### Accepted Manuscript

Synthesis, spectroscopic, coordination and biological activities of some transition metal complexes containing ONO tridentate Schiff base ligand

A.A.M. Belal, I.M. El-Deen, N.Y. Farid, Rosan Zakaria, Moamen S. Refat

PII:	S1386-1425(15)00593-4
DOI:	http://dx.doi.org/10.1016/j.saa.2015.05.005
Reference:	SAA 13672
To appear in:	Spectrochimica Acta Part A: Molecular and Biomo- lecular Spectroscopy
Received Date:	4 November 2014
Revised Date:	21 April 2015
Accepted Date:	4 May 2015



Please cite this article as: A.A.M. Belal, I.M. El-Deen, N.Y. Farid, R. Zakaria, M.S. Refat, Synthesis, spectroscopic, coordination and biological activities of some transition metal complexes containing ONO tridentate Schiff base ligand, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2015), doi: http://dx.doi.org/ 10.1016/j.saa.2015.05.005

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

### Synthesis, spectroscopic, coordination and biological activities of some transition metal complexes containing ONO tridentate Schiff base ligand

A.A.M. Belal<sup>1</sup>, I.M. El-Deen<sup>1</sup>, N.Y. Farid<sup>1</sup>, Rosan Zakaria<sup>1</sup> and Moamen S. Refat<sup>1,2\*</sup>

 <sup>1</sup> Department of Chemistry, Faculty of Science, Port Said University, Port Said, Egypt
 <sup>2</sup> Department of Chemistry, Faculty of Science, Taif University, Al-Hawiah, Taif, P.O. Box 888 Zip Code 21974, Saudi Arabia

Email: msrefat@yahoo.com

#### Abstract

The main target of this paper is to get an interesting data for the preparation and characterizations of metal oxide (MO) nanoparticles using H<sub>2</sub>L Schiff base complexes as precursors through the thermal decomposition procedure. Five Schiff base complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) metal ions were synthesized from 2-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-benzoic acid new adduct (H<sub>2</sub>L). Theses complexes were characterized using infrared, electronic, mass and <sup>1</sup>HNMR spectroscopic techniques. The elemental analysis data was confirmed that the stoichiometry of (metal: H<sub>2</sub>L) is 1:1 molar ratio. The molar conductance indicates that all of complexes are non electrolytic. The general chemical formulas of these complexes is  $[M(L)(NH_3)].nH_2O$ . All complexes are tetrahedral geometry. The thermal decomposition behavior of H<sub>2</sub>L hydrated and anhydrous complexes has been discussed using thermogravimetric analysis (TG/DTG) and differential thermal analyses (DTA) under nitrogen atmosphere. The crystalline phases of the reaction products were checked using X-ray diffractometer (XRD) and scanning electron microscopy (SEM).

Keywords: Schiff base; transition metals; nano-particles; XRD; SEM; thermal analysis.

#### **1- Introduction**

Schiff base compounds with the azomethine group (-RC=N-) were usually formed by the condensation of amine –NH<sub>2</sub> group with active –C=O carbonyl group [1]. The field of Schiff bases is fast developing because of the wide variety and potential applications of their industrial, biological, analytical, medicinal, pharmaceutical and catalytical applications [2-7]. Complexes of Schiff bases with some transition metals show significant biological notification including antimicrobial, antibacterial, antifungal and anticancer activities [7-10]. In literature survey [11-15] a number of research articles have been published on transition metal complexes of Cu(II), Co(II), Ni(II), Fe(III), Zn(II) with Schiff bases derived from the condensation of salicyladehyde and o-amino phenol or 2-amino benzoic acid. Azo compounds have been studied widely because of their excellent thermal, antibacterial activity and optical properties in applications such as optical recording medium, toner, ink-jet printing and oil-soluble lightfast dyes [16-19].

Based on the previous considerations, we are initiating a line of investigation on the coordination chemistry of Schiff base compounds containing azo group attached with organic moieties. In this paper, we report the characterization by elemental analysis, magnetic properties, infrared spectra (IR), ultraviolet and visible spectra (UV–Vis), X-ray diffraction, scanning electron microscopy, proton nuclear magnetic resonance (<sup>1</sup>H-NMR), and mass spectra of 2-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-benzoic acid Schiff base (H<sub>2</sub>L) and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes. Thus, the complexes have been isolated and there are well characterized. The ligand H<sub>2</sub>L acts

as tridentate through two oxygen atoms (–OH phenolic and carboxylic acid) and nitrogen atom of azomethine group deduced from the chemical interaction between anthranilic acid and 2-hydroxy-naphthalene-1-carbaldehyde moieties. The Cu(II) and Zn(II) oxides nano-particles are collected through thermal decomposition process of copper(II) and zinc(II) H<sub>2</sub>L complexes which has many advantages like controlling on the process conditions, particle size, particle crystal structure, decreasing the calcinations temperature, and high purity.

### 2- Experimental

#### 2-1- Reagents

All chemicals used in this paper were of analytical grade and used without further purification as transition metal salts MnCl<sub>2</sub>.4H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, and ZnCl<sub>2</sub>. Organic compounds like anthranilic acid and 2-hydroxy-naphthalene-1-carbaldehyde were obtained from BDH chemical company. The distilled water, methanol and diethyl ether solvents were used without distillation.

### 2-2- Synthesis of new H<sub>2</sub>L Schiff base ligand

New 2-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-benzoic acid Schiff base  $(H_2L)$  chelat (Fig. 1) was obtained by a procedure in two steps as follows.

The Schiff base (H<sub>2</sub>L) was prepared by mixing 50 mL methanol solution of 2hydroxy-naphthalene-1-carbaldehyde (50 mmol) with a solution of anthranilic acid (50 mmol) in methanol (50 mL) under reflux for 3 h. at 70 °C on a hot plate [20, 21]. After cooling, the precipitate was filtered, washed several times with methanol and diethyl ether to remove all organic impurities, dried in *vacuo* over calcium chloride. The purity of the ligand was evaluated by thin layer chromatography and the composition was confirmed by elemental analysis CHN, and (IR, mass, and <sup>1</sup>H-NMR) spectra.



### C<sub>18</sub>H<sub>13</sub>NO<sub>3</sub> Mol. Wt.: 291.30 m/e: 291.09 (100.0%) C, 74.22; H, 4.50; N, 4.81; O, 16.48

Fig. 1: The structural formula of  $H_2L$  2-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]benzoic acid Schiff base ligand

#### 2-3- Synthesis of complexes

To a hot solution (1 mmol) of  $H_2L$  Schiff base ligand in (50 mL) methanol, a hot solution of corresponding metal(II) salts (MnCl<sub>2</sub>.4H<sub>2</sub>O, CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuCl<sub>2</sub>.2H<sub>2</sub>O, and ZnCl<sub>2</sub>) (1 mmol, in 50 mL methanol) were added slowly. The resulting mixtures were neutralized at pH= 7-8 using ammonia solution, stirred and refluxed on a

hot plate at 70 °C for 1 hr, and then concentrated to half its initial volume. After cooling for the mixtures overnight, the solid complexes are precipitated and separated, washed with methanol and diethyl ether. The synthesized complexes was re-crystallized from methanol and dried under vacuum over anhydrous CaCl<sub>2</sub>. The purity was checked by thin layer chromatography.

