



## Preparation, analytical and X-ray diffraction studies of 4-hydroxy-3-[3-(4-isopropyl phenyl)-acryloyl]-6-methyl-2H-pyran-2-one and its some transition metal's complexes

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### 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, UV-visible, IR, <sup>1</sup>H-NMR spectroscopy, Mass & X-ray diffraction. 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. Monoclinic system for Cu (II) and Ni(II) complexes on the basis of X-ray diffraction investigations.

**Keywords:** Dehydroacetic acid; Transition metal complexes; Chalcone;

### 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.

### Experimental

#### Material and Methods:

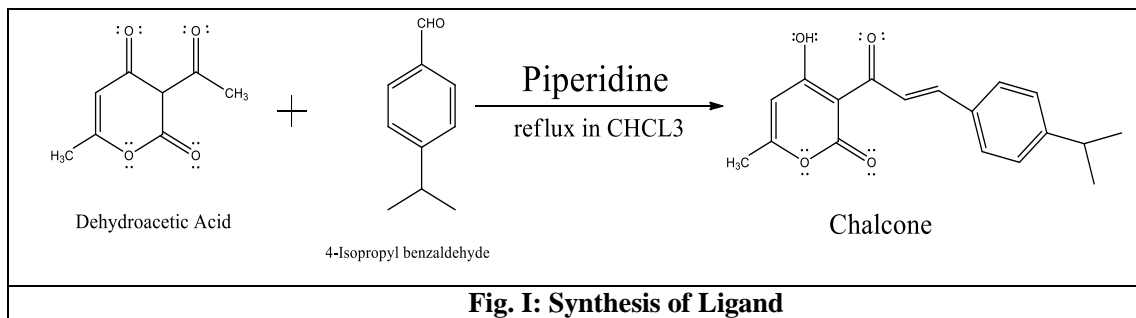
DHA (purity = 99%) for synthesis was

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 CDCl<sub>3</sub> 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 Hg [Co (SCN)<sub>4</sub>] as the calibrant.

#### General procedure for the synthesis of the ligand:

A solution of 0.01 mol of dehydroacetic acid, 10 drops of piperidine & 0.01 mole of 4-isopropyl benzaldehyde in 25ml chloroform were refluxed for 8-10 hrs, see fig.I, 10 ml of the chloroform-water azeotrope mixture was 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).



### General procedure for the synthesis of metal complexes :

To a chloroform solution ( 30ml ) of the ligand ( 2 mmol ), 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.

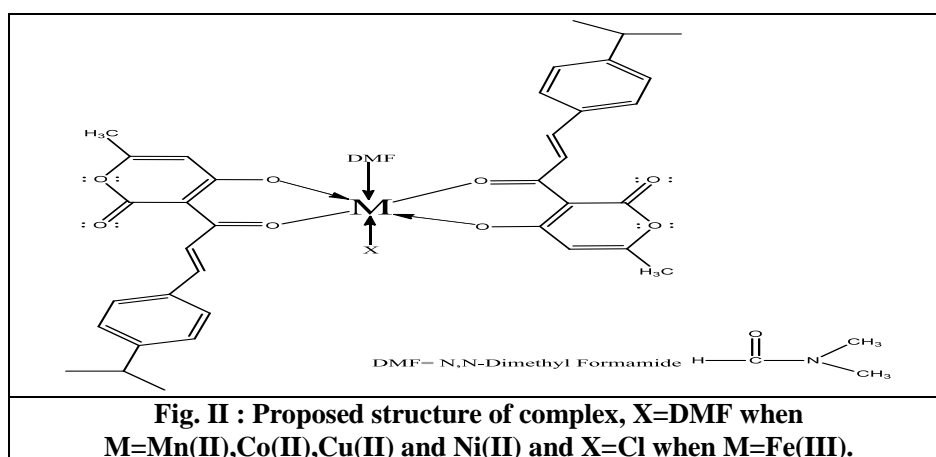
To evaluate the fungicidal activity of the ligands and the metal complexes, their effects on the growth of *Saccharomyces Cerevisiae*, *Aspergillus*

*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.

### Results and Discussion

The elemental analyses showed 1:2 (metal: ligand) stoichiometry for all the complexes (Fig. II). 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.



