



# Synthesis, Spectral Characterization, Molecular Modeling, and Antimicrobial Studies of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) Complexes of ONO Schiff Base

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**Abstract:** A series of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) complexes have been synthesized from the schiff base ligand L. The schiff base ligand [(4-oxo-4H-chromen-3-yl) methylene] benzohydrazide (L) has been synthesized by the reaction between chromone-3-carbaldehyde and benzoyl hydrazine. The nature of bonding and geometry of the transition metal complexes as well as schiff base ligand L have been deduced from elemental analysis, FT-IR, UV-Vis, <sup>1</sup>HNMR, ESR spectral studies, mass, thermal (TGA and DTA) analysis, magnetic susceptibility, and molar conductance measurements. Cu(II), Ni(II), Co(II), and Mn(II) metal ions are forming 1:2 (M:L) complexes, Zn(II) is forming 1:1 (M:L) complex. Based on elemental, conductance and spectral studies, six-coordinated geometry was assigned for Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) complexes. The complexes are 1:2 electrolytes in DMSO except zinc complex, which is neutral in DMSO. The ligand L acts as tridentate and coordinates through nitrogen atom of azomethine group, oxygen atom of keto group of  $\gamma$ -pyrone ring and oxygen atom of hydrazoic group of benzoyl hydrazine. The 3D molecular modeling and energies of all the compounds are furnished. The biological activity of the ligand and its complexes have been studied on the four bacteria *E. coli*, *Edwardella*, *Pseudomonas*, and *B. subtilis* and two fungi *penicillium* and *trichoderma* by well disc and fusion method and found that the metal chelates are more active than the free schiff base ligand.

**Keywords:** Chromone-3-carbaldehyde, Tridentate Schiff base, Transition metal complexes, Molecular modeling, Biological activity.

## Introduction

Investigations on the complexing ability of metal ions with model ligands assist in the understanding of the function of physiological systems. Among the complexing ligands, Schiff bases have special interest due to their industrial and biological applications<sup>1-10</sup>.

Earlier work reported that some drugs showed increased activity when administered as metal complexes rather than as organic compound<sup>11-13</sup>.

Chromone derivatives have received great attention for their applications. These compounds exhibit a wide spectrum of biological activities including antimicrobial<sup>14,15</sup>, antibacterial<sup>16,17</sup>, antitumor<sup>18</sup>, antifungal<sup>19-21</sup>, antiallergic<sup>22</sup>, antiviral<sup>23</sup>, anti-inflammatory<sup>24</sup>, and anticancer<sup>25</sup> activities. Additionally, chromone derivatives are essential for the synthesis of many important oxygen heterocyclic's, pyrazoles, and xanthenes<sup>26</sup>.

There are several reports about the coordination behaviors of metal ions with Schiff-base ligands derived from chromone-3-carbaldehyde derivatives and benzoyl hydrazine derivatives<sup>27,28</sup>. However, no report on the synthesis of transition metal complexes with the schiff base ligand derived from benzoyl hydrazine and chromone -3-carbaldehyde.

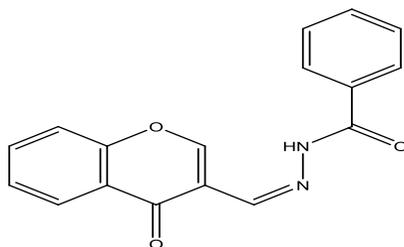
The schiff base derived from chromone-3-carbaldehyde and benzoyl hydrazine has important biological applications. Hence, we have synthesized the transition metal complexes with this ligand and we have carried characterization by various spectroscopic techniques, mass, elemental analysis, molecular modeling analysis, and antimicrobial studies.

## Experimental

Chromone-3-carbaldehyde, benzoyl hydrazine were purchased from Sigma-Aldrich chemicals and remaining all chemicals were purchased from commercial sources and used as such without purification.

### *Synthesis of the Schiff Base Ligand (L)*

The Schiff base ligand is prepared by condensation of chromone-3-carbaldehyde (1.74 g, 0.01 M) and benzoyl hydrazine (1.36 g, 0.01 M) in absolute ethanol (25 mL), by adding traces of glacial acetic acid the mixture was refluxed for 2 h with continuous stirring, then the yellow color compound was separated out. The compound is collected by filtration, washed several times with double distilled water, recrystallized from hot ethanol and dried in a vacume desiccator. The melting point of the resulting Schiff base ligand (Figure 1) is 176 °C. The yield is 94%.