### 2-4- Instruments

The elemental analyses (e.g., carbon, hydrogen and nitrogen) were collected at the Microanalytical unit of Ain Shams, University Egypt, by a Perkin-Elmer CHN 2400 elemental analyzer. The metal contents were determined gravimetrically by converting the compounds to its corresponding stable oxides. The chloride ions were gravimetrically determined using a standard method [22] and the data reflect the high conformity with that theoretically proposed. The molar conductivities of freshly prepared  $1.0 \times 10^{-3}$ mol/cm<sup>3</sup> dimethylsulfoxide solutions were measured for the soluble complexes using Jenway 4010 conductivity meter. The magnetic measurements were performed using magnetic susceptibility balance Sherwood Scientific Cambridge, England. The infrared spectra, as KBr discs, were recorded on a Bruker FT-IR Spectrophotometer (4000 - 400 cm<sup>-1</sup>) at Cairo University. The electronic and <sup>1</sup>H-NMR (200 MHz) spectra were recorded on Perkin-Elmer Precisely Lambda 25 UV/Vis double beam Spectrometer fitted with a quartz cell of 1.0 cm path length, and a Varian Gemini Spectrophotometers, respectively at Cairo universities. The thermal studies were carried out on a Shimadzu thermo gravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup> under nitrogen till 800 °C in Cairo University. The purity of  $H_2L$  Schiff base ligand was checked via mass spectra at 70 eV by using AEI MS 30 mass spectrometer at room temperature. The X-ray diffraction patterns were recorded on Bruker AXS configuration X-ray powder diffraction. Scanning electron microscopy (SEM) images were taken in Joel JSM-639OLA equipment, with an accelerating voltage of 20 KV.

#### 3. Results and discussion

3-1- Elemental analyses and physical properties

The %carbon, %hydrogen, %nitrogen and %chloride percentages with some physicochemical data are listed in Table 1. The colored solid isolated Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) H<sub>2</sub>L complexes are stable in air, having high melting points >250 °C, insoluble in H<sub>2</sub>O and most organic solvents except DMSO and DMF soluble with gently heating.

### 3-2- Conductance measurements

The molar conductivities measurements of  $H_2L$  divalent complexes were measured in DMSO solvent with  $1.0 \times 10^{-3}$  mol concentration. The magnitudes of  $\Lambda_m$  ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ) recorded in Table 1 found that all of complexes are non-electrolytic nature [23]. The very low conductivity values indicate no any conjugated chloride anion existed in the discussed complexes. This result agreement with the analytical data assigned to the absence of any chloride anion covalently or ionically attached with the central metal ions in M–H<sub>2</sub>L complexes.

Empirical formula	Color	Λm	Elem	ental ana	lysis, % F	Found % (	Calcd.)
Empirical formula		(µS)	С	Η	Ν	Cl	М
H <sub>2</sub> L	Yellow	9.28	74.06 (74.22)	4.43 (4.50)	4.77 (4.81)		
[Mn(L)(NH <sub>3</sub> )]	Reddish brown	5.59	59.22 (59.85)	4.23 (3.91)	7.70 (7.75)		15.10 (15.21)
[Co(L)(NH <sub>3</sub> )].H <sub>2</sub> O	Light brown	2.76	57.16 (56.41)	3.80 (4.21)	7.51 (7.31)		15.21 (15.38)
[Ni(L)(NH <sub>3</sub> )]	Greenish brown	2.45	58.22 (59.23)	3.57 (3.87)	7.58 (7.67)		15.77 (16.08)
[Cu(L)(NH <sub>3</sub> )].H <sub>2</sub> O	Dark green	2.17	56.90 (55.74)	3.72 (4.16)	7.44 (7.22)		16.09 (16.38)
[Zn(L)(NH <sub>3</sub> )].H <sub>2</sub> O	Dark brown	2.72	55.91 (55.47)	3.45 (4.14)	7.51 (7.19)		16.44 (16.78)

#### Table1: Physicochemical data of H<sub>2</sub>L Schiff base and its metal complexes

#### 3-3- Mass spectral analysis

Mass spectrometry an interesting technique successfully used to confirm the molecular ion peaks of H<sub>2</sub>L Schiff base and investigate the fragment species. The fragment pattern of mass spectrum gives an impression for the successive degradation of the target compound with the series of peaks corresponding to various fragments. Also, the peaks intensity gives an idea about the stability of fragments especially with the base peak. The recorded mass spectrum of H<sub>2</sub>L ligand (Fig. 2) reveals molecular ion peak confirms strongly the proposed formula. The spectrum of the ligand having peak at m/z = 291 (85 %) which is referring to the molecular ion peak (M<sup>+</sup>) and confirming the purity of the ligand prepared. The degradation pattern have prominent peaks at m/z= 231(100%) base peak, 207(83%), 181(60%), 159(80%), 78(7%) and 29(52%) as displayed in degradation scheme 1.

FAB mass spectra of the  $[Ni(L)(NH_3)]$  and  $[Cu(L)(NH_3)]$ .H<sub>2</sub>O complexes have been performed. The peaks revealed a distinctive set of ions with masses corresponding to the cation and fragments of parent ions derived by loss of the ligand.



Fig. 2: Mass spectrum of H<sub>2</sub>L Schiff base ligand



Scheme 1: The fragmentation pattern proposed for H<sub>2</sub>L Schiff base ligand

3-4- Infrared spectral data

The characteristic infrared spectra of  $H_2L$  and its complexes are shown in Fig. 3 as well as their bands assignments are listed in Table 2. These bands give essential information about the nature of the functional group attached to the metal atom [14, 15]. The IR spectra of  $H_2L$  ligand and its complexes are found to be quite complex as they in general exhibit large number of bands of varying intensities.

i- The spectrum of the free Schiff base ligand shows the peak of azomethine group -CH=N at 1589 cm<sup>-1</sup>, which is shifted to lower frequencies in the spectra of all complexes within the range 1542-1537 cm<sup>-1</sup>. This result indicate that the nitrogen atom of -CH=N sharing in the coordination with metal ions [14].

ii- The stretching vibration motion of v(C=O) of carboxylic group in H<sub>2</sub>L free ligand located at 1709 cm<sup>-1</sup> is disappeared in all complexes, this ascribe to the deprotonation of carboxylic group and participate in the chelation process.

iii- Two essential strong-to-medium strong bands were found in the range 1626– 1587 and 1428–1384 cm<sup>-1</sup> which could be assigned to ( $v_{as}$ COO) (antisymmetric) and (vsCOO) (symmetric) vibrations of the carboxylate ions, respectively [26]. The differences between the asymmetric and symmetric stretching vibration motions,  $\Delta$ [ $v_{as}$ (COO)-  $v_s$ (COO)] were in the range 213–198 cm<sup>-1</sup>, which were matched with monodentate ligational [22]. These values confirm that the carboxylate group was coordinated to Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions in a monodentate mode involving coordination of the oxygen atom of the ligand [26].

iv- In the IR spectrum of ligand (H<sub>2</sub>L), v(OH) band appeared at 3425 cm<sup>-1</sup>. This band is absence in the complexes but alternated in the same place by other bands within 3450-3420 cm<sup>-1</sup> which assigned to the stretching motions of uncoordinated water molecules.

Compound	v(OH)	v(NH); NH <sub>3</sub>	v(C=N)	v <sub>s</sub> (COO)	$v_{as}(COO)$	v(C-O)	v(M-O)	v(M-N)
H <sub>2</sub> L	3425	-	1589	1615	1483	1277	-	-
[Mn(L)(NH <sub>3</sub> )]	-	3260	1539	1587	1384	1210	572 530	494 448
$[Co(L)(NH_3)].H_2O$	3426	3306	1537	1614	1404	1244	516	419
[Ni(L)(NH <sub>3</sub> )]	3420	3304	1539	1612	1405	1242	551 521	478 431
[Cu(L)(NH <sub>3</sub> )].H <sub>2</sub> O	3440	3275	1546	1626	1428	1242	575 538	486 439
[Zn(L)(NH <sub>3</sub> )].H <sub>2</sub> O	3450	3298	1542	1615	1402	1211	561 509	457 410

**Table 2**: Assignments of the IR and Raman Spectral bands  $(cm^{-1})$  for H<sub>2</sub>L Schiff base and its metal complexes

v- The new bands exhibit at the frequency of  $3306-3260 \text{ cm}^{-1}$  in the spectra of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes are assigned to v(NH) of  $-NH_3$  group, which indicate the participation of nitrogen atom of  $-NH_3$  group in coordination with metal ions.

vi- The phenolic C–O stretching vibrations appeared at 1277  $\text{cm}^{-1}$  in the Schiff base free ligand is shifted towards lower frequencies (1244–1210  $\text{cm}^{-1}$ ) in the complexes

(Table 2). This shift confirms the participation of oxygen atom of phenolic group in the chelation with C–O–M bond [24, 25].

vii- In case of H<sub>2</sub>L complexes, there are number of medium-to-weak bands in the two ranges (572–509 cm<sup>-1</sup>) and (494–410 cm<sup>-1</sup>) are assigned to the stretching frequencies of the v(M–O) and v(M–N) [26] bands, respectively, which confirmed the attached of H<sub>2</sub>L ligand to the center metal ions through the phenolic oxygen atoms and the azomethine nitrogen.

viii- The spectra of H<sub>2</sub>L complexes exhibited a broad band around 3450-33420 cm<sup>-1</sup>, which is assigned to water molecules, v(OH), associated with the complexes.



