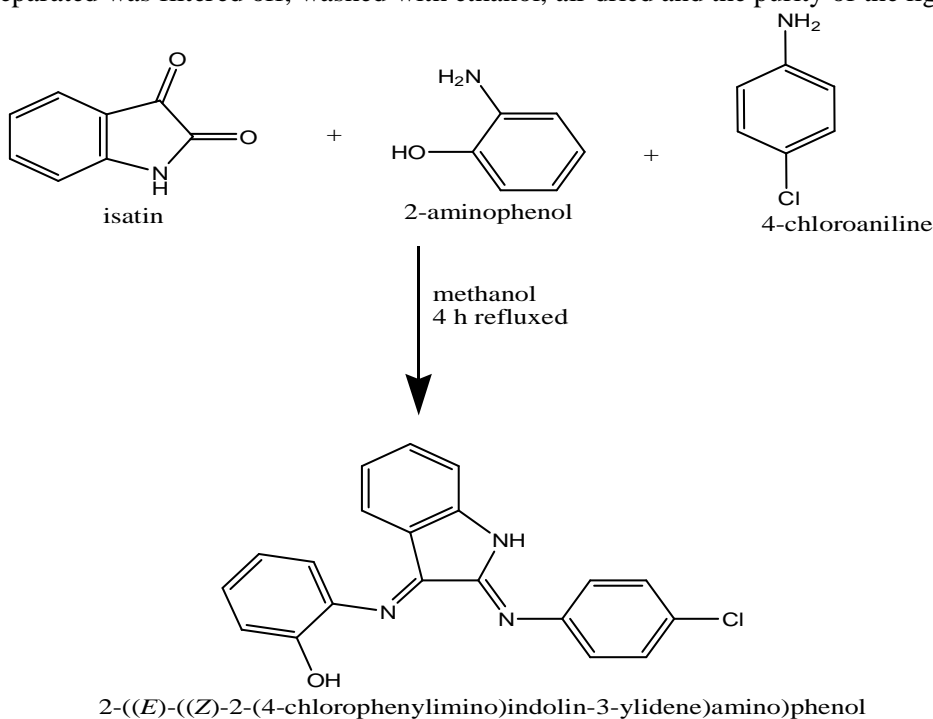
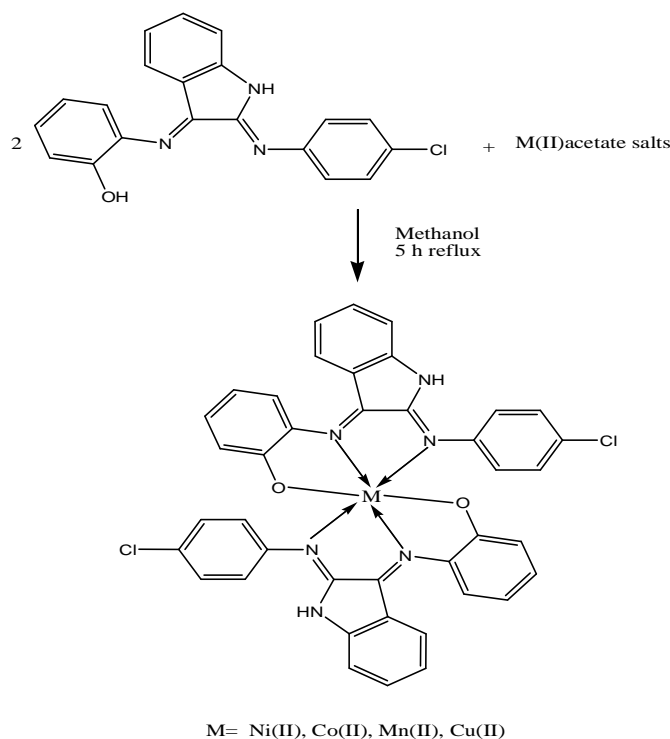


Fig.1 Synthesis of Schiff base ligand

**Preparation of Complexes:** A methanolic solution of ligand was added with a solution of metal acetate salts ( $\text{M}(\text{COOCH}_3)_2 \cdot n\text{H}_2\text{O}$ ;  $\text{M}=\text{Mn, Co, Ni, Cu}$ ) in methanol with constant stirring. The mixture was refluxed for 5 hr. On cooling the solution, the solid settled was filtered off with cold methanol and dried.



