

# Synthesis, spectral, thermal and antimicrobial studies on transition metal complexes of 4-hydroxy-3-[3-(4-isopropyl phenyl)-acryloyl]-6-methyl-2H-pyran-2-one

Balaji H. Jawale<sup>1</sup> and Shridhar D. Salunke<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, B.S.S. Arts Science & Commerce College, Makni-413 604

<sup>2</sup>Department of Chemistry, Rajarshi Shahu College, Latur-413 512, M.S, India

\*Corresponding author: E-Mail: salunke\_shridhar@yahoo.co.in

## ABSTRACT

Five coordination compounds of Cu(II), Ni(II), Co(II), Mn (II) & Fe(III) with bidentate ligand derived from 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid) & 4- isopropyl benzaldehyde, were synthesized & characterized by elemental analysis, TGA-DTA analysis, magnetic susceptibility, UV-visible, IR, <sup>1</sup>H-NMR spectroscopy, Mass & antimicrobial activity. From the analytical & spectral data, the stoichiometry of these coordination compounds was found to be 1:2 (metal: ligand). The physic-chemical data propose a distorted octahedral and octahedral geometry for the Cu (II) and all the other complexes respectively. The thermal analysis of all the prepared coordination compounds was studied by the TG-DTA method. The synthesized ligand and its coordination compounds were evaluated for their *in vitro* antimicrobial activity against Gram-negative (*Shigella boydii*) and Gram-positive (*Bacillus Cereus*) bacterial strains and against *Saccharomyces Cerevisiae* and *Penicillium notatum* antifungal strains. It is observed that some of the coordination compounds are antimicrobial active & show higher potency than the sole ligand. Complex formation changes significantly the antibacterial as well as antifungal/bioactive behavior of the sole ligands.

**KEY WORDS:** Dehydroacetic acid, Transition metal complexes, Chalcone, Antimicrobial activity.

## 1. INTRODUCTION

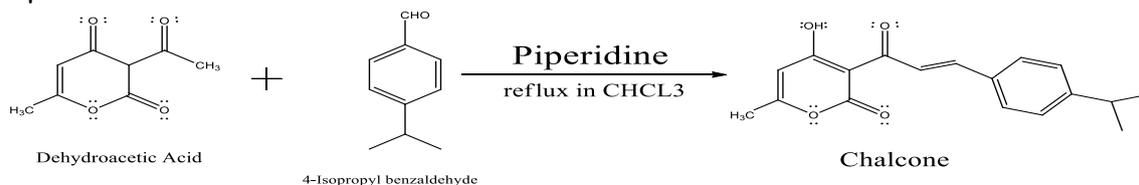
In recent times, numerous  $\beta$ -dicarbonyl compounds in which the carbonyl functions bonded to olefinic linkages have gained considerable importance (Krishanankutty, 2003) mainly because of such unsaturated  $\beta$ -dicarbonyl compounds & corresponding coordination compounds possess interesting biochemical properties such as antitumor, antioxidant, antifungal & antimicrobial activities (John, 2002; Oyedapo, 2004; Anto, 1995).

One of the oxygen heterocyclic compounds 3-acetyl-6-methyl-2H-pyran-2, 4(3H)-dione (DHA) was reported to be an excellent chelating agent & to possess promising fungicidal, bactericidal, herbicidal & insecticidal activities (Rao, 1980; Rao, 1978; Schleiffenbaum, 1992; Stanley, 1996). In addition, DHA is resourceful moiety for the preparation of various bioactive heterocyclic compounds (Levai, 2006). A search of the literature revealed that no work has been done on d-block metal coordination compounds of the chalcones derived from 4-isopropylbenzaldehyde and dehydroacetic acid (DHA). In this paper, we disclose the synthesis, characterisation, properties, antibacterial and antifungal activity of transition metals [Cu (II), Ni (II), Co (II), Mn (II) & Fe (III)] coordination compounds obtained from bidentate ligand (chalcone) containing a carbonyl group directly linked to the  $\alpha$ ,  $\beta$ -unsaturated system derived from DHA & 4-isopropyl benzaldehyde.