7



#### Fig. 3B

Fig. 3: Infrared spectra of A-H<sub>2</sub>L, and its B-Mn(II) Schiff base complex

3-5- Electronic spectra and magnetic measurements

The electronic spectral data of the free H<sub>2</sub>L Schiff base ligand (Table 3) was collected in DMSO solvent with four absorption bands at 295, 320, 355 and 420 nm. The spectral bands at 295 and 320 nm were assigned to transition motions of phenyl rings [27-29]. The transition band at 355 nm corresponded to  $n \rightarrow \pi^*$  transition of azomethine group –CH=N, while, the band at 420 nm assigned to  $n \rightarrow \pi^*$  transitions of donating atoms like oxygen and nitrogen which are overlapped with the intermolecular L<sub>CT</sub> from aromatic rings. The peaks within the transition motions of phenyl rings have been relatively unaffected in the spectra of the complexes; this is expected for the relatively unshared of aromatic ring in chelation. The transition bands up to 350 nm which assigned to  $n \rightarrow \pi^*$  transition due to involving molecular orbitals of the –CH=N chromophore. The bands of  $n \rightarrow \pi^*$  transition have been shifted upon complexation of H<sub>2</sub>L ligand towards all metal ions. This is indicating that, the azomethine group nitrogen atom appears to be coordinated to the metal ions [14].

The tetrahedral manganese(II) complex was reddish brown. This color is a guide to confirm that the formed Mn(II) complex has tetrahedral geometry rather than octahedral [30]. The Mn[(L)(NH<sub>3</sub>)] complex in DMSO solvent shows absorption bands at 27777 cm<sup>-1</sup> assigned to  ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$  transition. Moreover, there are two charge transfer bands at 33898 and 31250 cm<sup>-1</sup>. The tetrahedral Mn(II) complex gives an essentially spin-only magnetic moment value of 5.92 B.M., which does not vary much since the magnetic moment is temperature independent. The observed magnetic moment value 5.92 B.M. in Mn(II) complex is appreciably close to the calculated spin value only. The observed magnetic moment value and electronic spectrum suggest a tetrahedral geometry [31] for the Mn(II) complex.

For the cobalt(II) tetrahedral complex, there are two orbital forbidden absorptions, which are rarely observed [32]. There is a complex absorption in the visible region and the intensity of the band is due to spin-orbit coupling [33]. For Co(II) complex, two bands at 20618 and 25000 cm<sup>-1</sup> assigned to  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)$  and  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$  transitions, respectively. There are another two charge transfer bands at 31250 cm<sup>-1</sup> and 33898 cm<sup>-1</sup>, were recorded. The effective magnetic moment for a tetrahedral Co(II) species is 4.06 B.M., while the calculated value is 3.89 B.M., this give a close matching data between experimental and theoretical data.

The greenish brown tetrahedral nickel(II) complex has three absorption bands at 23809, 28571 and 32258 cm<sup>-1</sup>, assigned to  ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{2}(F)$ ,  ${}^{3}T_{1}(F) \rightarrow {}^{3}A_{2}(F)$  and  ${}^{3}T_{1}(F) \rightarrow {}^{3}T_{1}(P)$  transitions, respectively. There is one bands at 33898 cm<sup>-1</sup> due to charge transfer complexation [34]. The magnetic moment of a common tetrahedral nickel(II) should be approximately 3.52 B.M. (calculated magnetic moment of tetrahedral Ni(II) ion is lies between 3.5-3.2 B.M), so, the experimental magnetic moment value was existed within the logical limits [35].

Concerning the copper(II) complex, only one band at 19047 cm<sup>-1</sup> of lower energy was assigned to the d-d transition, which is considered sensitive to the ligand field strength and changes in the molecular geometry and corresponds to the  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$  transition [28, 36]. On the basis of d-d transitions, it is difficult to distinguish between a square-planar and a tetrahedral Cu(II) ion because it occurs in the same region for both the geometries [32]. The experimental magnetic moment value for Cu(II) ion is 2.17 B.M. which is in the range for a square-planar geometry.

Compound Magnetic		Electronic spectral values/ (cm <sup>-1</sup> )	Proposed Geometry	
	moments/			
	$\mu_{eff}$			
$H_2L$	-	33898, 31250, 28169, 23809	-	
$[Mn(L)(NH_3)]$	5.92	33898, 31250, 277777, 23256, 19608	Tetrahedral	
[Co(L)(NH <sub>3</sub> )].H <sub>2</sub> O	4.06	33898, 31250, 25000, 20618	Tetrahedral	
$[Ni(L)(NH_3)]$	3.52	33898, 32258, 28571, 23809	Tetrahedral	
$[Cu(L)(NH_3)].H_2O$	2.17	33898, 30303, 25974, 22727, 19047	Square planar	
[Zn(L)(NH <sub>3</sub> )].H <sub>2</sub> O	Dia- magnetic	33898, 30303, 23529, 19230	Tetrahedral	

**Table 3**: Electronic spectral bands  $(cm^{-1})$  and magnetic moments of the H<sub>2</sub>L ligand and its complexes

#### 3-6- ESR spectra

The X-band of ESR spectrum of  $[Cu(L)(NH_3)]$ .H<sub>2</sub>O Schiff base complex was shown in Fig. 4. The ESR spectrum of the Cu(II) complex was analyzed. The spin Hamiltonian parameters ( $g_{11} = 2.04$  and  $g_{12} = 2.02$ ) and the G value (G= 2) of solid state Cu(II) complex were calculated. Its ESR spectrum displayed axially symmetric g tensor parameters with  $g_{11} > g_{\perp} > 2.0023$  indicating that the  $d_{x-y}^{2}$  orbital as a ground state [28]. In axial symmetry the g-values are related to the G-factor by the expression,  $G = (g_{11} - 2) / (g_{11} - 2)$  $(g_{\perp}-2) = 4$ , which measures the exchange interaction between copper centers in the solid. According to Hathaway [37], if the value of G is greater than 4, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction exists in the solid complex. The G value is less than 4, this supports the little presence of exchange coupling between copper(II) centers in the solid state [38]. This hyperfine interaction observed for the complex is attributed to the interaction with nitrogen and oxygen nuclei adjacent to copper ion. Kivelson and Neiman, [39] have reported the  $g_{11}$  value < 2.3 for covalent character of the metal-ligand bond and > 2.3 for ionic character. Applying this criterion the covalent character of the metal-ligand bond in the complex under study can be predicated. The square-planar geometry has a ground state configuration  ${}^{2}B_{1g}$  (unpaired electron in d<sub>X</sub>2-<sub>Y</sub>2 orbital) and  $^{2}A_{1}$  (unpaired electron in d<sub>Z</sub>2 orbital), respectively. Molecular orbital coefficients,  $\alpha^{2}$  (A measure of the covalence of the in-plane  $\sigma$ -bonding between a copper 3d orbital and the ligand orbital) and  $\beta^{2}$  (covalent in-plane  $\pi$ -bonding), were calculated by using the following equations [39-43], where  $\alpha^2 = 1$  indicates complete ionic character, whereas  $\alpha^2 = 0.5$  denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral.