**Fig.2** Synthesis of Schiff base metal complexes

**In vitro antibacterial activity:** Antibacterial activity of the ligand and their complexes were tested against the bacterial species like *Staphylococcus aureus* and *Escherichia coli* by paper disc method [7]. The tested organisms were grown on nutrient agar medium in Petri plates. The compounds ( $50$  and  $100 \mu\text{g mL}^{-1}$ ) were prepared in DMSO and soaked in filter paper disc of  $5 \text{ mm}$  diameter [8]. The inhibition zone around each disc was measured after  $24 \text{ h}$  for bacteria.

#### Antioxidant activity

**DPPH (2,2-diphenyl-1-picryl-hydrazyl) Radical scavenging activity (RSA) evaluation:** It is a standard assay in antioxidant activity studies and offers a rapid technique for screening the radical scavenging activity of specific compounds like complexes, extracts etc., DPPH is a stable free radical that can accept an electron or hydrogen radical and get converted to a stable, diamagnetic molecule. DPPH shows a strong absorption band at  $517 \text{ nm}$  due to odd electron present in it. When this electron becomes paired off, the absorption decreases with respect to the uptake of number of electrons or hydrogen atoms. Such a change in the absorbance by this reaction has been extensively adopted to test the capacity of several molecules to act as free radical scavengers. Hence, more rapidly the absorbance decrease, the more potent is the antioxidant activity of the compound. The free radical scavenging effects of Schiff base and their complexes with the DPPH radical were evaluated under the same condition. Various concentrations ( $200$ - $1000 \mu\text{g mL}^{-1}$ ) of the test complexes in  $1 \text{ mL}$  DMF were added to  $4 \text{ mL}$  of  $0.004 \%$  (w/v) methanol solution of DPPH. After  $30 \text{ min}$  incubation period at room temperature, the absorbance was measured against blank at  $517 \text{ nm}$ . This absorption depends on the hydrogen atom or electron donation ability of the complexes in methanolic solution of DPPH. The percent of inhibition (I %) of free radical production from DPPH was calculated by using the following equation.

$$\% \text{ inhibition} = \left[ 1 - \frac{A_{\text{sample}}}{A_{\text{control}}} \right] \times 100$$

## RESULTS AND DISCUSSION

The analytical and physical data of the ligand and metal complexes are depicted in table 1. The complexes gave satisfactory analytical data indicating 1:2 metal-to-ligand stoichiometry for all complexes.

**Table.1.** Elemental analysis data and some physical properties of the Schiff base and metal complexes

Compounds	Molecular formula	Color	Yield (%)	M.pt (°C)	Calcd.(Found) %				
					C	H	N	M	Cl
L	C <sub>20</sub> H <sub>14</sub> ON <sub>3</sub> Cl	Dark brown	85	151	69.07	4.06	12.08	-	10.19
[Ni(L) <sub>2</sub> ]	NiC <sub>40</sub> H <sub>26</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	Brown	65	>250	63.86	3.48	11.17	7.80	9.43
[Co(L) <sub>2</sub> ]	CoC <sub>40</sub> H <sub>26</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	Red	65	>250	63.84	3.48	11.17	7.83	9.42
[Mn(L) <sub>2</sub> ]	MnC <sub>40</sub> H <sub>26</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	Pale brown	65	>250	64.18	3.50	11.23	7.34	9.47
[Cu(L) <sub>2</sub> ]	CuC <sub>40</sub> H <sub>26</sub> O <sub>2</sub> N <sub>6</sub> Cl <sub>2</sub>	Brown	65	>250	63.45	3.46	11.10	8.39	9.37

**Conductivity measurements:** The molar conductance of the metal complexes (10<sup>-3</sup> M) in DMSO solvent were measured at room temperature and the results are listed in table 2. The values (3.44 - 7.95) showed that all the complexes are non electrolytic in nature [9].