**Figure 1.** Proposed structure of schiff base ligand (L).

### *Synthesis of Metal Complexes*

The Schiff base ligand L (0.01 M) is dissolved in hot methanol and hot methanol solution of corresponding salts (0.01M)  $MX_2$  [where M = Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) and X= chloride/acetate/nitrate] were mixed together and refluxed with constant stirring for 2-3 h at refluxing temperature. On cooling colored solids were precipitated out. The products were filtered, washed with cold methanol, petroleum ether and dried in air and desiccator over anhydrous  $CaCl_2$  and stored in an airtight sample bottle. All the compounds are colored and are stable when exposed to air and moisture.

### *Instruments Used*

The percentage composition of C, H, and N of complexes and ligand L were determined using micro analytical methods on Perkin Elmer 240C (USA) elemental analyzer. FT-IR spectra of the ligand and its complexes were recorded by using KBr pellets in the range 4000-400  $\text{cm}^{-1}$  on Perkin Elmer Infra red model 337. The UV-Visible spectra of the Schiff base ligand and its metal complexes were carried out in DMSO using a Shimadzu UV-1601 spectrophotometer.  $^1\text{H}$  NMR spectrum of the ligand was recorded at 200MHz on Varian Gemini Unity Spectrometer using TMS as internal standard. The mass spectra of the compounds were recorded by ESI technique on VG AUTOSPEC mass spectrometer. The X-band ESR spectra was recorded with a EPR VARIAN-E-112 at RT. TGA and DTA analysis of complex was carried on Mettler Toledo Star system in the temperature range 0-1000°C. The heating rates were controlled by 10°C  $\text{min}^{-1}$ . Magnetic measurements were carried out on a Gouy balance model 7550 using  $\text{Hg}[\text{Co}(\text{NCS})_4]$  as standard. The conductivity measurements were carried out in DMSO ( $10^{-3}\text{M}$ ) using Digisun Electronic Digital conductivity meter, 0.01 M KCl solution is used for calibration. Melting points of the ligand and decomposition temperature of complexes were determined on Polmon instrument (model No.MP-96). Molecular modeling and analysis of the compounds were carried out using Chem Office software.

### *Biological Activity*

The antimicrobial tests were performed by the standard well disc and diffusion method. The complexes were screened for their antifungal activity against fungi *viz. penicillium* and *trichoderma*. These fungal species were isolated from the infected parts of the host plants of potato dextrose agar. The cultures of the fungi were purified by single spore isolation technique. A concentration of 1 mg/mL of each metal complex compound in DMSO solution was prepared for testing against spore germination of each fungus. Filter paper discs of 5 mm in size, prepared by using Whatman filter paper no. 1 (sterilized in an autoclave) were saturated with 10  $\mu\text{L}$  of the metal complex compounds dissolved in DMSO solution or DMSO as negative control. The fungal culture plates were inoculated and incubated at 37°C for 48 h. The plates were then observed and the diameters of the inhibition zones (in mm) were measured and tabulated.

The antibacterial activity of the complexes was studied against *E.coli*, *Edwardella*, *Pseudomonas*, and *B.subtilis*. Each of the metal complex compounds dissolved in DMSO at a concentration of 1 mg/mL was prepared. Paper discs of Whatman filter paper no. 1 were cut and sterilized in an autoclave. The paper discs were saturated with 10  $\mu\text{L}$  of the metal complex compounds dissolved in DMSO solution or DMSO as negative control and were placed aseptically in the Petri dishes containing Nutrient agar media inoculated with the above mentioned two bacteria separately. The petridishes were incubated at 37°C and the inhibition zones were recorded after 24 h of incubation.