 $\alpha^{2} = ((A_{//} / 0.036) + (g_{//} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04)$  $\beta^{2} = (g_{//} - 2.0023) E / -8\lambda\alpha^{2},$ 

Where  $\lambda = -828$  cm<sup>-1</sup> for the free copper ion and E is the electronic transition energy. The  $\alpha^2$  (0.45) and  $\beta^2$  (0.24) values indicate that the in-plane  $\sigma$ -bonding and the in-plane  $\pi$ -bonding are highly covalent. The lower value of  $\beta^2$  compared to  $\alpha^2$  indicates that the in-plane  $\pi$ -bonding is more covalent than the in-plane  $\sigma$ -bonding. The  $\alpha^2$  value for copper(II) complex indicates a considerable covalency in the bonding between the Cu(II) ion and the ligand.



**Fig. 4**: ESR spectrum of [Cu(L)(NH<sub>3</sub>)].H<sub>2</sub>O Schiff base complex

### 3-7-<sup>1</sup>HNMR spectra

The <sup>1</sup>HNMR spectrum of H<sub>2</sub>L Schiff base ligand was recorded to confirm the structural. The spectrum of H<sub>2</sub>L ligand (Fig. 5) showed two weak broad peaks at  $\delta$  = 13.42 and 15.14 ppm, that are assigned to –OH and –COOH protons. These peaks are disappeared in the spectrum of zinc(II) complex (Fig. 5B). The singlet peak of –NH (azomethine) in the H<sub>2</sub>L ligand (9.36 ppm) was shifted to lower value at 9.16 ppm in zinc(II) complex, this confirm the participation of –NH group in the complexation. The higher values of protons for the –OH, –COOH and –NH groups can be assigned to the presence of intermolecular hydrogen bonding. The group of peaks (m, 10H) at  $\delta$  = 6.79 – 8.40 ppm range are assigned to aromatic protons of the three aromatic rings and (s, 2H) at  $\delta$  = 2.50 and 3.30 ppm for DMSO and H<sub>2</sub>O/ DMSO, respectively.





#### Fig. 5B



3-8- Thermal analysis

The TG/DTG and DTA thermal curves of H<sub>2</sub>L, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes in nitrogen environment with a heating rate 10 °C/min were given in Figs. 6&7 and the decomposition steps are assigned in Table 4. This table illustrated to the behavior of the thermal degradation according to TG curves for each step in the decomposition sequence of the H<sub>2</sub>L, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes. The mass losses obtained from TG curves are in a good

agreement with the calculated values. The pathway of these complexes is the same sequences with overlapping steps vary from one complex to another as the following:

The H<sub>2</sub>L ligand melts at 256 °C with simultaneous decomposition, (Fig. 6A). From the TG curve, it appears that the sample decomposes in three main stages over the temperature range 25-1000 °C. The first step occurs at (25-271 °C) with a mass loss of (obs. = 11.91%, calc. = 11.68%). The second step falls in the range of 271-422 °C with a mass loss (obs. = 7.72%, calc. = 9.27%). The last one within the range 422-1000 °C was accompanied by mass loss (obs. = 67.44%, calc. = 66.68%). From the corresponding DTA curve (Fig. 6B), two exothermic peaks are noted. The first maximum is at 183 °C and the second at 566 °C, respectively.



The thermal decomposition of Mn(II) complex occurs at strong  $DTG_{max}$  decomposition steps (Fig. 7A). The first degradation step take place within the range of 21-300 °C and it is corresponds to the decomposition of L Schiff base ligand and NH<sub>3</sub> molecules due to a weight loss of (obs. = 61.83%, calc. = 62.05%). The second step falls in the range of 300-1000 °C which is assigned to loss of three carbon monoxide CO molecules with a weight loss (obs = 22.24%, calc= 23.27%). The manganese pure metal is the final product remains stable till 1000 °C. The following is the mechanism of achievement of Mn metal at the final decomposition products. MnO<sub>2</sub> resulted from the decomposition of manganese carbonate is conversed upon the carbothermal reduction to manganese metal using coke (few carbon atoms produced from decomposition of H<sub>2</sub>L moiety.



From the corresponding DTA curve (Fig. 7B), two exothermic peaks are noted. The first maximum is at 92 °C and the second at 243 °C, respectively.

The Co(II) complex decomposed in two steps. The first step ranged at 20-136 °C corresponding to the loss of H<sub>2</sub>O molecules representing a weight loss of (obs. = 4.64%, calc. = 4.70%). The second step occurring at 136-800 corresponding to the loss of NH<sub>3</sub> and Schiff base ligand molecules, the weight loss associated with this stage (obs. = 78.78%, calc. = 79.89%). The final residue at the end of this stage is cobalt metal residue. From the corresponding DTA curve, one very strong exothermic peak is noted at 390 °C. The CoO produced from the thermal decomposition of cobalt(II) carbonate is conversed upon the carbothermal reduction to cobalt metal using coke (few carbon atoms produced from decomposition of H<sub>2</sub>L moiety.



To make sure about the proposed formula and structure for the Ni(II) complex, thermogravimetric and differential thermal analysis were carried out for this complex under N<sub>2</sub> flow. The thermal decomposition of the nickel(II) complex proceeds approximately with main three degradation steps. The first stage occurs at maximum temperature of  $DTG_{max}$ = 207 °C (temperature range 22-272 °C), the weight loss associated with this stage (obs. = 61.71%, calc. = 60.82%) corresponding to the loss of C<sub>15</sub>H<sub>14</sub>N<sub>2</sub> (decomposition of L Schiff base ligand). The second step occurs at the maximum temperature DTG<sub>max</sub>= 316 and 480 °C (temperature range 272-1000 °C). The weight loss at this step (obs. = 17.15%, calc. = 15.34%) associated with the loss of 2CO gas molecules. The final residue at the end of this stage is NiO+C (residual carbon).



The thermal degradation of the Cu(II) complex take place in mainly five degradation stages with DTG<sub>max</sub>= 81 (20-92 °C), 207 (155-245 °C), 283 and 324 (245-372 °C), and 417 (372-800) °C. The first stage of decomposition occurs at a temperature maximum of DTG<sub>max</sub>= 81 °C, the found weight loss associated with this step is (obs. = 9.17%, calc. = 9.02%) and may be attributed to the loss of H<sub>2</sub>O and NH<sub>3</sub> molecules. The decomposition steps from second-to fifth were occurs at a temperature maximum of 207, 283, 324 and 417 °C. The weight loss found at these steps equals to (obs. = 69.70%, calc. = 70.36%) corresponds to the loss of C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub> (decomposition L Schiff base ligand). The final thermal product obtained at 800 °C is CuO as a residue. The interesting point for this system is the resulted of copper(II) oxide at low temperature 475 °C (calcinations point).



From the corresponding DTA curve, four exothermic peaks are noted at 208, 291, 331 and 420 °C, respectively.

The thermal decomposition of the Zn(II) complex occurs in definite five degradation stages with  $DTG_{max}$ = 130 (30-249 °C), 342 (249-356 °C), 389 and 445 (356-465 °C), and 510 (465-800) °C. The first stage of decomposition occurs at a temperature

maximum of  $DTG_{max}$ = 130 °C, the found weight loss associated with this step is (obs. = 8.97%, calc. = 8.97%) and may be attributed to the loss of H<sub>2</sub>O and NH<sub>3</sub> molecules. The decomposition steps from second-to fifth were occurs at a temperature maximum of 342, 389, 445 and 510 °C. The weight loss found at these steps equals to (obs. = 74.26%, calc. = 74.10%) corresponds to the loss of C<sub>18</sub>H<sub>11</sub>NO<sub>2</sub> (decomposition L Schiff base ligand). The final thermal product obtained at 800 °C is zinc metal as a residue. From the corresponding DTA curve, two exothermic peaks are noted at 457 and 511 °C, respectively, and oly one endothermic peak at 131 °C.