**Infrared spectroscopy:** IR Spectra of the ligand and its complexes were recorded in order to find the binding nature of ligand in their corresponding complexes. The IR spectrum of ligand exhibits the stretching frequencies of the OH and NH bonds at 3364 cm<sup>-1</sup> and 3026 cm<sup>-1</sup> respectively. The two azomethine stretching vibrations were observed around 1650 cm<sup>-1</sup>. The disappearance of OH frequency in complexes clearly shows the binding mode of the phenolic oxygen atom with the metal *via* deprotonation [10]. The decrement of stretching vibrations in complexes corresponds to the two C=N bonds from 1628 cm<sup>-1</sup> - 1609 cm<sup>-1</sup> [11]. The appearance of new band ranges from 413-416 and 514-542 cm<sup>-1</sup>, which are assigned to  $\nu$ (M-N) and  $\nu$ (M-O), respectively [12]. This evidence supported the stretching frequency of the imine nitrogen and phenolic oxygen coordinated to metal ion. These observations suggest tridentate binding mode of the ligand through ONN donor atoms. The infrared spectral data for the ligand and their metal complexes are summarized in table 2.

**Table.2.** Infrared spectral and Molar Conductance data of Schiff base and its metal complexes

Compounds	$\nu$ (C=N) cm <sup>-1</sup>	$\nu$ (O-H) cm <sup>-1</sup>	$\nu$ (C-N) cm <sup>-1</sup>	$\nu$ (M-N) cm <sup>-1</sup>	$\nu$ (M-O) cm <sup>-1</sup>	$\Lambda_m$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )
L	1650	3364	1325	-	-	-
[Ni(L) <sub>2</sub> ]	1609	-	1393	414	514	7.95
[Co(L) <sub>2</sub> ]	1610	-	1399	413	516	3.44
[Mn(L) <sub>2</sub> ]	1686	-	1322	414	523	3.94
[Cu(L) <sub>2</sub> ]	1628	-	1271	416	542	5.17

**<sup>1</sup>H NMR Spectra:** The <sup>1</sup>H NMR Schiff base was recorded in DMSO-d<sub>6</sub> at room temperature. Three different type of protons were identified i) characteristic resonance due to azomethine proton in the Schiff base appears at 8.38 ppm was observed, ii) the signal at 10.62 ppm exhibits due to phenolic -OH protons and iii) the other signals in the region 6.59–7.39 ppm exhibits due to aromatic protons [13]. All these observations support the infrared conclusions.

**Magnetic susceptibility and electronic spectral studies:** The electronic absorption spectral data of the complexes in DMSO at room temperature are presented in table 3. The electronic spectra of ligand shows two bands at 291 nm ( $34,364\text{ cm}^{-1}$ ) and 353 nm ( $28,328\text{ cm}^{-1}$ ) ranges are most probably due to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition of the aromatic and imine groups [14]. The diffused reflectance spectrum of the nickel(II) complex exhibits a band at 697 nm ( $14,347\text{ cm}^{-1}$ ) which may be assigned to the  ${}^3A_{2g} \rightarrow {}^3T_{2g}$  transition and the room temperature magnetic moment value of 3.70 B.M. indicating that the Ni(II) complex is octahedral [15-16]. The electronic spectra of the Co(II) complex consists of a broad band at 734 nm ( $13,623\text{ cm}^{-1}$ ) which may be assigned to the  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  respectively. The measurement of Co(II) complex display magnetic moment value of 4.54 B.M. which is in the octahedral range 4.40 to 4.54 B.M [17]. The room temperature magnetic moment of Mn(II) complex is 5.64 B.M. and is close to the spin only value for an octahedral Mn(II) ion corresponding to five unpaired electrons. The electronic spectra of Mn(II) complex exhibit two very low intense bands, at 676 nm ( $14,792\text{ cm}^{-1}$ ) which may rise due to  ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$  transition and the another band at 735 nm ( $13,605\text{ cm}^{-1}$ ) may be assigned to  ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g(G)$  transition for Mn(II) ion in octahedral environment [18]. The reflectance spectrum of the Cu(II) complex gives two bands at 589, 781 nm ( $16,977$  and  $12,804\text{ cm}^{-1}$ ). These bands observed are assigned to the transitions  ${}^2B_{1g} \rightarrow {}^2E_g$  and  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ , respectively. The magnetic moment 1.79 B.M. fits well in the region 1.73–2.20 B.M. reported for the octahedral Cu(II) complexes [19]. The band at 412-436 nm ( $24271$ - $22935\text{ cm}^{-1}$ ) and 355-362 nm ( $28169$ - $27624\text{ cm}^{-1}$ ) which attributed to ligand to metal charge transfer and  $n \rightarrow \pi^*$  transition of metal complexes.

