Synthesis and Thermal Studies of Chalcone Ligand Complexes of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) with 4-Dimethylamino benzaldehyde and Dehydroacetic Acid

Abstract: Some novel transition metal [Cu(II), Ni(II), Co(II), Mn(II) and Fe(III)] complexes of substituted Dehydroacetic acid Chalcone have been prepared and characterized by physical, spectral and analytical data. The synthesized Chalcone act as bidentate for the complexation reaction with Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) ions. In order to evaluate the effect of metal ions upon chelation, the Chalcone and their complexes have been screened for antibacterial activity against the strains such as Shigella Boydii, Bacillus Cereus, Bacillus Megaterium and Escherichia Coli and antifungal activity against the strains such as Saccharomyces Cerevisiae, Penicillium Natatum and Aspergillus Oryzae. The complexed Chalcone have shown to be more antimicrobial against species as compared to uncomplexed Chalcone.

Keywords: Dehydroacetic acid, metal complexes, chalcone, antimicrobial activity.

INTRODUCTION

The field of coordination chemistry is one of the most scholarly, attractive and experimentally demanding frontiers in modern chemical sciences. It has grown in a half century from a readily defined and limited area into the most active research field of inorganic chemistry. Coordination compounds brought about a synthetic revolution in inorganic chemistry which leads to new products of equally novel applications in wide range of areas such as pharmaceuticals, fungicidal, bactericidal, herbicidal & insecticidal activities. Complexation reactions are used in qualitative as well as quantitative analysis of metals. There are some extremely sensitive and selective organic reagents for the determination of metal ions. Coordination chemistry, by its very nature, deals with metals and ligands. Metal coordination occurs when lone pair electrons from a ligand are donated to an empty orbital in a metal ion. There are many broad classes of ligands such as classical, organo-metallic, cluster and bioinorganic. A classical ligand, also called a Werner complex after coordination chemistry’s founder Alfred Werner, is a ligand that binds through the lone pairs of the main group atom of the ligand. Many metal-ligand interactions seen in nature are classical ligands. Metals are known to have first choice for certain ligands and for certain geometries. Classical cases are the so-called chalcone couplings; in other cases rather unique ligands can be formed only when the metal is present.

Chalcones are the condensation product of acetophenone with aromatic aldehydes in the presence of strong base. Chalcones and their metal complexes play a prominent role in modern coordination chemistry. These compounds possessing novel structural features, interesting spectral and magnetic properties, have been the subject of intensive research due to their importance in medical, agricultural, analytical, biological and industrial fields. In recent years a number of β-dicarbonyl compounds in which the carbonyl function(s) bonded to olefinic linkage(s) have gained considerable importance mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants. For instance, curcuminoids, the active chemical component present in Indian medicinal plant turmeric (curcuma longa, linn, zingiberacea family) contain three β-dicarbonyl compounds in which the diketo function is directly linked to olefinic group. Such unsaturated β-dicarbonyl compounds and their metal complexes possess interesting biochemical properties such as antitumour, antioxidant, antifungal and antimicrobial activities. A search of the literature revealed that no work has been done on transition metal complexes of the chalcone derived from dehydroaceticacid and 4-Dimethylaminobenzaldehyde. The complexes of Ni(II), Cu(II), Mn(II), Co(II) and Fe(III) with this ligand were also prepared in the solid state and characterized by different physico-chemical methods, investigate antimicrobial activities.

EXPERIMENTAL

Dehydroacetic acid (purity ≥ 99%) for synthesis was obtained from Merck, Germany & used as supplied. 4-Dimethylamino benzaldehyde 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 preparation of the complexes. The carbon, hydrogen & nitrogen content in each sample were measured on a Perkin Elmer(2400) CHNS analyzer. The IR spectra (KBr), in the range of 4000-450 cm⁻¹ were recorded...
on a Perkin Elmer (C-75430) IR spectrometer. The 1H-NMR spectrum of the ligand was measured in CDCl₃ on Bruker instrument. The mass spectrum of the ligand was measured in Qc-01 DAD Mas-spectrometer, thermogravimetric analysis differential thermal analysis (TGA-DTA) were realised on a METTLER-TOLEDO–DB V13.00 instruments. The UV-VIS spectra of the complexes were recorded on a Shimadzu UV-2202 Spectrophotometer. Magnetic susceptibility measurements of the complexes were performed using a Gouy balance at room temperature using Hg [Co (SCN)₄] as the calibrant.

SYNTHESIS OF THE LIGAND (HL) :-

A solution of 0.01 mol of dehydroacetic acid, 10 drops of piperidine & 0.01 mol of 4-Dimethylaminobenzaldehyde in 25 ml chloroform were refluxed for 8-10 hrs, 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.

Scheme : Synthesis of Ligand

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 desicator.