Table 4: Thermogravimetric data of the H<sub>2</sub>L and its Schiff base complexes

Complex	Steps	Temp. range	DTG peak	DTA peak	Decomposed	Weight loss
		(°C)	(°C)	(°C)	assignments	Found (Calcd.
					-	%)
$H_2L$	$1^{st}$	25 - 271	193	183	- H <sub>2</sub> O <sub>2</sub>	11.91 (11.68)
	$2^{nd}$	271-422	331	566	- HCN	7.72 (9.27)
	3 <sup>rd</sup>	422 - 1000	590		- C <sub>14</sub> H <sub>10</sub> O	67.44 (66.68)
	residue				3C	
Mn(II)	$1^{st}$	21 - 300	222	92	$-NH_3+C_{15}H_{11}N$	61.83 (62.05)
	$2^{nd}$	300 - 1000	364	243	-3CO	22.24 (23.27)
	residue				Mn metal	
Co(II)	$1^{st}$	20 – 136	261	390	- H <sub>2</sub> O	4.64 (4.70)
	$2^{nd}$	136 - 800	384		$-C_{18}H_{11}NO_3 + NH_3$	78.78 (79.89)
	residue				Co metal	
Ni(II)	$1^{st}$	22 – 272	207	74	$- C_{15}H_{14}N_2$	61.71 (60.82)
	$2^{nd}$	272 - 1000	316, 480	219	- 2CO	17.15 (15.34)
	residue			507	NiO + C	
Cu(II)	1 <sup>st</sup>	20 - 92	81	-	$- H_2O + NH_3$	9.17 (9.02)
	$2^{nd}$	155 - 800	207, 283	208, 291	$- C_{18}H_{11}NO_2$	69.70 (70.36)
			324, 417	331,420		
	residue				CuO	
Zn(II)	$1^{st}$	30 - 249	130	131	$- H_2O + NH_3$	8.97 (8.97)
	$2^{nd}$	249 - 800	342, 389	-	$- C_{18}H_{11}NO_3$	74.26 (74.10)
			445, 510	457, 511		
	residue				Zn metal	









Base on the spectroscopic and thermal analyses data of the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes the suggested structure can be formulated as shown in Fig. 8.



**Fig. 8**: Suggested structures of  $[M(L)(NH_3)].nH_2O$  Schiff base complexes (where M= Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); n= 0 or 1)

### 3-9- XRD and SEM studies

The main target of this paper beside the synthesis and characterization of the novel Schiff base and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes is to study of the final thermal decomposition products at calcinations temperatures. These residuals were checked using scanning electron microscopy (SEM), and x- ray diffraction (XRD) techniques. SEM is a simple method can be used to check the deposited samples which clearly indicated that the nanoparticles have been formed. According to the images of SEM and XRD, the diameters of the residual samples for Co(II) and Ni(II) are about 50 and 65 nm, respectively. Figure 9 show the scanning electron microscopy pictures of [Co(L)(NH<sub>3</sub>)].H<sub>2</sub>O and [Ni(L)(NH<sub>3</sub>)] particles. By comparison between the residual products in this study, the cobalt(II) and nickel(II) oxides nanoparticles in the literature

[44, 45], it is obvious that the particles (50 and 65 nm diameters) are smaller and the H<sub>2</sub>L Schiff base ligand can be used as a good precursors with low calcinations temperatures. The x-ray powder diffraction patterns in the range of  $4^{\circ} < 2\theta < 70^{\circ}$  for the Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes and the residual products at 600 °C were carried in order to obtain an idea about the lattice dynamics of the resulted oxides of cobalt and nickel. X-ray diffraction of the residual products of cobalt and nickel H<sub>2</sub>L complexes were recorded between  $4^{\circ}$  and  $70^{\circ}$  2 $\theta$  and are given in Fig. 10. The values of 2 $\theta$ , full width at half maximum (FWHM) of prominent intensity peak, relative intensity and particle size of cobalt and nickel residual products were calculated. The crystallite size of the cobalt and nickel residuals at 600 °C (Fig. 11) could be estimated from XRD patterns by applying FWHM of the characteristic peaks using Deby-Scherrer equation 1 [46].

### $D = K\lambda/\beta Cos\theta \dots (equ. 1)$

Where D is the particle size of the crystal gain, K is a constant (0.94 for Cu grid),  $\lambda$  is the x-ray wavelength (1.5406 Å),  $\theta$  is the Bragg diffraction angle and  $\beta$  is the integral peak width. The particle size was estimated according to the highest value of intensity compared with the other peaks. The particle size for the cobalt and nickel thus obtained were 50 and 65 nm, respectively. These data gave an impression that the particle size located within nano scale range.







Fig. 9B





















Fig. 10D



Fig. 10E





Fig. 10F Fig. 10: XRD spectra of A-H<sub>2</sub>L, and its B-Mn(II), C-Co(II), D-Ni(II), E-Cu(II) and F-Zn(II) Schiff base complexes



Fig. 11: XRD spectra of cobalt and nickel oxides produced after thermal decomposition of  $[Co(L)(NH_3)]$ .H<sub>2</sub>O and  $[Ni(L)(NH_3)]$  Schiff base complexes at 600 °C

3-10- Kinetic thermodynamic parameters

The kinetic thermodynamic studies upon the thermal degradation processes are a powerful indication to provide sufficient knowledge about Arrhenius parameters viz. activation energy (E\*), frequency factor (A), enthalpy of activation (H\*), entropy of activation (S\*) and free energy of activation (G\*). From TG/DTG curves, Coats-Redfern and Horowitz-Metzger [47, 48] were employed to calculate mentioned kinetic parameters. The data was summarized and tabulated in Table 5. In fact the increasing in (A) value led to decreasing in (E\*), so, when the activation energy has a higher value the thermal stability increased. The higher values of (E\*) and lower values of (A) are supported the reaction to proceed slower than normal [49, 50]. This fact has been applicable for the H<sub>2</sub>L complexes studied in the present paper. The negative values of (S\*) indicate that the activated complex has a more ordered [51] than that of either the reactants. The values of both E\* and H\* are equivalent.