**Table.3.** Electronic spectral data ( $\text{cm}^{-1}$ ) of the Schiff base and its metal complexes

Compounds	$\pi\text{-}\pi^*$	$n\text{-}\pi^*$	LMCT	d-d	Geometry	$\mu_{\text{eff}}$ B.M
L	34364	28338	-	-	-	-
[Ni(L) <sub>2</sub> ]	28169	-	23331	14347	Octahedral	3.70
[Co(L) <sub>2</sub> ]	33670	28089	24271	13623	Octahedral	4.54
[Mn(L) <sub>2</sub> ]	41841, 33444	28168	23809	14792, 13605	Octahedral	5.64
[Cu(L) <sub>2</sub> ]	34722	27624	22935	16977, 12804	Octahedral	2.70

**Electrochemical properties :** Electrochemical behaviour of metal(II) complexes were studied by cyclic voltammetry technique in DMSO containing  $10^{-1}$  M tetra(n-butyl)ammonium perchlorate in the potential range 0 to -2 V and the electrochemical data are summarized in table 4. All the complexes show a single quasi-reversible one electron transfer reduction process in the negative potential region. The copper complex is redox active and show a cyclic voltamogram response in the negative potential range of -0.64 to -1.32 V [20-21] assigned to the Cu(II)/Cu(I) couple [22]. It has been shown that the formal redox potential of Cu(II)/Cu(I) couple is dependent on factors such as coordination number, hard/soft nature of the ligands and bulkiness of the ligands [23]. The cobalt complex exhibit one electron quasi reversible transfer process with a peaks at  $E_{\text{pa}} = -0.67$  V,  $E_{\text{pc}} = -1.4$  V and  $\Delta E_{\text{p}} = 730$  V. This gives evidence for quasi reversible Co(II)/Co(I) couple. The cyclic voltamogram of nickel complexes shows well defined redox process corresponding to the formation of the quasi-reversible Ni(II)/Ni(I) couple. The anodic peak at  $E_{\text{pa}} = -0.68$  V and the associated cathodic peak at  $E_{\text{pc}} = -1.31$  V and  $\Delta E_{\text{p}} = -313.27$  V corresponds to Ni(II)/Ni(I) couple [24-25]. The one electron cyclic response for manganese complexes was observed at  $E_{\text{pc}} = -1.33$  V,  $E_{\text{pa}} = -0.66$ , and  $\Delta E_{\text{p}} = 629$  V. corresponds to Mn(II)/Mn(I).

**Table 4.** Electrochemical data (Negative potential) of Schiff base metal complexes

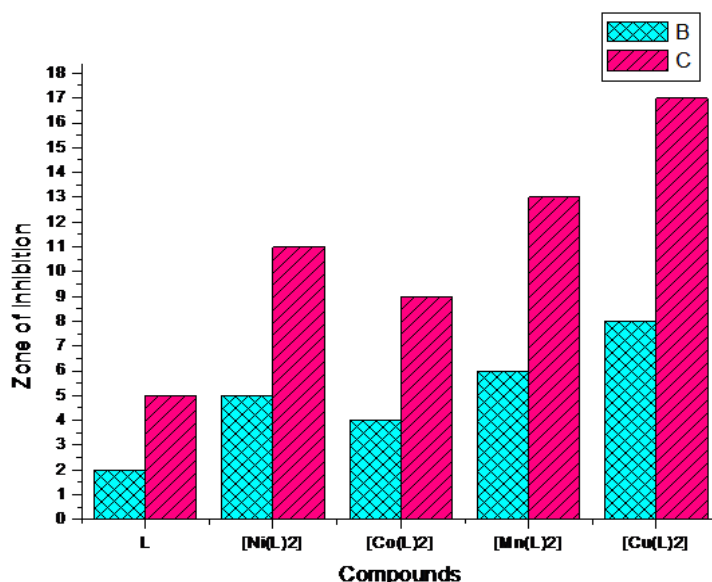
Complexes	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E_{1/2}$ (V)	$\Delta E_{\text{p}}$ (mV)
[Ni(L) <sub>2</sub> ]	-1.31	-0.68	-0.97	629
[Co(L) <sub>2</sub> ]	-1.40	-0.67	-1.03	730
[Mn(L) <sub>2</sub> ]	-1.33	-0.66	-1.99	670
[Cu(L) <sub>2</sub> ]	-1.32	-0.64	-0.98	680