## **Results and Discussion**

The analytical and physical data of Schiff base ligand and its metal complexes are given in Table 1. The data shows that the ligand L forms a 1:2 (M : L) complexes with Cu(II), Ni(II), Co(II) and Mn(II), 1:1 (M:L) with Zn(II) ions. The prepared complexes are found to have the formula  $[\text{CuL}_2]\text{Cl}_2$ ,  $[\text{NiL}_2](\text{NO}_3)_2$ ,  $[\text{CoL}_2]\text{Cl}_2$ ,  $[\text{MnL}_2]\text{Cl}_2$ , and  $[\text{Zn}(\text{L})(\text{Ac})_2(\text{H}_2\text{O})]$  and L is Schiff base ligand, it coordinates as a neutral ligand. The C, H and N analysis of Schiff base ligand and its complexes are found in good agreement with the expected values.

*Molar Conductance*

Molar conductance of the complexes are measured in DMSO at a concentration of 0.001 M. The observed conductance values falls in the range of 102-148  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  in case of Cu(II), Ni(II), CO(II), and Mn(II) complexes, indicates that these complexes are 1:2 electrolytes<sup>29</sup>. The observed conductance value for zinc complex is 26  $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ , indicates that the complex is non-electrolyte.

**Table 1.** Analytical and physical data of schiff base ligand L and its complexes.

Compound	Empirical formula	Molecular weight	Color	Yield, %	Melting Point in °C	Molar Conductance ( $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ )
Schiff base ligand (L)	$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$	292	yellow	94	176	-
Cu(II) complex	$[\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	648	green	71	196	136
Ni(II) complex	$[\text{Ni}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2](\text{NO}_3)_2$	643	light green	69	210	148
Co(II) complex	$[\text{Co}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	643.5	green	63	222	102
Mn(II) complex	$[\text{Mn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	639.5	greenish yellow	61	>250	103
Zn(II) complex	$[\text{Zn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)(\text{ac})_2(\text{H}_2\text{O})]$	493.8	yellow	65	>300	26

*IR Spectra and Mode of Bonding*

The FT-IR spectral data of few important functional groups of the Schiff base ligand and its transition metal chelates are presented in Table 2.

**Table 2.** Characteristic IR stretching bands of Schiff base ligand and its metal complexes in  $\text{cm}^{-1}$ .

Compound	$\nu_{\text{C=O}}$ ( $\gamma$ -pyrone ring)	$\nu_{\text{C=N}}$ (azomethine)	$\nu_{\text{C=O}}$ of benzoyl hydrazine	Coor-dinat-ed water	$\nu_{\text{as}}(\text{OAc})$	$\nu_{\text{s}}(\text{OAc})$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$	1679	1617	1638	-	-	-	-	-
$[\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	1643	1578	1604	-	-	-	541	449
$[\text{Ni}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2](\text{NO}_3)_2$	1646	1572	1608	-	-	-	511	418
$[\text{Co}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	1644	1584	1612	-	-	-	527	420
$[\text{Mn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	1626	1590	1626	-	-	-	527	420
$[\text{Zn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)(\text{ac})_2(\text{H}_2\text{O})]$	1626	1588	1626	755	1484	1278	527	415

The IR spectrum of the Schiff base ligand show a very strong absorption band at  $1679\text{ cm}^{-1}$ , which is characteristic of the  $\nu(\text{C}=\text{O})$  of  $\gamma$ -pyrone. In the spectra of analyzed complexes, this absorption band has been shifted to lower region by  $33\text{--}53\text{ cm}^{-1}$ , indicating the coordination of the Schiff base ligand through the oxygen atom present in the 4-position of  $\gamma$ -pyrone ring<sup>30</sup>. The spectrum of free Schiff base ligand show another strong absorption band at  $1617\text{ cm}^{-1}$  assigned for the  $\nu(\text{C}=\text{N})$  of azomethine group. In the spectra of analyzed complexes, this absorption band have been shifted to lower region by about  $27\text{--}45\text{ cm}^{-1}$ , which confirms the coordination of azomethine group through nitrogen atom<sup>31</sup>.

The IR spectrum of schiff base ligand shows a band at  $1638\text{ cm}^{-1}$ , which is assigned for  $\nu(\text{C}=\text{O})$  of carbonyl group of benzoyl hydrazine. This band has been shifted to lower region by  $12\text{--}34\text{ cm}^{-1}$ , indicates the coordination of ligand through carbonyl oxygen atom of benzoyl hydrazine<sup>32</sup>.