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

Ligand/complexes	F.W.	M.P./decomp . Temp.( <sup>o</sup> 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)

$C_{42}H_{48}CuN_2O_{10}$	804	242	42	Celadon	7.82 (7.90)	62.51 (62.71)	5.95 (6.01)	3.41 (3.48)
$C_{42}H_{48}CoN_2O_{10}$	799	248	32	Orange	7.30 (7.37)	62.85 (63.07)	5.90 (6.05)	3.41 (3.50)
$C_{42}H_{48}MnN_2O_{10}$	795	250	33	Brown	6.71 (6.90)	62.80 (63.39)	5.96 (6.08)	3.50 (3.52)
$C_{42}H_{48}NiN_2O_{10}$	799	256	60	Green Yellow	7.22 (7.34)	62.63 (63.09)	5.97 (6.05)	3.45 (3.50)

### $^1H$ NMR spectra of ligand :

The  $^1H$  NMR spectra of free ligand in  $CDCl_3$  at room temperature shows the following signals. d 1.30 (d, 6H,  $-CH(CH_3)_2$ ), 2.30 (s, 3H,  $-CH_3$ ), 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. III).

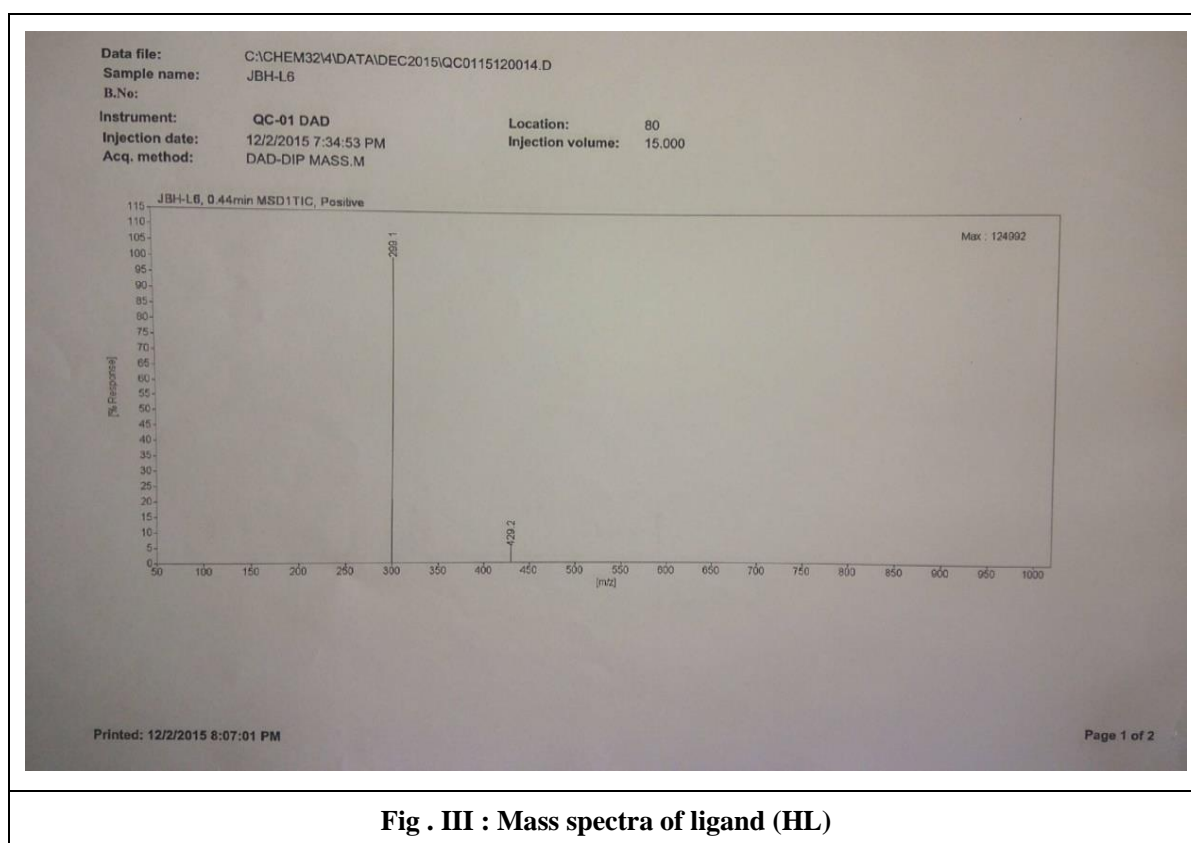


Fig . III : Mass spectra of ligand (HL)