## APPLICATIONS

**Antibacterial study:** The *in vitro* biological screening effects of the investigated compounds were tested against some bacterial species by the paper disc method. The antibacterial activities are given in table 5. The results shows that both the Schiff base ligand have moderate activity in the antibacterial species of *S. aureus*, *E. coli*. The antibacterial activity of all the complexes exhibited promising results than the ligand against all the test bacterial strains. The biological activity of the complexes follow the order: Cu(II) > Mn(II) > Ni(II) > Co(II). It is known that chelation tends act as more powerful and potent bactericidal agent [26]. This enhancement in the activity may be rationalized on the basis that ligands mainly possess C=N bond. It has been suggested that the ligands with nitrogen and oxygen donor atoms inhibit enzyme activity, since the enzymes which require these groups for their activity appear to be especially more susceptible to deactivation by metal ions on coordination. Moreover, coordination reduces the polarity of the metal ion essentially because of the partial sharing of its positive charge with the donor groups within the chelate ring system formed during coordination [27, 28]. It also shows that the activity increases with increase in concentration of the synthesized compounds.

**Table.5.** Antibacterial activity of the Schiff base and its metal complexes

Compounds	Zone of inhibition (mm)			
	Staphylococcus aureus		Escherichia coli	
	Concentrations ( $\mu\text{g mL}^{-1}$ )			
	50	100	50	100
L	2	5	2	4
[Ni(L) <sub>2</sub> ]	5	11	4	9
[Co(L) <sub>2</sub> ]	4	9	3	7
[Mn(L) <sub>2</sub> ]	6	13	5	11
[Cu(L) <sub>2</sub> ]	8	17	10	12



**Fig 3.** Antibacterial activity of the Schiff base and its metal complexes against *Staphylococcus aureus* (B=50  $\mu\text{g mL}^{-1}$ , C=100  $\mu\text{g mL}^{-1}$ )

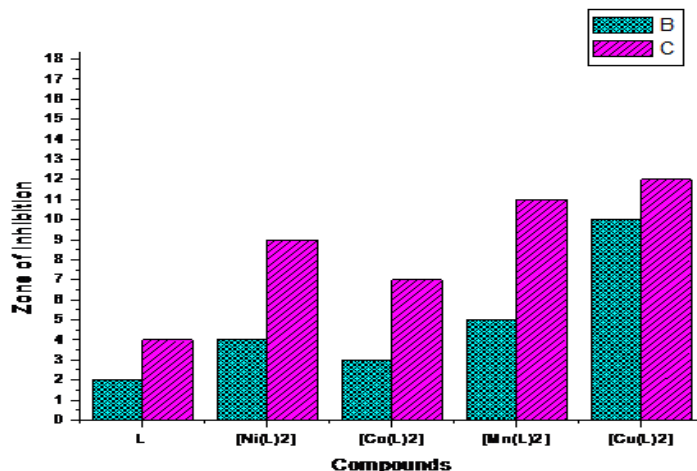


Fig 4. Antibacterial activity of the Schiff base and its metal complexes against Escherichia coli (B=50 µg mL<sup>-1</sup>, C=100 µg mL<sup>-1</sup>)

**Antioxidant studies - DPPH radical:** The scavenging of DPPH radicals is a convenient method used to evaluate the antioxidant properties of the Schiff and its metal complexes. The DPPH radicals are stable but in the presence of synthesized compounds capable of donating hydrogen atoms and the radical property is destroyed resulting in a colour change from purple to yellow. In this experiment, ascorbic acid is used as a standard for comparison. It was observed that the Schiff base and their complexes can indeed reduce the concentration of the initial DPPH radical in solution and this is taken as evidence of their antioxidant capabilities [29]. The inhibitory effect and IC<sub>50</sub> values on DPPH radical are shown in fig.5 and 6.