## 2. EXPERIMENTAL

**Material and Methods:** DHA (purity = 99%) for synthesis was purchased from Merck, Germany & used as it is. 4-isopropylbenzaldehyde of A.R. grade obtained from AVRA chemicals were used for the synthesis of the ligands. A.R. grade hydrated metal chlorides from Thomas Baker were used for the synthesis of the chelates. The carbon, hydrogen & nitrogen content in each sample were measured on a Perkin Elmer (2400) CHNS analyzer. The IR spectra (KBr), between 4000-450  $\text{cm}^{-1}$  were recorded on a Perkin Elmer (C-75430) IR spectrometer. The <sup>1</sup>H-NMR spectrum of the ligand was recorded in  $\text{CDCl}_3$  on Bruker instrument. The mass spectrum of the ligand was recorded in Qc-01 DAD Mass-spectrometer, thermo gravimetric analysis (TGA-DTA) were realized on a METTLER-TOLEDO-DB V13.00 instruments. The UV-VIS spectra of the chelates were recorded on a Shimadzu UV-2202 Spectrophotometer. Magnetic susceptibility measurements of the chelates were performed using a Gouy balance at room temperature using  $\text{Hg} [\text{Co} (\text{SCN})_4]$  as the calibrant.

**General procedure for the synthesis of the ligand (HL):** A solution of 0.01 mol of dehydroacetic acid, 10 drops of piperidine & 0.01 mole of 4-isopropyl benzaldelyde in 25 ml chloroform were refluxed for 8-10 hrs, 10 ml of the chloroform-water azeotrope mixture way separated by distillation. Crystal of product separated on slow evaporation of the remaining chloroform. The resulting precipitate was filtered, washed several times with ethanol & recrystallized from chloroform (Patange, 2007; Munde, 2009).



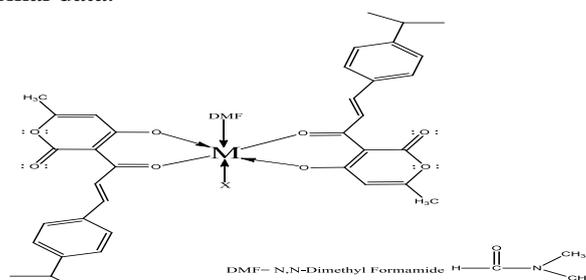
**Figure.1. Synthesis of Ligand**

**General procedure for the synthesis of metal complexes:** To a chloroform solution (30ml) of the ligand (2mmol), methanolic solution (20ml) of metal chlorides was added with constant stirring. The PH of the reaction mixture was maintained around 7.5 by adding 10% methanolic solution of ammonia. It was then refluxed for 2hr. the resulting metal complex was filtered in hot condition & washed with ethyl acetate methanol, pet-ether & dried over calcium chloride in vacuum desiccator.

**General procedure for the antimicrobial activity:** The ligand and its metal complexes were screened for *in vitro* antibacterial activity against Gram-positive i.e. *Bacillus Cereus*, *Bacillus Megaterium* and Gram-negative i.e. *Shigellaboydii* and *Escherichia Coli* by the paper disc plate method (Thornberry, 1950). The compound were tested at concentrations of 1.0 mg ml<sup>-1</sup> in DMF (0.1ml) was placed on a paper disk (6mm in diameter) with the help of micropipette and compared with a known antibiotic, viz. *Ciprofloxacin* at the same concentrations. To evaluate the fungicidal activity of the ligands and the metal complexes, their effects on the growth of *Saccharomyces Cerevisiae*, *Aspergillus Oryzae* and *Penicillium notatum* were studied. The ligand and their corresponding metal chelates in DMF were screened *in vitro* by the disc diffusion method (Bauer, 1966). The ligands and complexes were dissolved separately in DMF to obtain concentration of 500 µg disc<sup>-1</sup>. The linear growth of the fungus was recorded by measuring the diameter of the colony after 96 hr. The diameters of the zone of inhibition produced by the complexes were compared with Griseofulvin, an antifungal drug.

### 3. RESULTS AND DISCUSSION

The elemental analyses showed 1:2 (metal: ligand) stoichiometry for all the complexes (Fig.2). The analytical data of the ligand and its metal complexes corresponded well with the general formula [M(L)<sub>2</sub>(DMF)<sub>2</sub>], where M=Mn (II), Co(II), Ni(II), Cu (II), and [M(L)<sub>2</sub>(DMF)(CL)], where M=Fe(III), L=C<sub>18</sub>H<sub>18</sub>O<sub>4</sub>. The absence of chlorine except in the Fe (III) complex was evident from the Vol-hard test. The complexes were coloured, stable in air, insoluble in water and common solvents, except for DMF and DMSO. Since a single crystal of the complexes could not be isolated from any common solvent, the possible structure was predicted based on analytical, spectroscopic, magnetic and thermal data.