					parameter			
Compound	stage	method	$E^*$	• < −1>	$\Delta S^*$	$\Delta H^*$	$\Delta G^*$	r
			$(J mol^{-1})$	A(s)	$(J mol^{-1} K^{-1})$	$(J mol^{-1})$	$(\text{Jmol}^{-1})$	
	1 st	CR	$1.50 \times 10^{5}$	$2.00 \times 10^{11}$	-3.88×10	$1.44 \times 10^{5}$	$1.70 \times 10^{5}$	0.9960
шт	1	HM	$1.61 \times 10^{5}$	$6.11 \times 10^{11}$	-2.59×10	$1.50 \times 10^{5}$	$1.65 \times 10^{5}$	0.9970
$\Pi_2 L$	$2^{nd}$	CR	$1.34 \times 10^{5}$	$2.45 \times 10^7$	$-1.10 \times 10^{2}$	$1.25 \times 10^{5}$	$2.60 \times 10^5$	0.9952
	2	HM	$1.32 \times 10^{5}$	$2.14 \times 10^{7}$	$-1.14 \times 10^{2}$	$1.30 \times 10^{5}$	$2.22 \times 10^{5}$	0.9982
	1 st	CR	4.83×10 <sup>4</sup>	$8.42 \times 10^4$	$-1.50 \times 10^{2}$	$4.50 \times 10^{4}$	$9.80 \times 10^{5}$	0.9945
M <sub>m</sub> (II)	1	HM	$4.62 \times 10^4$	$2.39 \times 10^{4}$	$-1.44 \times 10^{2}$	$5.24 \times 10^{4}$	$9.51 \times 10^{5}$	0.9993
MIN(II)	and	CR	$5.14 \times 10^{5}$	$6.70 \times 10^{44}$	$-6.11 \times 10^2$	$5.10 \times 10^{5}$	$1.64 \times 10^{5}$	0.9930
	Z	HM	$4.92 \times 10^{5}$	$1.72 \times 10^{43}$	$-5.80 \times 10^{2}$	$4.81 \times 10^{5}$	$1.60 \times 10^{5}$	0.9966
	1 st	CR	$6.20 \times 10^4$	$9.55 \times 10^{6}$	$-1.11 \times 10^{2}$	5.80×10 <sup>4</sup>	$9.80 \times 10^4$	0.9941
$C_{0}(\mathbf{II})$	1	HM	$6.78 \times 10^4$	$2.00 \times 10^{8}$	-8.82×10	$6.50 \times 10^4$	$9.64 \times 10^4$	0.9973
C0(II)	2 <sup>nd</sup>	CR	$6.65 \times 10^{5}$	9.33×10 <sup>49</sup>	$-7.11 \times 10^{2}$	$6.60 \times 10^{5}$	$1.83 \times 10^{5}$	0.9931
	2	HM	$6.80 \times 10^5$	$1.08 \times 10^{51}$	$-7.20 \times 10^{2}$	$6.71 \times 10^{5}$	$1.81 \times 10^{5}$	0.9975
	1 st	CR	$4.80 \times 10^4$	$5.61 \times 10^4$	$-1.50 \times 10^{2}$	$4.46 \times 10^{4}$	$1.22 \times 10^{5}$	0.9974
NE(II)	1	HM	$5.60 \times 10^4$	$1.78 \times 10^{6}$	$-1.33 \times 10^{2}$	$5.23 \times 10^{4}$	$9.80 \times 10^{5}$	0.9975
INI(II)	and	CR	$2.10 \times 10^{5}$	$6.00 \times 10^{12}$	-7.62×10	$2.22 \times 10^{5}$	$2.13 \times 10^{5}$	0.9822
	Z	HM	$2.30 \times 10^{5}$	$2.24 \times 10^{14}$	-2.24×10	$2.16 \times 10^{5}$	$2.09 \times 10^{5}$	0.9981
	1 st	CR	$7.00 \times 10^4$	$5.63 \times 10^{8}$	-7.81×10	$6.70 \times 10^4$	$9.40 \times 10^4$	0.9915
C <sub>W</sub> (II)	1	HM	$7.04 \times 10^{4}$	$2.80 \times 10^{9}$	-6.50×10	$7.14 \times 10^{4}$	$9.48 \times 10^{4}$	0.9971
Cu(II)	and	CR	$1.20 \times 10^{5}$	$4.44 \times 10^{8}$	-8.44×10	1.13×10 <sup>5</sup>	$1.64 \times 10^{5}$	0.9980
2	Z	HM	$1.44 \times 10^{5}$	$2.12 \times 10^{10}$	-5.33×10	$1.30 \times 10^{5}$	$1.62 \times 10^{5}$	0.9941
$Zn(II) = \frac{1^{st}}{2^{nd}}$	1 st	CR	6.20×10 <sup>4</sup>	$1.90 \times 10^{7}$	$-1.11 \times 10^{2}$	5.96×10 <sup>4</sup>	$9.72 \times 10^4$	0.9944
	1	HM	$6.51 \times 10^4$	$8.70 \times 10^{7}$	-9.21×10	$6.44 \times 10^4$	$9.69 \times 10^4$	0.9955
	and	CR	$1.10 \times 10^{5}$	$1.12 \times 10^{6}$	$-1.30 \times 10^{2}$	$1.12 \times 10^{5}$	$2.44 \times 10^{5}$	0.9809
	2	HM	$1.23 \times 10^{5}$	$1.20 \times 10^7$	$-1.14 \times 10^{2}$	1. $16 \times 10^5$	$2.32 \times 10^{5}$	0.9950

**Table 5**: Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for the  $H_2L$ , and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes

### 3-11- Biological and anticancer assessments

3-11-1- Antibacterial assay of ligand and its metal complexes

Centrifuged pellets of bacteria from a 24 h old culture containing approximately 104-106 CFU (colony forming unit) per mL were spread on the surface of nutrient agar (typtone 1%, yeast extract 0.5%, NaCl 0.5%, agar 1%, 1000 mL of distilled water, pH 7.00), which was autoclaved under 121°C for at least 20 min. Wells were created in medium with the help of a sterile metallic bores and then cooled down to 45 °C. The activity was determined by measuring the diameter of the inhibition zone (in mm.). 100 mL of the tested samples (10 mg/mL and 50 mg/mL) were loaded into the wells of the plates. All compounds were prepared in dimethylsulfoxide (DMSO), DMSO was loaded as control. The plates were kept for incubation at 37 °C for 24 h and then the plates were examined for the formation of zone of inhibition. Each inhibition zone was measured three times by caliper to get an average value. The test was performed three times for each bacteria culture. Ciprofloxacin was used as antibacterial standard drug.

Antibacterial activities were investigated using agar well diffusion method. The activity of ligand H<sub>2</sub>L and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were studied against Gram Positive bacteria such as, *Bacillus Subtillus* (RCMB 00010) and *Staphylococcus aureas* (RCMB 000106)] and Gram negative bacteria namely, *Escherichia Coli* (RCMB 000103) and *Pseudomanas aeruginose* (RCMB 000102)] [52-60]. The zone of inhibition was measured in mm and was compared with standard drug.

DMSO was used as a blank and Ciprofloxacin was used as antibacterial standard. All the compounds were tested at 10 and 50 mg concentrations. The data is summarized in Table 6.

Compound	Gram Positive Bacteria			Gram Negative Bacteria				
	Bacilli	us sub.	Staphyl	ococcus	E.Coli		Pseudomonas sp.	
	10 mg	50 mg	10 mg	50 mg	10 mg	50 mg	10 mg	50 mg
H <sub>2</sub> L	-	3	-	-	-	1	-	2
Co(II)	1	8	-	9	3	9	1	10
Zn(II)	3	18	5	14	9	14	6	13
Ni(II)	5	22	7	19	11	15	8	18
Cu(II)	8	29	8	20	14	19	12	19
Mn(II)	12	25	11	25	18	22	16	23
Ciprofloxacin	11	25	9	23	15	19	13	20

Table 6: Antibacterial activity of  $H_2L$  ligand and its metal complexes with different concentrations

In comparison with standard antibacterial drug ciprofloxacin, manganese(II) complex was found to be the most active than the standard drug ciprofloxacin against Gram positive and Gram negative bacteria. The Zn(II) and N(II) and Cu(II) tested complexes were found to be less active than the standard drug ciprofloxacin against Gram positive and Gram negative bacteria. The ligand and cobalt(II) complex were found to be inactive against Gram positive and Gram negative bacteria. The ligand and cobalt(II) complex were found to be inactive against Gram positive and Gram negative bacteria. The ligand and cobalt(II) complex were found to be inactive against Gram positive and Gram negative bacteria. The order of inhibition was found to be:

 $H_2L < Co(II) < Zn(II) < Ni(II) < Cu(II) < Mn(II)$ 

3-11-2- Antifungal evaluation of ligand and its metal complexes

Fungal strain was grown in 5 mL sabouard dextrose broth (glucose: peptone; 40.10) for 3-4 days to achieve 105 CFU/mL cells. The fungal (culture ca. 1 mL) was spread out uniformly in the sabourad dextrose agar plates by sterilized triangular folded glass rod. Plates were left for 5-10 min. So that culture is properly adsorbed on that surface of sabourad dextrose agar plates. Now small wells of size (4 mm x 2 mm) were cut in to the plates with the help of well culture and bottom of the wells were sealed with 0.8% soft agar to prevent the flow of test sample at the bottom of the well. 100  $\mu$ L of the tested samples (10 mg/mL and 50 mg/mL) were loaded into the wells of the plates. All compounds were prepared in dimethylsulfoxide (DMSO), DMSO was loaded as control. The plates were kept for incubation at 30 °C for 3-4 days and then the plates were examined for the formation of zone of inhibition. Each inhibition zone was measured three times by caliper to get an average value. The test was performed three times for each fungus. Fluconmazole was used as antifungal standard drug. The results of antifungal studies are presented in Table 6. The results show that the Mn(II) complex is more active in comparison to standard drug Fluconazole against the Aspergillus niger and penicillium sp. under the identical experimental conditions. The other complexes and ligand are less active in comparison to standard drug Fluconazole against the Aspergillus niger and penicillium sp. (Table 7).