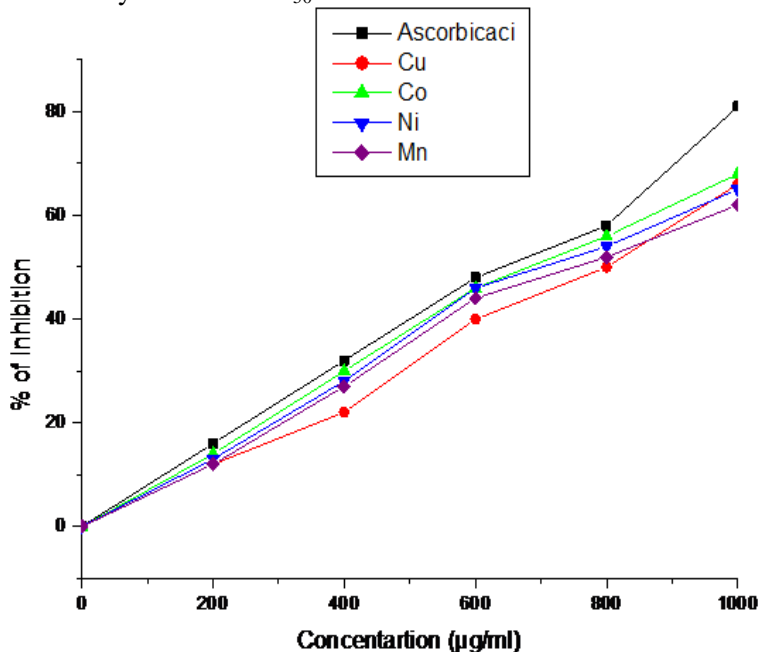


Fig 5: DPPH Scavenging Activity of Schiff base and its Metal Complexes (B= Ascorbic acid; C=Ligand D= [Cu(L)<sub>2</sub>]; E= [Co(L)<sub>2</sub>]; F=[Ni(L)<sub>2</sub>]; G = [Mn(L)<sub>2</sub>])

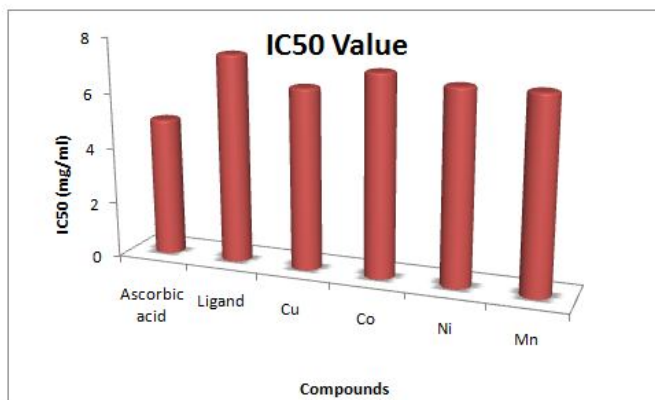


Fig 6: DPPH Scavenging Capacities (IC<sub>50</sub>) of Schiff base and its Metal Complexes

## CONCLUSIONS

The synthesized new Schiff base and its metal complexes have been confirmed by the analytical data, IR, Electronic, <sup>1</sup>H NMR, magnetic moment, molar conductance and electrochemical studies. These spectral studies confirm octahedral arrangement around the metal ion. The antibacterial activity results shows that all complexes have been found to be more effective than its ligand as the process of chelation dominantly affects the overall biological behaviour of the compounds.