**Figure.2. Proposed structure of complex, X=DMF when M=Mn (II), Co(II),Cu(II) and Ni(II) and X=Cl when M=Fe(III)**

**Table.1. Physical Characterization and analytical data of ligand and its metal complexes**

Ligand/ complexes	F.W.	M.P./decomp. Temp. (°C)	Yield %	Colour	Found (Calcd.), %			
					M	C	H	N
Ligand HL C <sub>18</sub> H <sub>18</sub> O <sub>4</sub>	298	141	55	Yellow	-	72.02 (72.47)	6.06 (6.08)	-
C <sub>39</sub> H <sub>41</sub> ClFeNO <sub>9</sub>	759	260	40	Golden	7.26 (7.36)	60.99 (61.71)	5.31 (5.44)	1.80 (1.85)
C <sub>42</sub> H <sub>48</sub> CuN <sub>2</sub> O <sub>10</sub>	804	242	42	Celadon	7.82 (7.90)	62.51 (62.71)	5.95 (6.01)	3.41 (3.48)
C <sub>42</sub> H <sub>48</sub> CoN <sub>2</sub> O <sub>10</sub>	799	248	32	Orange	7.30 (7.37)	62.85 (63.07)	5.90 (6.05)	3.41 (3.50)
C <sub>42</sub> H <sub>48</sub> MnN <sub>2</sub> O <sub>10</sub>	795	250	33	Brown	6.71 (6.90)	62.80 (63.39)	5.96 (6.08)	3.50 (3.52)
C <sub>42</sub> H <sub>48</sub> NiN <sub>2</sub> O <sub>10</sub>	799	256	60	Green Yellow	7.22 (7.34)	62.63 (63.09)	5.97 (6.05)	3.45 (3.50)

**$^1\text{H}$  NMR spectra of ligand:** The  $^1\text{H}$  NMR spectra of free ligand in  $\text{CDCl}_3$  at room temperature shows the following signals. d 1.30 (d, 6H,  $-\text{CH}(\text{CH}_3)_2$ ), 2.30 (s, 3H,  $-\text{CH}_3$ ), 2.96 (m, 1H, methylene), 5.97 (s, 1H, C5-hydrogen of DHA moiety), 7.29-7.66 (m, 4H, Ar-H), 8.01 (d, 1H, olefinic proton), 8.32 (d, 1H, olefinic proton) and 13.51 (s, 1H, phenolic OH of DHA moiety).

**Mass spectra of ligand:** Mass spectral data confirmed the structure of the ligand (HL) as indicated by the peaks corresponding to their molecular mass shown in (fig.3).

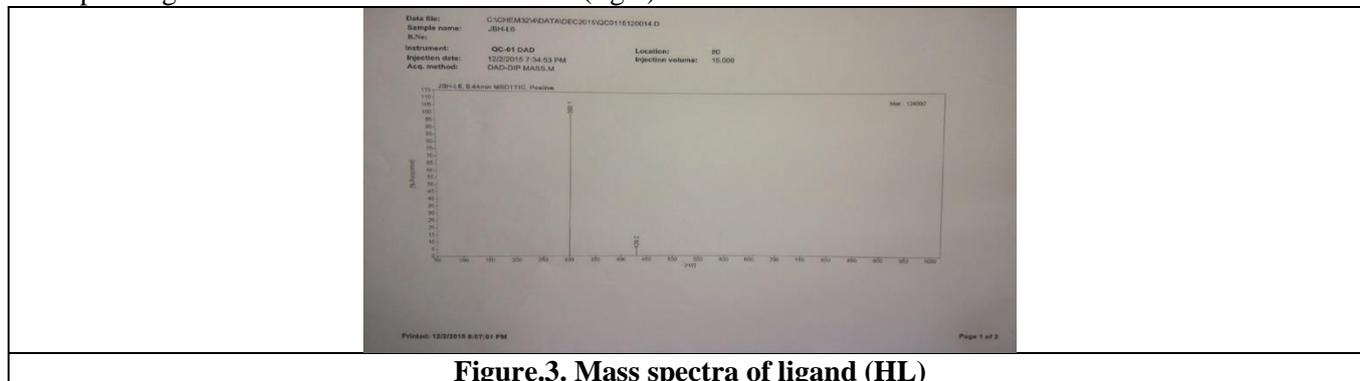


Figure.3. Mass spectra of ligand (HL)