Compound	A. Niger		Penicillium sp.		
no.	10 mg	50 mg	10 mg	50 mg	
H <sub>2</sub> L	-	4	1	5	
Co(II)	1	9	8	11	$\leq$
Zn(II)	-	15	11	17	
Ni(II)	5	17	13	20	
Cu(II)	3	19	15	24	
Mn(II)	11	27	19	31	
Fluconazole	10	21	16	28	

 Table 7: Antifungal activity of ligand and its metal complexes with different concentrations

The increase in antifungal and antibacterial activities of the complexes can be ascribed to the effect of the metal ion on the normal cell process. The toxicity increase in the light of chelation theory [61, 62] as chelation considerably reduces the polarity of the metal ion mainly because of partial sharing of its positive charge with donor groups and possible  $\pi$ -delocalization over the chelation ring. Such chelation could enhance the lipophilic character of the central metal atom, which subsequently favors are permeation through the lipid layer of the cell membrane. The presence of lipophilic and polar substituents such as C=N, O-H and COOH are expected to enhance the fungal and bacterial toxicity and therefore magnesium(II) complex have a greater chance of interaction with the nucleotide bases.

### 3-11-3- Cytotoxic assay of ligand and its metal complexes

Human hepatocellular carcinoma (HepG-2) cells were obtained from the American type culture collection (ATCC, Rock, Villa, and MD). The cells were grown on RPMI –  $1640^+$  medium supplemented with 10% inactivated fetal calf serum and 50 µg/mL gentamycin. The cells were maintained at 37 °C in a humidified atmosphere with 5% CO<sub>2</sub> and were subcultured two to three times a week. The antitumor activity was evaluated on HepG-2 cell. The cells were grown as monolayer in growth RPMI - 1640 medium supplemented with 10% inactivated fetal calf serum and 50 µg/mL gentamycin. The monolayernof 10.000 cells adhered at the bottom of the wells in a 96-well microtiter plate incubated for 24 h at 37 °C in a humidifier incubator with 5% CO<sub>2</sub>. The monolayers were then washed with sterile phosphate buffered saline (0.01 M pH 7.20) and simultaneously the cells were treated with 100 µL from different dilution of the test sample in fresh maintenance medium and incubated at 37 °C. A control of untreated cells was made in the absence of the test sample. Six wells were used for each concentration of the test sample. Every 24 h the observation under the inverted microscope was made. The number of the surviving cells was determined by staining the cells with crystal violet followed by cell lysing using 33 % glacial acetic acid and read the absorbance at 490 nm using ELISA reader (SunRise, TECAN, Inc, USA) after well mixing. The absorbance values from untreated cells were considered as 100 % proliferation. The number of viable cells was determined using ELISA reader as previously mentioned before and the percentage of viability was calculated as [1 - (ODt/ODc)] 100% were ODt is the mean optical density of wells treated with the test sample and ODc is the mean optical density of untreated cells. The 50 % inhibitor concentration (IC<sub>50</sub>), the concentration required to cause toxic effects on 50 % of intact cells, was estimated from graphic plots.

In this study, the anticancer activity of the prepared compounds (Ligand and its metal complexes) bearing naphthalidene moiety has been evaluated on human cancer cell lines, representing breast cancer. The cytotoxic activities of ligand and its metal complexes were tested against MCF-7 cell line according to method Masmann and Vijayen et al., [63, 64]. The inhibitory activity against Breast carcinoma cells (MCF-7) was detected by using different concentrations of tested samples (50, 25, 12.5, 6.25, 3.125 and 1.65  $\mu$ g) and the viability cells (%) were determined by colorimetric method. The IC<sub>50</sub> was calculated from Table 8.

Sample	Viability (%)								
concentration (mg)	Ligand	Co(II)	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Vinblastine standard		
50	34.92	38.68	6.68	21.94	6.14	6.85	14.38		
25	56.49	50.13	12.05	37.55	12.68	11.03	16.13		
12.5	67.26	67.24	18.64	69.31	30.26	21.48	24.25		
6.25	86.78	86.94	41.34	82.46	45.34	37.54	45.13		
3.125	94.64	93.85	84.94	91.34	59.94	69.21	55.00		
1.65	98.68	96.39	97.55	96.27	88.94	92.37	72.13		
0.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00		

**Table 8**: Evaluation of cytotoxicity of ligand and its metal complexes

The results of 50 % inhibitory concentration (IC<sub>50</sub>) data are summarized in Table 9.

**Table 9**:  $IC_{50}$  (µg) values of ligand and its metal complexes after 24 h continuous exposure of tumor cell line.

Compound	L	Co(II)	Zn(II)	Ni(II)	Cu(II)	Mn(II)	Vinblastine (Standard)
Tumor type/Cell line MCF- 7	32.5	26.00	5.70	20.10	5.26	5.02	4.60

The IC<sub>50</sub> value is the concentration that induces 50 % growth inhibition compared with untreated control cell MCF-7: Human breast carcinoma cell lines. According to the results of 50 % inhibitory concentration (IC<sub>50</sub>), the complexes Mn(II) (IC<sub>50</sub>=  $5.02 \mu g$ ), Cu(II) (IC<sub>50</sub>=  $5.26\mu g$ ) and Zn(II) (IC50= $5.70\mu g$ ) showed good antitumor activity nearly from the standard antitumor drug vinblastine (IC<sub>50</sub>= $4.60 \mu g$ ) against human breast carcinoma cell lines (MCF-7). In comparison with standard antitumor drug vinblastine (IC<sub>50</sub>= $4.60 \mu g$ ), the ligand (IC<sub>50</sub>= $32.5\mu g$ ), complex Ni(II) (IC<sub>50</sub>= $20.10\mu g$ ) and complex Co(II) (IC50= $26.00\mu g$ ) showed weak antitumor activity than the vinblastine standard against breast carcinoma cell lines (MCF-7). As a result of the cell culture studies, all of the tested compounds have shown antitumor activity for breast cancer cells. In conclusion, some prepared complexes might be potentially useful in the field of cancer treatment, finally complexes, Mn(II), Cu(II) and Zn(II) can be suggested as potent candidates for breast cancer.