IR absorption spectrum of the Schiff base ligand and its metal complexes shows bands in the region  $3300\text{--}2700\text{ cm}^{-1}$  which are characteristic of the (N-H) of benzoyl hydrazine. Same types of bands are observed in case of schiff base ligand and its metal complexes, indicating that N-H of benzoyl hydrazine is not coordinating<sup>33</sup>.

In addition to the above, the IR spectra of metal chelates shows absorption bands at  $527\text{--}541\text{ cm}^{-1}$  and  $415\text{--}449\text{ cm}^{-1}$  are due to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  respectively<sup>34</sup>. These bands are absent in the spectrum of free Schiff base ligand.

Zinc complex shows the IR bands at  $1484$  and  $1278\text{ cm}^{-1}$  due to  $\nu_{\text{as}}(\text{OAc})$  and  $\nu_{\text{s}}(\text{OAc})$  stretching vibrations respectively. The  $\Delta\nu$  is  $206\text{ cm}^{-1}$ , indicating the coordination of acetate ligand as unidentate<sup>35</sup>. Zinc complex shows a band at  $755\text{ cm}^{-1}$ , indicates the presence of water molecule in the coordination sphere<sup>36</sup>.

### *<sup>1</sup>H NMR Spectra*

The <sup>1</sup>H NMR spectrum of the Schiff base ligand is recorded in DMSO-d<sub>6</sub>. In the <sup>1</sup>H NMR spectra of schiff base ligand a peak at  $11.95\ \delta$  is assigned for the proton of N-H of schiff base and a singlet at  $8.84\ \delta$  assignable for proton of azomethine group.

### *Mass Spectra of the Compounds*

The mass spectral data of Schiff base ligand and its metal chelates are given in Table 3. Mass spectra of the ligand and its metal chelates show molecular ion peaks, which are in good agreement with the expected values. The mass spectrum of ligand L gives a peak at  $293\ m/Z$ , which is assigned for [L+H] peak. Copper complex gives molecular ion peak at  $646\ m/Z$ , which is assigned as [M-2] peak. The mass spectrum of Ni(II) complex gives a peak at  $643\ m/Z$  and is assigned for [M] peak. Cobalt complex gives a peak at  $646\ m/Z$ , is assigned for [M+2] peak, Mn(II) complex gives a molecular ion peak at  $648\ m/Z$ , which is assigned for [M-1] peak and zinc complex gives a peak at  $495\ m/Z$ , which is assigned for [M+1] peak.

**Table 3.** Mass spectral data of schiff base ligand and its metal chelates.

Compound	Calculated mass <i>m/Z</i>	Obtained mass <i>m/Z</i>	Peak assigned
$\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3$	292	293	L+H
$[\text{Cu}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	648	646	M-2
$[\text{Ni}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2](\text{NO}_3)_2$	643	643	M
$[\text{Co}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	644	646	M+2
$[\text{Mn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)_2]\text{Cl}_2$	649	648	M-1
$[\text{Zn}(\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_3)(\text{ac})_2(\text{H}_2\text{O})]$	494	495	M+1

*Magnetic Moment and Electronic Absorption Spectra*

The electronic absorption spectral data and magnetic moment values of Schiff base ligand and its transition metal chelates are given in Table 4. The electronic spectra of Schiff base ligand shows strong absorption bands at 31847 cm<sup>-1</sup> and 42553 cm<sup>-1</sup>, which are attributed to n → π\* and π → π\* transitions respectively<sup>37</sup>.

**Table 4.** Electronic absorption spectral data and magnetic moment values of Schiff base ligand and its metal complexes.

Compound	Absorption (ν) in cm <sup>-1</sup>	Transition	Mag. Moment μ (B.M.)	Geometry
C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub>	31847	n → π*	-	-
	42553	π → π*		
[Cu(C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	11778	<sup>2</sup> E <sub>g</sub> → <sup>2</sup> T <sub>2g</sub>	2.10	Octahedral
	15060	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>2g</sub> (F)	3.24	Octahedral
[Ni(C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	17667	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (F)		
	23809	<sup>3</sup> A <sub>2g</sub> (F) → <sup>3</sup> T <sub>1g</sub> (P)		
	14450	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>2g</sub> (F)		
[Co(C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	19011	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> A <sub>2g</sub> (F)	4.95	Octahedral
	22222	<sup>4</sup> T <sub>1g</sub> (F) → <sup>4</sup> T <sub>1g</sub> (P)		
	14858	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>1g</sub> (S)		
[Mn(C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ]Cl <sub>2</sub>	18832	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G)	5.81	Octahedral
	21505-22675	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub>		
	[Zn(C <sub>17</sub> H <sub>12</sub> N <sub>2</sub> O <sub>3</sub> )(ac) <sub>2</sub> (H <sub>2</sub> O)]	18832-22624		