**FTIR spectra:** The FTIR spectrum of free ligand shows characteristic bands at 3100, 1725, 1626, 1233-1211  $\text{cm}^{-1}$  assignable to  $\nu(\text{OH})$  of the intramolecular phenolic group of the dehydroacetic acid moiety,  $\nu(\text{C}=\text{O})$  (lactone carbonyl),  $\nu(\text{C}=\text{O})$  (acetyl carbonyl) &  $\nu(\text{C}-\text{O})$  (phenolic) stretching mode, respectively (Ramarao, 1985; Carugo, 1990). In the IR spectra of all the metal chelates, no band was observed in the region of 3200-3000  $\text{cm}^{-1}$ . Instead, in its place, a broad band characteristic of  $\nu(\text{OH})$  of coordination water was observed in the region 3570-3200  $\text{cm}^{-1}$ . The absence of  $\nu(\text{OH})$  (Phenolic) at 3100  $\text{cm}^{-1}$  suggests subsequent deprotonation of the phenolic group and coordination of phenolic oxygen to the metal ion. This was supported by an upward shift in  $\nu(\text{C}-\text{O})$  (phenolic) (Rao, 2003) by 20-40  $\text{cm}^{-1}$ . The  $\nu(\text{C}=\text{O})$  (acetyl carbonyl) was shifted to lower energy with respect to the free ligand, suggesting the participation of the acetyl carbonyl in the coordination (Ramarao, 1985; Carugo, 1990; Rao, 2003). The IR spectra of all the compounds showed a prominent band at 1377 & 970  $\text{cm}^{-1}$ , typical of  $\nu(\text{C}-\text{O}-\text{C})$  and *trans*  $-\text{CH}=\text{CH}-$  absorption. The presence of new bands in the region 600-450  $\text{cm}^{-1}$  can be assigned to  $\nu(\text{M}-\text{O})$  vibration (Nakamoto, 1970).

Hence, the ligands coordinated with the metal ions as monodeprotonated bi-dentate and the coordination occurs via the acetyl & phenolic oxygen of dehydroacetic acid moiety, as shown in Fig.2.

Table.2. Characteristic IR frequencies ( $\text{cm}^{-1}$ ) of the ligand and its metal complexes

Compound	$\nu(\text{OH})$ (dehydroacetic acid moiety)	$\nu(\text{C}=\text{O})$ (lactone)	$\nu(\text{C}=\text{O})$ (acetyl carbonyl)	$\nu(\text{C}-\text{O})$ (phenolic)	$\nu(\text{C}=\text{C})$ (trans)	$\nu(\text{M}-\text{O})$
Ligand HL $\text{C}_{18}\text{H}_{18}\text{O}_4$	3100(s)	1725(s)	1626(m)	1714(w)	1645(s)	1690(s)
$\text{C}_{39}\text{H}_{41}\text{ClFeNO}_9$	-	1648(m)	1622(w)	1626(s)	1621(w)	1619(s) 488(s)
$\text{C}_{42}\text{H}_{48}\text{CuN}_2\text{O}_{10}$	-	1645(w)	1619(s)	1264(s)	977(s)	560(w) 480(s)
$\text{C}_{42}\text{H}_{48}\text{CoN}_2\text{O}_{10}$	-	1690(s)	1626(s)	1235(w)	968(m)	531(m) 476(w)
$\text{C}_{42}\text{H}_{48}\text{MnN}_2\text{O}_{10}$	-	1648(m)	1603(w)	1247(m)	1001(m)	585(m) 533(s)
$\text{C}_{42}\text{H}_{48}\text{NiN}_2\text{O}_{10}$	-	476(m)	585(w)	533(s)	551(m)	531(s)

**Magnetic moment and Ultra-violet-Visible analysis:** The electronic spectra of all the complexes were recorded in DMF solution. The electronic spectrum of the Mn(II) complex exhibited three bands at 18345  $\text{cm}^{-1}$  ( $\epsilon = 26 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 19763  $\text{cm}^{-1}$  ( $\epsilon = 16 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 23154  $\text{cm}^{-1}$  ( $\epsilon = 28 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), which are assigned to  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{G})$ ,  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{G})$  and  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}$ ,  $^4\text{E}_{1g}(\text{4G})$  transitions, respectively, indicating an octahedral configuration around the Mn(II) ion. The octahedral geometry of Mn(II) was further confirmed by the value of the magnetic moment (5.84  $\mu_B$ ). Three electronic transitions were observed in the electronic spectrum of the Fe(III) complex, at 14472  $\text{cm}^{-1}$  ( $\epsilon = 22 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), 21322  $\text{cm}^{-1}$  ( $\epsilon = 26 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ) and 24272  $\text{cm}^{-1}$  ( $\epsilon = 32 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ), which are assigned to  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g}(\text{G})$ ,  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}(\text{G})$  and  $^6\text{A}_{1g} \rightarrow ^4\text{E}_g(\text{G})$ , respectively, suggesting an octahedral complex of Fe(III), which was confirmed by the value of magnetic moment (5.93  $\mu_B$ ) (Lever, 1968). The electronic