### FTIR Spectra:

The FTIR spectrum of free ligand shows characteristic bands at 3100, 1725, 1626, 1233-1211  $cm^{-1}$  assignable to  $\nu(OH)$  of the intramolecular phenolic group of the dehydroacetic acid moiety,  $\nu(C=O)$  (lactone carbonyl),  $\nu(C=O)$  (acetyl carbonyl) &  $\nu(C-O)$  (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  $cm^{-1}$ . Instead, in its place, a broad band characteristic of  $\nu(OH)$  of coordination water was observed in the region 3570-3200  $cm^{-1}$ . The absence of  $\nu(OH)$  (Phenolic) at 3100  $cm^{-1}$  suggests subsequent deprotonation of the phenolic group and coordination of phenolic oxygen to the metal ion. This was supported by an upward

shift in  $\nu(C-O)$  (phenolic) (Rao, 2003) by 20-40  $cm^{-1}$ . The  $\nu(C=O)$  (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  $cm^{-1}$ , typical of  $\nu(C-O-C)$  and *trans*  $-CH=CH-$  absorption. The presence of new bands in the region 600-450  $cm^{-1}$  can be assigned to  $\nu(M-O)$  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.II.

Table.II. Characteristic IR frequencies (cm-1) of the ligand and its metal complexes

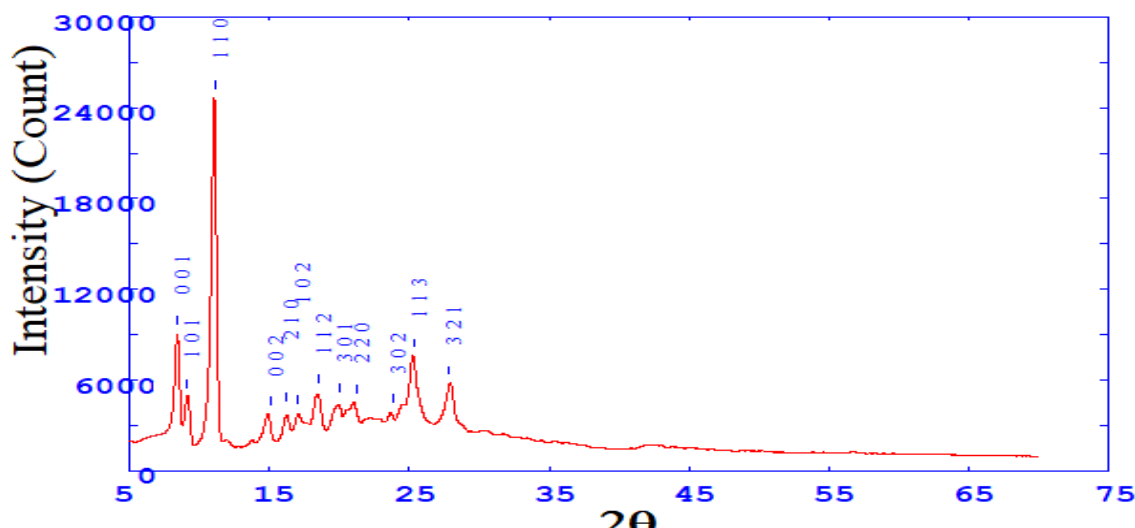
Compound	$\nu$ (OH) (dehydroacetic acid moiety)	$\nu$ (C=O) (lactone)	$\nu$ (C=O) (acetyl carbonyl)	$\nu$ (C-O) (phenolic)	$\nu$ (C=C) (trans)	$\nu$ (M-O)
Ligand HL $C_{18}H_{18}O_4$	3100 <sub>(s)</sub>	1725 <sub>(s)</sub>	1626 <sub>(m)</sub>	1211 <sub>(w)</sub>	985 <sub>(s)</sub>	-
$C_{39}H_{41}ClFeNO_9$	-	1714 <sub>(m)</sub>	1621 <sub>(w)</sub>	1214 <sub>(s)</sub>	1002 <sub>(w)</sub>	530 <sub>(s)</sub> 488 <sub>(s)</sub>
$C_{42}H_{48}CuN_2O_{10}$	-	1645 <sub>(w)</sub>	1619 <sub>(s)</sub>	1264 <sub>(s)</sub>	977 <sub>(s)</sub>	560 <sub>(w)</sub> 480 <sub>(s)</sub>
$C_{42}H_{48}CoN_2O_{10}$	-	1690 <sub>(s)</sub>	1626 <sub>(s)</sub>	1235 <sub>(w)</sub>	968 <sub>(m)</sub>	531 <sub>(m)</sub> 476 <sub>(w)</sub>
$C_{42}H_{48}MnN_2O_{10}$	-	1648 <sub>(m)</sub>	1603 <sub>(w)</sub>	1247 <sub>(m)</sub>	1001 <sub>(m)</sub>	585 <sub>(m)</sub> 533 <sub>(s)</sub>
$C_{42}H_{48}NiN_2O_{10}$	-	1662 <sub>(m)</sub>	1626 <sub>(w)</sub>	1238 <sub>(s)</sub>	1004 <sub>(m)</sub>	551 <sub>(s)</sub> 531 <sub>(s)</sub>