The observed magnetic momentum value of Cu(II) complex is 2.10 BM, falls within the range observed for octahedral geometry. Further, the electronic spectra of Cu(II) complex shows one broad peak at 11778 cm<sup>-1</sup> due to transition between <sup>2</sup>E<sub>g</sub> → <sup>2</sup>T<sub>2g</sub> indicating octahedral geometry<sup>38</sup>.

The Ni(II) complex exhibits peaks at 15060, 17667 and 23809 cm<sup>-1</sup> attributed to the <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>2g</sub>(F), <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(F), and <sup>3</sup>A<sub>2g</sub>(F) → <sup>3</sup>T<sub>1g</sub>(P) transitions respectively, suggests octahedral geometry. The magnetic moment value of Ni(II) complex is found to be 3.24 BM, falls within the range of 2.8-3.5 BM for octahedral complexes, suggesting octahedral geometry<sup>39</sup>.

The magnetic moment of Co(II) complex has been found to be 4.95 B.M, and it lies within the range expected for octahedral geometry. The electronic spectrum of Co(II) complex shows three peaks at 14450, 19011 and 22222 cm<sup>-1</sup> corresponding to <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>2g</sub>(F), <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>A<sub>2g</sub>(F), and <sup>4</sup>T<sub>1g</sub>(F) → <sup>4</sup>T<sub>1g</sub>(F), suggesting octahedral geometry<sup>40</sup>.

The Mn(II) complex shows three absorption peaks at 14858 cm<sup>-1</sup> expected for <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>1g</sub>(S), at 18832 cm<sup>-1</sup> corresponding to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>T<sub>2g</sub>(G) and a broad band at 21505-22675 cm<sup>-1</sup> may be due to <sup>6</sup>A<sub>1g</sub> → <sup>4</sup>A<sub>1g</sub>, suggesting octahedral geometry<sup>41</sup>. Further, the octahedral geometry is proposed based on magnetic moment. The magnetic moment of the complex is found to be 5.81 BM, falls within the range expected for octahedral geometry.

The electronic spectrum of Zn(II) complex show one peak at 18832-22624 cm<sup>-1</sup> due to charge transfer from ligand to metal. The observed magnetic moment value for this complex is zero, indicating diamagnetic nature of the complex. On the basis of analytical, conductance and spectral data, octahedral geometry<sup>42</sup> is assigned to zinc complex.

### ESR Spectral Studies

ESR spectra of Cu(II) complex (Figure 5) was recorded at room temperature in the polycrystalline state, on X- band at frequency of 9.1 GHZ under the magnetic field strength of 3000G. The spectrum show one intense absorption in the high field and is isotropic due to tumbling of the molecule. The g values of the complex are  $g_{\parallel}$  (2.333) >  $g_{\perp}$  (2.077) > 2.0023, indicating that the unpaired electron in the ground state of Cu(II) is predominantly in  $d_{x^2-y^2}$ . The value of exchange interaction term G, estimated from the following expression is 4.4.

$$G = g_{\parallel} - 2.0023 / g_{\perp} - 2.0023.$$

If  $G > 4.0$ , the local tetragonal axes are aligned parallel or only slightly misaligned. If  $G < 4.0$ , significant exchange coupling is present and misalignment is appreciable. The observed value for the exchange interaction term G suggests that the complex has regular octahedral geometry.