spectra of the Co(II) chelate exhibited three bands at  $9487\text{ cm}^{-1}$  ( $\epsilon = 17\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ),  $18656\text{ cm}^{-1}$  ( $\epsilon = 59\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) and  $21551\text{ cm}^{-1}$  ( $\epsilon = 98\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ), which are allotted to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$  and  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ , respectively, indicating octahedral configuration around the Co(II) ion. The magnetic moment of the Co(II) complex was  $4.54\ \mu_B$ . The calculated spectral parameters  $\nu_2/\nu_1$ ,  $10Dq$ ,  $B$ ,  $\beta$  and the ligand field stabilizing energy (LFSE) have the values  $1.96$ ,  $9169\text{ cm}^{-1}$ ,  $783.1\text{ cm}^{-1}$ ,  $0.81$  and  $26.20\text{ kcal mol}^{-1}$ , respectively, which are in good accord with the reported values of an octahedral Co(II) complex (Lever, 1968). The electronic spectra of the Ni(II) chelate exhibited three bands at  $9345\text{ cm}^{-1}$  ( $\epsilon = 34\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ),  $15698\text{ cm}^{-1}$  ( $\epsilon = 67\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) and  $22471\text{ cm}^{-1}$  ( $\epsilon = 188\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ), which are allotted to  ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ ,  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  and  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ , respectively. The ligand field parameters  $\nu_2/\nu_1$ ,  $10Dq$ ,  $B$ ,  $\beta$  and the LFSE have the values  $1.68$ ,  $9345\text{ cm}^{-1}$ ,  $675.6\text{ cm}^{-1}$ ,  $0.65$  and  $26.69\text{ kcal mol}^{-1}$ , respectively. These values, as well as the magnetic moment value ( $3.13\ \mu_B$ ), support an octahedral geometry of the Ni(II) complex (Lever, 1968). The spectra of the Cu(II) chelate consisted of a broad band at  $14225\text{ cm}^{-1}$  ( $\epsilon = 94\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ), assigned to the  ${}^2E_g \rightarrow {}^2T_{2g}$  transition of a distorted octahedral geometry (Eichhorn, 1953). In addition to this band, the band observed at  $25316\text{ cm}^{-1}$  ( $\epsilon = 1143\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ ) arises from intra ligand charge transfer. The LFSE value of the Cu (II) complex is  $42.64\text{ kcal mol}^{-1}$ . The obtained values of LFSE determine the stability of the chelates and follows the order in terms of metal ions  $\text{Cu (II)} > \text{Ni(II)} > \text{Co(II)}$ .