#### References

- [1] S.C. Bell, G.L. Conklin, S.J. Childress, J. Am. Chem. Soc. 85 (1963) 2868.
- [2] A.A. Abou-Hussein, W. Linert, Spectrochim. Acta Part A, 141 (2015) 223.
- [3] H.M. Aly, M.E. Moustafa, M.Y. Nassar, E.A. Abdelrahman, J. Mol. Struct., 1086 (2015) 223.
- [4] C. Shiju, D. Arish, N. Bhuvanesh, S. Kumaresan, Spectrochim. Acta Part A, 145 (2015) 213.
- [5] P. Tyagi, S. Chandra, B.S. Saraswat, D. Sharma, Spectrochim. Acta Part A, 143 (2015) 1.
- [6] H.-D. Bian, J. Wang, Y. Wei, J. Tang, F.P. Huang, D. Yao, Q. Yu, H. Liang, Polyhedron, 90 (2015) 147.
- [7] G. Kumar, D. Kumar, C.P. Singh, A. Kumar, V.B. Rana, J. Serb. Chem. Soc. 75 (5) (2010) 629.
- [8] D. Sinha, A.K. Tiwari, S. Singh, G. Shukla, P. Mishra, H. Chandra, A.K. Mishra, Eur. J. Med. Chem. 43 (2008) 160.
- [9] S. Adsule, V. Barve, D. Chen, F. Ahmed, Q.P. Dou, S. Padhye, F.H. Sarkar, J. Med. Chem. 49 (2006) 7242.
- [10] S. Ren, R. Wang, K. Komatsu, P. Bonaz-Krause, Y. Zyrianov, C.E. McKenna, C. Csipke, Z.A. Tokes, E.J. Lien, J. Med. Chem. 45 (2002) 410.
- [11] E.A. Elzahany, K.H. Hegab, S.K.H. Khalil, N.S. Youssef, Aust. J. Basic Appl. Sci. 2 (2008) 210.
- [12] F.M. Morad, M.M. El-Ajaily, S. Ben Gweirif, J. Sci. Appl. 1 (2007) 72.
- [13] V.S. Kshirsagar, A.C. Garade, R.B. Mane, K.R. Patil, A. Yamaguchi, M. Shirai, C.V. Rode, Applied Catalysis A 370(1-2) (2009) 16.
- [14] M.S. Refat, I.M. El-Deen, H.K. Ibrahim, S. El-Ghool, Spectrochim. Acta Part A 65 (2006) 1208.
- [15] S. Brooker, S.S. Iremonger, P.G. Plieger, Polyhedron, 22(5) (2003) 665.
- [16] H.E. Katz, K.D. Singer, J.E. Sohn, C.W. Dirk, L.A. King, H.M. Gordon, J. Am. Chem. Soc. 109(21) (1987) 6561.
- [17] T. Abe, S. Mano, Y. Yamada, A. Tomotake, J. Imag. Sci. Tech. 43 (1999) 339.
- [18] S. Wang, S. Shen, H. Xu, Dyes Pigments 44 (2000) 195.
- [19] K. Maho, T. Shintaro, K. Yutaka, W. Kazuo, N. Toshiyuki, T. Mosahiko, Jpn. J. Appl. Phys. 42 (2003) 1068
- [20] A.A. Khandar, Z. Rezvani, Polyhedron 18 (1999) 129.
- [21] R.J. Fessenden, J.S. Fessenden, Inorganic Chemistry, vol. 13, fourth ed., Cole Publishing Company, California, 1990, pp. 587.
- [22] A.I. Vogel, "A text Book of Quantitative Inorganic Analysis", Longmans, London, 1994.
- [23] W.J. Geary, Coord. Chem. 7 (1971) 81.
- [24] S. Sarawat, G.S. Srivastava, R.C. Mehrotra, J. Organomet. Chem. 129 (1977) 155.
- [25] G. Wang, J.C. Chang, Synth. Inorg. Met.-Org. Chem. 24 (1994) 1091.
- [26] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds. Willey, New York, 1970.
- [27] J.R. Platt, J. Chem. Phys. 17 (1949) 484.
- [28] A.B.P. Lever, Inorganic Electronic Spectroscopy, 2<sup>nd</sup> ed., Elsevier, Amsterdam (1997).
- [29] A.A.A. Emara, Spectrochim. Acta Part A 77(1) (2010) 117.
- [30] F.A. Cotton, D.M.L. Goodgame and M. Goodgame, J. Am. Chem. Soc. 84 (1962) 167.

- [31] F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, "Advanced Inorganic Chemistry", John Wiley and Sons, New York, 1999, p.784.
- [32] Lutfullah, A. Umar, M.M. Rahman, M.M. Khan, Y.B. Hahn, Turk. J. Chem., 31 (2007) 179.
- [33] N. Shirasawa, T.T. Nguyet, S. Hikichi, Y. Moro-Oka and M. Akita, Organomet. 20 (2001) 3582.
- [34] A. Christensen, H.S. Jensen, V. McKee, C.J. McKenzie and M. Munch, Inorg. Chem. 36 (1997) 6080.
- [35] F.A. Cotton, G. Wilkinson, C.A. Murillo and M. Bochmann, "Advanced Inorganic Chemistry", John Wiley and Sons, New York, 1999, p.841.
- [36] A.L. Nivorozhkin, H. Toftlund, P.L. Jorgensen and L.E. Nivorozhkin, J. Chem. Soc.; Dalton. Trans. 1215 (1996).
- [37] (a) B.J. Hathaway, D.E. Billing, Coord. Chem. Rev. 5 (1970) 143; (b) B.J. Hathaway, Struct. Bonding (Berlin) 57 (1984) 55.
- [38] H. Montgomery, E.C. Lingefetter, Acta Cryst. 20 (1966) 728.
- [39] D. Kivelson, R. Neiman, J. Chem. Phys. 35(1961)149
- [40] R. K. Ray and G. R. Kauffman, Inorg. Chem. Acta, 173 (1990) 207.
- [41] K. Jayasubramanian, S. A. Samath, S. Thambidurai, R. Murugesan and S. K. Ramalingam ,Trans. Met. Chem. 20 (1995) 76.
- [42] V. S. X. Anthonisamy and R. Murugesan, Chem. Phys. Lett. 287 (1998) 353.
- [43] V. S. X. Anthonisamy, R .Anantharam and R .Murugesan, Spectra Chim. Acta. A55 (1999) 135.
- [44] M. Salavati-Niasari, F. Mohandes, F. Davar, M. Mazaheri, M. Monemzadeh, N. Yavarinia, Inorg. Chim. Acta 362 (2009) 3691.
- [45] B.P. Baranwal, T. Fatma, A. Varma, A.K. Singh, Spectrochim. Acta Part A, 75 (2010) 1177.
- [46] C.X. Quan, L.H. Bin, G.G. Bang, Mater. Chem. Phys. 91 (2005) 317.
- [47] A.W. Coats, J. P. Redfern, Nature 201 (1964) 68.
- [48] H.W. Horowitz, G.A. Metzger, Anal. Chem. 35 (1963) 1464.
- [49] S.S. Sawney, A.K. Bausal, Thermochim. Acta 66 (1983) 347.
- [50] P. Chourasia, K.K. Suryesh, A.P. Mishra, Proc. Ind. Acad. Sci. 105 (1993) 173.
- [51] A.A. Frost, R.G. Pearson, "Kinetics and Mechanism" New York; Wiley, 1961.
- [52] Schelz, Z.; Molnar, J.; Hohmann, J. Antimicroial and antiplasmid avtivities of essential oils. Fitoterapia, 77 (2006) 279.
- [53] Bauer A w, Kirby W M, Sherris J C and Turck M, Am J ClinPathol., 39(5) (1966) 493.
- [54] Robert G petersdorf and John C Sherris, Am J Med. 39(5) (1995) 766.
- [55] Pharmacopoeia of India, 1996, II, A-100, A-108.
- [56] National Committee for Clinical Laboratory Standards. Reference Method for Broth Dilution Antifungal Susceptibility Testing of Yeats. Approves Standard M27-A2, 3<sup>rd</sup> ed.; NCCLS: Wayne, PA, USA2002; Vol.22, No.15, pp. 1-30.
- [57] Bauer, A. W.; Kirby, W. M. M.; Sherris, J.C.; Turck, M. Antibiotic Susceptibility Testing by a Standardized Single Disk Method. Am. J. Clin. Pathol. 1966, 36, 493-496.
- [58] Jorgensen, J. H.; Turnidge, J. D. Manual of Clinical Microbiology, 9<sup>th</sup> ed.; Murray, P. R., Baron, E. J., Jorgensen, J. H., Landry, M. L., Pfaller, M. A., Eds.; ASM Press: Washington, DC, USA, 2007; pp. 1152-1172.
- [59] National Committee for Clinical Laoratory Standards. Methods for Dilution Antimicrobial Susceptibility Tests for Bacteria that Grow Aerobically. Approved standard M7-A6, 6<sup>th</sup> ed.; NCCLS: Wayne, PA, USA, 2003.

- [60] National Committee for Clinical Laboratory Standards. Performance Standards for Antimicrobial Susceptibility Testing. Informational supplement M100-S13, 12<sup>th</sup> ed.; NCCLS: Wayne, PA, USA, 2003.
- [61] Gillespie S H, Medical Microbiology-Illustrated, Butterworth Heinemann: London, 1994, 234-247.
- [62] Chatterjee S., Das S. N., Ind. J. of Pharmacology, 28 (1996) 116.
- [63] Musmann, T.; J. Imunol. Methods, 65 (1983) 55.

[64] Nijayan, P.; Rayhu, C.; Dhanaraj, S. A.; Suresh, B.; Indian J. Med. Res., 120 (2004) 24.





- New Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) Schiff base complexes were synthesized.
- Metal ions coordinate in a tetra-dentate manner with ONO chelating agent.
- Spectroscopic and thermal analyses were performed to suggest the structural.
- All the complexes are tetrahedral geometry.
- Preparation and characterizations of single phases of metal oxide (MO) • A COLORING COLORINA COLORINA COLORINA COLORINA COLORINA COLORINA COLORINA COLORINA C nanoparticles.