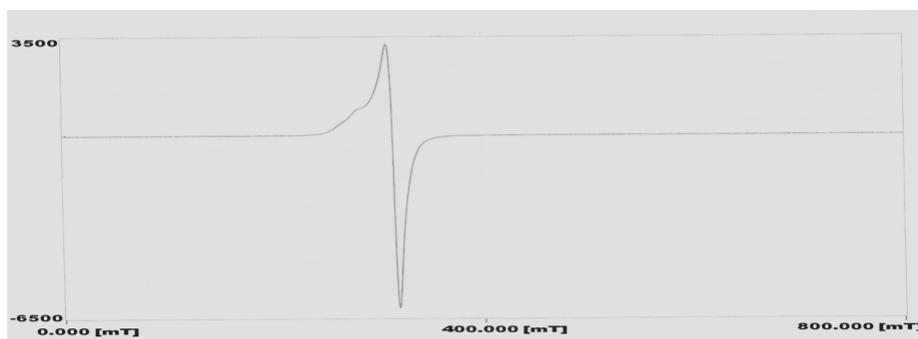


Figure 2. ESR spectra of copper complex.

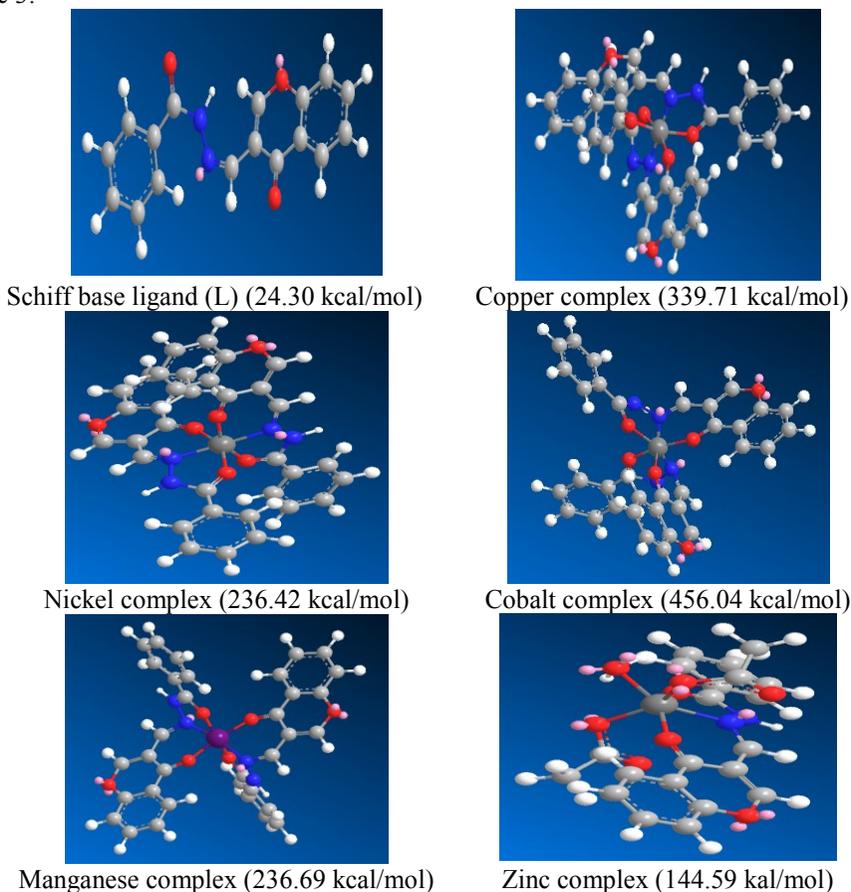
### Thermal Analysis

The thermal stability of Cu(II) complex is studied by controlling heating rates 10°C per minute under nitrogen atmosphere. Thermogram of Cu(II) complex is stable up to 250°C, indicates the absence of lattice water as well as coordinated water. Generally in TG lattice water loses at low temperature region between 60-120°C, where as coordinated water requires 120-250°C. Absence of water molecule in Cu(II) complex is supported by the DTA curve, which represents weight loss by endothermic bands. The DTA of copper complex has no endothermic band in the range of 60-250°C. Endothermic bands present at high temperature in DTA of Cu(II) complex is due to loss of organic molecules and finally metal may convert into its oxide<sup>43,44</sup>. In addition to endothermic bands, the DTA curves of the complex also show exothermic bands. These bands appeared at high temperature and represent phase transition, oxidation and/or decomposition of the complex.