**Thermal analysis:** All chelates showed high thermal stability and decomposed above  $250\text{ }^\circ\text{C}$ , showing the absence of any lattice or attached water molecules. The TG curve of Cu(II) chelate showed the first decomposition step between  $180\text{--}320\text{ }^\circ\text{C}$  with a mass loss of  $39.92\%$  (calcd.  $41.80\%$ ), and the exothermic peak on the TGA-DTA curve between  $200\text{--}300\text{ }^\circ\text{C}$  ( $\Delta T_{\text{max}} = 280\text{ }^\circ\text{C}$ ) corresponds to the loss of two attached DMF molecules and the non-coordinated element of the ligand. The second step of the decomposition occurred between  $340\text{--}700\text{ }^\circ\text{C}$  with a mass loss of  $42.0\%$  (calcd.  $41.62\%$ ) and a broad exotherm in DTA corresponds to the loss of the coordinated element of the ligand. The final residue  $15.08\%$  (calcd.  $14.86\%$ ) corresponds to CuO. The TG curve of the Mn(II) complex showed a rapid first step decomposition between  $240\text{--}350\text{ }^\circ\text{C}$  with  $48\%$  mass loss (calcd.  $48.14\%$ ), associated with an exothermic peak on the DTA curve ( $\Delta T_{\text{max}} = 247.38\text{ }^\circ\text{C}$ ), indicating the loss of two attached DMF molecules and the non-coordinated element of the complex, i.e., the aromatic ring with a beta carbon (Patange, 2008). The complex did not remain stable at higher temperatures and exhibited slow second step decomposition between  $360\text{--}950\text{ }^\circ\text{C}$  with a mass loss of  $42\%$  (calcd.  $42.22\%$ ). The broad endothermic peak for this step on the TGA-DTA curve corresponds to the oxidative degradation of the coordinated part of the ligand. The decomposition was completed at  $\sim 950\text{ }^\circ\text{C}$  leading to the formation of the stable metal oxide MnO (observed  $10\%$ , calcd.  $9.54\%$ ). The TGA-DTA study of the Fe (III) chelate shows stability up to  $325\text{ }^\circ\text{C}$ . The first step showed a rapid decomposition between  $340\text{--}400\text{ }^\circ\text{C}$  with a  $45\%$  mass loss (calcd.  $45.3\%$ ). A broad exotherm was observed in the DTA ( $\Delta T_{\text{max}} = 366.1\text{ }^\circ\text{C}$ ). This step may be ascribed to the removal of one coordinated DMF molecule, one chloride ion (may be oxidized as  $\text{Cl}_2$ ) and the non-coordinated element of the ligand. The complex continued slow decomposition with a mass loss of  $44\%$  (calcd.  $44.42\%$ ) between  $400\text{--}900\text{ }^\circ\text{C}$ . A broad endotherm was found for this step in the DTA. The mass of the final residue match to the stable FeO (observed  $11\%$ , calcd.  $10.2\%$ ). The Co (II) complex decomposed in two successive steps in between  $300\text{--}850\text{ }^\circ\text{C}$ . Two coordinated DMF molecules and the non-coordinated element of the ligand were removed in the first step at  $300\text{--}400\text{ }^\circ\text{C}$  with a mass loss  $47.5\%$  (calcd.  $47.88\%$ ). A broad exothermic peak was observed between  $200\text{--}400\text{ }^\circ\text{C}$  ( $\Delta T_{\text{max}} = 338.12\text{ }^\circ\text{C}$ ). The complex finally decomposed to CoO with the loss of the coordinated element of the ligand (observed  $42\%$ , calcd.  $42\%$ ) between  $400\text{--}850\text{ }^\circ\text{C}$ . The Ni (II) complex also decomposed in two steps between  $300\text{--}900\text{ }^\circ\text{C}$ . The first step between  $300\text{--}400\text{ }^\circ\text{C}$  in the TG analysis corresponded to the elimination of two attached DMF molecules and the non-coordinated element of the ligand with a mass loss of  $47.5\%$  (calcd.  $47.89\%$ ). A broad exotherm between  $200\text{--}400\text{ }^\circ\text{C}$  was observed ( $\Delta T_{\text{max}} = 332.51\text{ }^\circ\text{C}$ ). The second step of the decomposition was found between  $400\text{--}900\text{ }^\circ\text{C}$  with a mass loss of  $42.5\%$  (calcd.  $42.01\%$ ). A broad exotherm in DTA could be assigned to the loss of the coordinated element of the ligand. The final weight  $10\%$  (calcd.  $9.99\%$ ) corresponds to NiO.

**Antimicrobial activity:** The antibacterial and antifungal activity of ligand and metal chelates was tested *in vitro* against bacteria such as *Shigella Boydii*, *Bacillus Cereus*, *B. Megaterium* and *E. Coli* by paper disc plate method (Mane, 2001). The complexes were evaluated at the concentration  $1\text{ mg/ml}$  in DMF and compared with known antibiotics viz *Ciprofloxacin* (Table.3). The results of the *in vitro* fungicidal activity of the compounds against *Saccharomyces Cerevisiae*, *Penicillium Natatum* and *Aspergillus Oryzae* determined by the mycelia dry weight method (Tan, 1984) with glucose nitrate media, are shown in Table.4, in which the results of the control are also presented from table.3 and 4, it is clear that the inhibition by the metal complexes was higher than that of sole ligand and results are in good accord with earlier reported literature (Patange, 2008 & 2011, Rao, 2003; Mane, 2001).

**Table.3. Antibacterial activity of HL and its metal complexes**

Compounds	Inhibition zone diameter (mm)			
	<i>Shigella Boydii</i>	<i>Bacillus Cereus</i>	<i>Bacillus Megaterium</i>	<i>Escherichia Coli</i>
	Concentration, 1mg/ ml	Concentration, 1mg/ ml	Concentration, 1mg/ ml	Concentration, 1mg/ ml
<b>Ciprofloxacin</b>	30	54	36	32
Ligand HL C <sub>18</sub> H <sub>18</sub> O <sub>4</sub>	11	12	04	09
C <sub>39</sub> H <sub>41</sub> ClFeNO <sub>9</sub>	20	14	08	15
C <sub>42</sub> H <sub>48</sub> CuN <sub>2</sub> O <sub>10</sub>	12	16	08	21
C <sub>42</sub> H <sub>48</sub> CoN <sub>2</sub> O <sub>10</sub>	26	18	06	17
C <sub>42</sub> H <sub>48</sub> MnN <sub>2</sub> O <sub>10</sub>	20	22	12	16
C <sub>42</sub> H <sub>48</sub> NiN <sub>2</sub> O <sub>10</sub>	20	20	10	19