### XRD Studies of Complexing Agent and Their Metal Complexes

The XRD studies of the selected Copper(II) and Nickel(II) complexes derived from 4-hydroxy-3-(3-(4-isopropylphenyl)acryloyl)-6-methyl-2H-pyran-2-one (Complexing agent) were logged in between the  $2\theta$  range  $5-70^\circ$  at a  $\lambda$  of  $1.540598 \text{ \AA}$ . The X-ray diffractograms as well as associated figures define the  $2\theta$  value for every peak, the comparative intensity in addition inter-planar spaces (d-values). The X-ray diffractograms forms of Copper(II) and Nickel(II) chelates thru respect to leading peaks of relative intensity greater than 10% were indexed by a Powder-X Computer software

programme (Carvajal J. R., et al., 2004; Balaji H. Jawale, et al., 2017; Patange, 2008). This type of indexing system in the same way produces the Miller indices, the unit cell parameters in addition the unit cell volume. In agreement through these cell parameters, circumstances such as  $a \neq b \neq c$  also  $\alpha = \gamma = 90^\circ \neq \beta$  essential for a monoclinic sample were tried and observed to be adequate results. Evaluation of trial and hypothetical density value spectacles blameless arrangement inside the restrictions of trial error (Deshmukh M. B. et al., 2005). The XRD investigation of Copper(II) and Nickel(II) complexes are as follows

Fig. IV : X-ray Diffractogram of Copper(II) chelate of Complexing agent



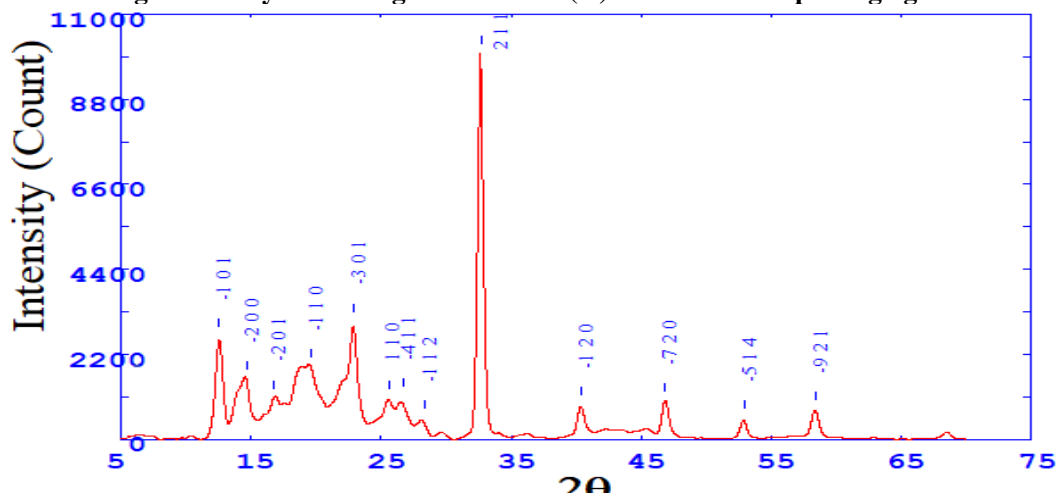
CRYSTAL SYSTEM : Monoclinic      LATTICE TYPE : P 2/m  
 RADIATION : Cu      WAVELENGTH :  $1.540598 \text{ \AA}$   
 VOLUME :  $2998.00 \text{ \AA}^3$       LAMBDA :  $1.54060 \text{ \AA}$   
 RECIP. LATTICE : 0.06756 0.06756 0.08438 90.000 90.000 60.000  
 LATTICE PARAMETER :  
 a= 4.9168       $\alpha= 90$   
 b= 4.9168       $\beta= 90$   
 c= 5.4089       $\gamma= 120$   
 2Theta Start= 5      2Theta End= 70