### Molecular Modeling and Analysis

Theoretical calculations (Geary, 1971; Allen *et al.*, 1991; Rappe and Casewit, 1997) have paid a considerable attention to the characterization and inferences of geometrical optimization of the prepared complexes, therefore we could obtain the optimized geometry for each complex by computing the minimum steric energy and the theoretical physical parameter such as bond length using MM2CS Chem Office version 11.0 molecular

modeling program. The steric energies of the prepared complexes are listed individually in Figure 3.



**Figure 3.** Molecular modelings of the proposed structures.

### Biological Activity Studies

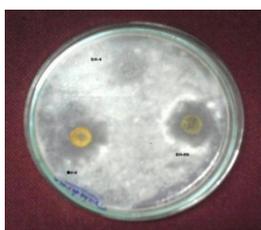
The antimicrobial activity of the Schiff base ligand and its metal chelates were tested against the four bacteria *E.coli*, *Edwardella*, *Pseudomonas* and *B.subtilis* and two fungi *penicillium* and *trichoderma* by the well disc and fusion method. The test solutions were prepared in DMSO at a concentration of 1 mg/mL. The zone of inhibition values were measured in millimeter after 24 h incubation at 37°C. The antibacterial results are given in Table 5.

**Table-5.** Antibacterial activity in centimeter (cm).

Compound	E.coli	B.subtilis	Edwardella	Pseudomonas	Pencillium	Trichoderma
$C_{17}H_{12}N_2O_3$	0.0	0.0	0.0	0.0	0.10	0.2
$[Cu(C_{17}H_{12}N_2O_3)_2]Cl_2$	0.6	0.78	0.7	1.92	1.70	0.6
$[Ni(C_{17}H_{12}N_2O_3)_2](NO_3)_2$	0.5	0.0	0.0	0.0	0.78	0.3
$[Co(C_{17}H_{12}N_2O_3)_2]Cl_2$	0.9	0.9	0.8	0.0	0.45	0.5
$[Mn(C_{17}H_{12}N_2O_3)_2]Cl_2$	0.0	0.0	0.0	0.0	0.63	1.0
$[Zn(C_{17}H_{12}N_2O_3)(ac)_2(H_2O)]$	0.73	0.73	0	1.8	0.3	0.2

The value in the above table indicates that the activity of the Schiff base ligand became more pronounced when coordinated with the metal ions. The presence of azomethine moiety and chelation effect with central metal enhances the antibacterial activities. Out of all the complexes, the Cu(II) complex shows maximum activity on the given micro organisms. This enhancement in antibacterial activity of these metal complexes can be explained based on the chelation theory<sup>45</sup>.

When a metal ion is chelated with a ligand, its polarity will be reduced to a greater extent due to the overlap of ligand orbital and the partial sharing of the positive charge of the metal ion with donor groups. Furthermore, the chelation process increases the delocalization of the  $\pi$ -electrons over the whole chelate ring, which results in an increase in the lipophilicity of the metal complexes. Consequently, the metal complexes can easily penetrate into the lipid membranes and block the metal binding sites of enzymes of the microorganisms. These metal complexes also affect the respiration process of the cell and thus block the synthesis of proteins, which restrict further growth of the organism.



Antifungal activity against *Trichiderma* of Manganese complex.



Antibacterial activity against *E.coli* of Copper complex.

**Figure 4.** Antimicrobial activity.

## Conclusion

The Schiff base ligand [(4-oxo-4*H*-chromen-3-yl) methylene] benzohydrazide (L) and its five transition metal complexes have been synthesized. They have been characterized based on the analytical, spectral, thermal and magnetic measurements. The results of these investigations support the suggested structure of the metal complexes. Cu(II), Ni(II), Co(II), and Mn(II) metal ions are forming 1:2 (M:L) complexes, Zn(II) is forming 1:1 (M:L) complex. Based on elemental, conductance and spectral studies, six-coordinated geometry was assigned for Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) complexes. The complexes are 1:2 electrolytes in DMSO except zinc complex, which is neutral in DMSO. ESR spectra of copper complex suggest regular octahedron geometry. Biological activity of the Schiff base ligand and its metal complexes were studied and results shows that the activity of the metal complexes is higher than the free Schiff base ligand.

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