**Table.4. Antifungal activity of HL and its metal complexes**

Compounds	Inhibition zone diameter (mm)		
	<i>Saccharomyces Cerevisiae</i>	<i>Penicillium Natatum</i>	<i>Aspergillus Oryzae</i>
	Concentration, 0.5mg/ ml	Concentration, 0.5mg/ ml	Concentration, 0.5mg/ ml
<i>Griseofulvin</i>	40	34	42
Ligand HL C <sub>18</sub> H <sub>18</sub> O <sub>4</sub>	08	16	07
C <sub>39</sub> H <sub>41</sub> ClFeNO <sub>9</sub>	12	21	12
C <sub>42</sub> H <sub>48</sub> CuN <sub>2</sub> O <sub>10</sub>	10	32	11
C <sub>42</sub> H <sub>48</sub> CoN <sub>2</sub> O <sub>10</sub>	13	30	14
C <sub>42</sub> H <sub>48</sub> MnN <sub>2</sub> O <sub>10</sub>	14	22	13
C <sub>42</sub> H <sub>48</sub> NiN <sub>2</sub> O <sub>10</sub>	18	31	12

The improved activity of these complexes can be elucidated on the basis of the overtone theory and the Tweedy Chelation Theory (Raman, 2004). According to the overtone theory of cell permeability, the lipid membrane that surrounds the cell favor the passage of only lipid soluble materials, for which reason liposolubility is an important factor controlling antimicrobial activity. On Chelation with metal ion, the polarity of metal ion is decreased to a greater extent due to overlap of the ligand orbital and partial sharing of its positive charge with the donor groups and also due to delocalization of the p-electrons over whole chelate ring, which improves the penetration of the coordination compounds into the lipid membranes and the blocking of the metal binding sites of the enzymes of the micro-organisms.

#### 4. CONCLUSION

The physic-chemical data propose a distorted octahedral and octahedral geometry for the Cu (II) and all (Mn(II), Fe(III), Co(II) and Ni(II)) other complexes respectively. The ligand act as a bidentate ligand coordinates through the phenolic oxygen and the acetyl carbonyl group of the dehydroacetic acid moiety. The complexes are biologically active and exhibit enhanced antifungal activities compared to their parent ligands, hence further study of these complexes could show desirable effects in agriculture field.

#### 5. ACKNOWLEDGEMENTS

The authors are thankful to the UGC (WRO) Pune, for the sanctioning Minor Research Project under XII<sup>th</sup> plan. The authors are also thankful to Chandrabanshi B.S. Head, Department of chemistry, Rajarshi Shahu Mahavidyalaya, Latur for providing laboratory facilities.

#### REFERENCES

- Anto R.J, Dineshababu K.N & Kuttan R, Antimutagenic and anticarcinogenic activity of natural and synthetic curcuminoid, Cancer let, 1995, 74-94.
- Bauer A.W, Kirby W.M.M, Shesies J.C, Turck M, Antibiotic susceptibility testing by a standardized single disk method, Am. J. Clin. Pathol. 44, 1966, 93.
- Carugo O, Castellani C.B, Rizzi M, Carugo O, Castellani C.B, Rizzi M, Influence of the complexation of copper (II) on the structure and reactivity of 4-hydroxy-6-methyl-3-[3-dimethylaminoacryloyl]-2Hpyran-2-one, Polyhedron, 9, 1990, 2061-2069.
- Eichhorn G. L, Bailar J. C, Metal ion catalysis in the hydrolysis of Schiff bases, J. Am. Chem. Soc, 75, 1953, 2905.

John V.D, Kuttan G & Krishanankutty K, Synthesis, characterization and crystal structures of molybdenum(VI) and (V) complexes with differently N-substituted  $\beta'$ -hydroxy- $\beta$ -enaminones J. exp. Clin. can. Res, 33, 2002, 343.

Krishanankutty K, John, V.D, Synthesis, characterization and antitumour studies of metal chelates of some synthetic curcuminoids. Synthesis and Reactivity in Inorganic Metal-Organic Chemistry, 28, 2003, 343.

Levai A, Jeke J, Physicochemical and spectral properties of octahedral dioxomolybdenum (VI) complexes, Monatsh. Chem, 137, 2006, 339.