## REFERENCES

- [1] Sargunam Caleb Noble Chandar, Kannappan Santhakumar, Mahadevimangalam Narayanasamy Arumugham, *Transition Met Chem.*, **2009**, 34,841–848.
- [2] Panayot R. Bontchev, Ivayla N. Pantcheva, Ranko P. Bontchev, Darvin S. Ivanov & Nikolay D. Danchev, *BioMetals*, **2002**,15, 79–86.
- [3] Da Silva JJRF, Williams RJP, The biological chemistry of the elements. Oxford: Clarendon Press, **1991**.
- [4] E.M Jouad, G. Larcher, M. Allain, A. Riou, G.M Bouet, M.A Khan, X.D Thanh, *J Inorg Biochem*, **2001**, 86,565–571.
- [5] S.S Konstantinovic, B.C Radovanovic, Z. Cakic, V. Vasic, *J Serb Chem Soc.*, **2003**, 68, 641–647.
- [6] Sandra S. Konstantinovic, Vanja S. Cakic, *Med Chem Res.*, **2010**, 19, 771–781.
- [7] A. W. M. M. Bauer, J. C. Sherries, and M. Truck, *Am. J. Clin. Pathol.*, 1996, 45,493-496.
- [8] Ferrari, M. B., Capacchi, S., Reffo, G., Tarasconi, P., Albertini, R., Penelli, S. and Lunghi, P., *Inorg. Chim. Acta.*, **1999**, 286,134-141.
- [9] W.J.Geary, *Coord.Chem.Rev.*, **1972**, 1-8.
- [10] M. Sayed G. Abdallah, Gehad, M.A. Mohamed, S. Zayed, Mohsen, Abou El-Ela, *Spectrochim. Acta Part A.*, **2009**, 833-840, 73.
- [11] G. Gehad, M.M. Mohamed, Amr. Omar, A. Ibrahim, *Eur. J. Med. Chem.*, **2009**, 44, 4801-4812.
- [12] Pampa Mukherjee, Michael G.B. Drew, Marta Estrader, Carmen Diaz, Ashutosh Ghosh, *Inorg. Chim. Acta*, **2008**, 161-172, 361.
- [13] Sayaji Rao, *Asian J. Chem.*, **2005**, 17, 2663–2668.
- [14] S.A. Abdel-Latif, H.B. Hassib, Y.M. Issa, *Spectrochim. Acta Part A*, **2007**, 67, 950-957.
- [15] F.A. Cotten, G. Wilkinson, C.A. Murillo, M. Bochmann, *Adv.Inorg. Chem.*, 6<sup>th</sup> edn., Wiley, New York, **1999**.



- [16] D.R. Zhu, Y. Song, Y. Xu, Y. Zhang, S.S.S. Raj, H.K. Fun, X.Z. You, *Polyhedron*, **2000**, 19, 2019-2025.
- [17] Mohammad Shakir, Yasser Azim, Hamida-Tun-Nisa Cbishti, Shama Praveen, *Spectrochim. Acta Part A.*, **2006**, 65,490-496.
- [18] K. T. Joshi, A. M. Pancholi, K. S. Pandya and A. S. Thakar, *J. Chem. Pharm. Res.*, **2011**, 3(4),741-749.
- [19] Sulekh Chandra, Lokesh Kumar Gupta, *Spectrochim. Acta Part A.*, **2005**, 61, 1181-1181.
- [20] XH. Bu, ZH. Zhang, XC. Cao, S. Ma, Y. Tichen, *Polyhedron*, **1997**, 16, 3525.
- [21] S. Dhar, D. Senapathi, P.K Das, P. Chattopadyay, M. Nethaji, A.R Chakravarthy, *J AM chem. Soc.*, **2003**, 125,12218.
- [22] S. Djebbar-Sid, O. Benali-Baitich, JP. Delaume, *Polyhedron*, **1997**,16,2175.
- [23] S. Chandra, L. K. Gupta, Sangeetika, *Synth. React. Inorg. Met.-Org. Chem.*, **2004**, 34:1591
- [24] A.S. Kumbhar, S.B. Padhye, D.X. West, A.E. Liberta, *Transition met chem.*, **1992**, 17, 247.
- [25] A.J. Bard and L.R. Izatt, *Electrochemical method: Fundamentals and Applications: 2<sup>nd</sup> Ed.*, Wiley: New York, **2001**.
- [26] K. Sudhakar Babu, T. Ravi Sankar, J. Latha, B. Ram Babu and M. SwarnaKumari, *Journal of Applicable Chemistry*, **2013**, 2 (4), 772-778.
- [27] Y. Anjaneyulu, R. P. Rao, *Synth. React. Inorg. Met. Org. Chem.* **1986**, 16 257.
- [28] Gehad Geindy Mohamed, Mohamed Mohamed Omar, Ahmed Mohamed Hindy, *Turk J.Chem.*, **2006**, 30, 361-382.
- [29] Zeng-Chen Liu, Zheng-Yin Yang, Tian-Rong Li, Bao-Dui Wang, Yong Li, Ming-Fang Wang, *Transition Met Chem.*, **2011**, 36:489-498.