Table III : X-ray Diffractogram data of Copper(II) chelate of Complexing agent

H	K	L	TH(OBS)	TH-ZERO	TH(CALC)	D(OBS)	D(CALC)	RI%
0	0	1	4.20511	3.96465	3.72656	11.14099	11.85167	29.8
1	0	1	4.54842	4.30796	4.7762	10.25462	9.25129	17.2
1	1	0	5.57834	5.33789	5.17179	8.2802	8.54538	82.2
0	0	2	7.58099	7.34053	7.46901	6.02897	5.92584	12.3
2	1	0	8.09595	7.85549	7.91446	5.63599	5.59426	12.1
1	0	2	8.49648	8.25602	8.04907	5.36432	5.5013	12.2
1	1	2	9.29754	9.05708	9.10166	4.89332	4.86956	16.7
3	0	1	10.04137	9.80092	9.73659	4.52517	4.55478	14.2
2	2	0	10.61356	10.3731	10.38633	4.27808	4.27269	14.3
3	0	2	11.92958	11.68912	11.72184	3.80204	3.79158	12
1	1	3	12.67342	12.43296	12.40457	3.57784	3.5859	24.2
3	2	1	13.93222	13.69176	13.6494	3.25435	3.26426	18.6

The cell records and crystal lattice of Copper(II) chelate of Complexing agent are apt in the Table III designates that the chelate make sure monoclinic arrangements (*Vaibhav N. Patange et al., 2008*).

Fig. V : X-ray Diffractogram of Nickel(II) chelate of Complexing agent



CRYSTAL SYSTEM : Monoclinic                      LATTICE TYPE : P 2/m  
 RADIATION : Cu    WAVELENGTH : 1.540598 Å<sup>0</sup>  
 VOLUME : 516.11Å<sup>3</sup>    LAMBDA : 1.54060 Å<sup>0</sup>  
 RECIP. LATTICE : 0.07813 0.24064 0.11909 90.000 88.052 60.000  
 LATTICE PARAMETER :  
 a= 4.9168    α= 90  
 b= 4.9168    β= 90  
 c= 5.4089    γ=120  
 2Theta Start= 5    2Theta End= 70

Table IV : X-ray Diffractogram data of Nickel(II) chelate of Complexing agent

H	K	L	TH(OBS)	TH-ZERO	TH(CALC)	D(OBS)	D(CALC)	RI%
-1	0	1	6.26496	6.20136	6.19943	7.13088	7.13309	22.3
-2	0	0	7.35211	7.28851	6.91354	6.07177	6.39935	13.6
-2	0	1	8.38204	8.31844	8.55971	5.32435	5.17535	9.2
-1	1	0	9.8125	9.7489	9.4266	4.54908	4.70314	16.8
-3	0	1	11.47183	11.40823	11.52081	3.89437	3.85682	25.2
1	1	0	12.78785	12.72425	12.80712	3.49724	3.47499	8.3
-4	1	1	13.36004	13.29644	13.51366	3.34928	3.29642	8.2
1	1	2	14.16109	14.09749	14.14663	3.1625	3.15174	5.1
-	1	1	16.3926	16.329	16.46432	2.73979	2.71789	92.1
2	2	0	20.22623	20.16263	20.15711	2.23478	2.23537	7.4
-1	2	0	23.43046	23.36686	23.47985	1.94217	1.93335	8.6
-7	1	4	26.46303	26.39943	26.29665	1.73246	1.73875	4.2
-5	2	1	29.20951	29.14591	29.00202	1.58161	1.58877	5.1

In the XRD investigation of Nickel (II) chelate of Complexing agent outcomes are monoclinic system on the basis of cell data and crystal parameters. These diffractogram and data are shown in above Fig. V and Table IV.

### 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. Monoclinic system for Cu (II) and Ni (II) complexes on the basis of X-ray diffraction investigations..

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