Lever A.B.P, Inorganic electronic spectroscopy, Elsevier, Amsterdam, 27, 1968, 256.

Mane P.S, Shirodkar S.G, Arbad B.R, Chondhekar T.K, Synthesis and Structural Studies of Transition Metal Complexes with Bidentate Schiff Base Derived from 3-Acetyl-6-methyl-(2H)-pyran-2,4(3H)-dione, Indian J.Chem, 40, 2001, 648.

Munde A.S, Jagdale A.N, Jadhav S.M, Chondhekar T.K, Synthesis and Characterization of Some Transition Metal Complexes of Unsymmetrical Tetradentate Schiff Base Ligand, J.Korean Chem. Soc, 53, 2009, 4.

Nakamoto K, Infrared spectra of inorganic & coordination compounds, Wiley, New York, 159, 1970, 167-214.

Oyedapo A.O, Makanju V.O, Adewunmi C.O, Iwalewa E.O & Adenowo T.K, Antitrichomonal activity of 1,3-diaryl-2-propen-1-ones on trichomonas gallinae, Afr. J. Trad. CAM, 1, 2004, 55.

Patange V.N, Arbad B.R, Mane V.G & Salunke S.D, Synthesis, spectral and antimicrobial study of chalcone and their metal complexes, Trans Met. Chem, 32, 2007, 944.

Patange V.N, Mane P.S, Mane V.G, Arbad B.R, Transition metal complexes with oxygen donor ligands, a synthesis, spectral, thermal and antimicrobial study, J. Indian Chem. Soc, 85, 2008, 792.

Raman N, Kulandaisamy A, Tungaraja C, Manishankar P, Viswanthan S, Vedhi C, Sythesis Spectral Redox and Antimicrobial Activity of Schiff Transition metal (II) complexes Derived from 4-aminoantipyrine and Benzil, Transition Met. Chem, 29, 2004, 129.

Ramarao N, Rao V.P, TyagaRaju V.J, Ganorkar M.C, Reaction of ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2-pyran-3-yl)-4-oxo-2-butenate with N-nucleophiles. Synthesis of isomeric pyronylpyrazoles and pyrano [4,3-c]pyrazoles Indian J.Chem. A24, 1985, 877.

Rao P.V, Narasaiah A.V, Synthesis, characterization and biological studies of oxovanadium (IV), manganese (II), iron (II), cobalt (II), nickel (II) and copper (II) complexes derived from DHA derivatives. Indian J. chem. A, 42, 2003, 1896.

Schleiffenbaum B, Spertini O, Tedder Thomas F, In vitro study of the insulin-like action of vanadyl-pyrone and -pyridinone complexes with a VO (O-4) coordination mode, J. cell. Biol, 119, 1992, 229.

Stanley V.G, Woldesenbet S, Cassandra G, Sensitivity of Escherichia coli 0157, H7 strain 932 to selected anticoccidial drugs in broiler chicks. Poult. Sci, 75, 1996, 42.

Suryarao D, Sadasivareddy C, John V.T, Gonorkar M.C, Synthesis and structure of cadmium and zinc complexes of dehydroacetic acid, Curr.Sco, 49, 1980, 511.

Suryarao D, Subharao B.L, John V.T, Gonorkar M.C. Synthesis and characterization of new dinuclear complexes of molybdenum(V) with  $\beta'$ -hydroxy-beta-enaminones, Nat. Acad. Sci.let, 1, 1978, 402.

Tan S.F, Ang K.P, Jatchandran H.L,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  nuclear magnetic resonance studies on the tautomerism of the Schiff's bases of 3-acetyl-6-methyl-2H-pyran-2,4 (3H)-dione and 3,5-diacetyltetrahydropyran-2,4,6-trione, Transition Met. Chem, 9, 1984, 390.

Thornberry H.H, Transition-metal complexes with dehydroacetic acid, crystal structure of bis (3-acetyl-4-hydroxy-6-methyl-2-pyrone) cobalt (II) bis (dimethylformamide), Phytopathology, 40, 1950, 419.

Vaibhav Patange N, Arbad B.R, Synthesis, spectral, thermal and biological studies of transition metal complexes of 4-hydroxy-3-[3-(4-hydroxyphenyl)-acryloyl]-6-methyl-2H-pyran-2-one, J. Serb. Chem. Soc. 76 (9), 2011, 1237-1246.

Vaibhav Patange N, Pardeshi R.K, Arbad B.R, Transition metal complexes with oxygen donor ligands, a synthesis, spectral, thermal and antimicrobial study, J. Serb. Chem. Soc, 73 (11), 2008, 1073-1082.