Scheme : Preparation of Metal Complex

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. Shigella boydii, Escherichia Coli by the paper disc plate method. The compound were tested at concentrations of 1.0 mg ml⁻¹ 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, Aspergillas Oryzae and Penicillium notatum were studied. The ligand and their corresponding metal chelates in DMF were screened in vitro by the disc diffusion method. The ligands and complexes were dissolved separately in DMF to obtain concentration 500 µg disc⁻¹. 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)₂(X)₂], where M=Mn (II), Co(II), Ni(II), Cu (II), and M=Fe(III), L=C₁₇H₁₇NO₄. The absence of chlorine in the 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.

<table>
<thead>
<tr>
<th>Ligand/complexes</th>
<th>F.W.</th>
<th>M.P/decomp. Temp.(°C)</th>
<th>Yield %</th>
<th>Colour</th>
<th>M (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>N (%)</th>
</tr>
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<tbody>
<tr>
<td>Ligand HL C₇H₆NO₄</td>
<td>299</td>
<td>225</td>
<td>70</td>
<td>Yellow</td>
<td>-</td>
<td>68.18</td>
<td>(68.21)</td>
<td>5.70</td>
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<tr>
<td>C₅H₅Fe(phen)O₄</td>
<td>652</td>
<td>248</td>
<td>60</td>
<td>Brown</td>
<td>8.51</td>
<td>(8.56)</td>
<td>62.55</td>
<td>4.89</td>
</tr>
<tr>
<td>C₅H₅Cu(NH)₂O₂</td>
<td>654</td>
<td>298</td>
<td>80</td>
<td>Apricot</td>
<td>9.60</td>
<td>(9.63)</td>
<td>61.82</td>
<td>4.85</td>
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<tr>
<td>C₅H₅Co(NH)₂O₂</td>
<td>655</td>
<td>300&lt;</td>
<td>80</td>
<td>Amber</td>
<td>8.95</td>
<td>(8.99)</td>
<td>62.22</td>
<td>4.86</td>
</tr>
<tr>
<td>C₅H₅Mn(NH)₂O₂</td>
<td>651</td>
<td>264</td>
<td>65</td>
<td>Bronze</td>
<td>8.41</td>
<td>(8.43)</td>
<td>62.51</td>
<td>4.90</td>
</tr>
<tr>
<td>C₅H₅Ni(NH)₂O₂</td>
<td>655</td>
<td>282</td>
<td>90</td>
<td>Lemon</td>
<td>8.86</td>
<td>(8.96)</td>
<td>62.31</td>
<td>4.91</td>
</tr>
</tbody>
</table>

¹H-NMR Spectra of ligand: -

The ¹H NMR spectra of free ligand in CDCl₃ at room temperature shows the following signals. 6.27 (s, 3H, -CH₃), 3.09 (s, 6H, two N–(CH₃)₂ gr), 5.92 (s,1H, C₅-hydrogen of DHA moiety), 6.71 (dd, 2H, Ar-H), 7.64(dd, 2H, Ar-H), 8.04(d,1H, olefinic proton), 8.16 (d,1H, olefinic proton) and 14.50 (s,1H, enolic OH of DHA moiety). The NMR spectra giving in the following fig.III.

Massspectra of ligand: -

Mass spectroscopy regard as clear and strong evidence to prove the formation of molecules via the observation of the mother ion at molecular weight equivalent value and this observed in the mass fragmentation spectra of ligand, that the mother ion appear clear band at (299 m/e ) , this was a good agreement for the formation of the new ligand.

IR Spectra of ligand: -

The FTIR spectrum of free ligand shows characteristic bands at 3081, 1725, 1648, 1456, 1242 cm⁻¹ assignable to v (OH) of the intramolecular phenolic group of the dehydroacetic acid moiety, v (C=O) (lactone carbonyl), v(C=O) (acetyl carbonyl), v(C=N) (P-substituted amine gr) & v (C-O) (phenolic ) stretching mode, respectively. In the IR spectra of all the metal chelates, no band was observed in the region 3200-3300 cm⁻¹. Instead, in its place, a broad band characteristic of v (OH) of coordination water was observed in the region 3570-3200 cm⁻¹. The absence of v (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 v (C=O) (phenolic) 20 by 10-45 cm⁻¹. The v (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. The IR spectra of all the compounds showed a prominent band at ~1377 & ~970 cm⁻¹, typical of v (C-O-C) and trans –CH=CH- absorption. The presence of new bands in the region 600-450 cm⁻¹ can be assigned to v (M-O) vibration. Important spectral bands for the ligand and its metal complexes are presented in Table II.

Hence, the ligands coordinated with the metal ions as mono-deprotonated 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

<table>
<thead>
<tr>
<th>Compound</th>
<th>v (OH) (dehydroacetic acid moiety)</th>
<th>v (C=O) (lactone)</th>
<th>v (C=O) (acetyl carbonyl)</th>
<th>v (C=O) (phenolic)</th>
<th>v (C=C) (trans)</th>
<th>v (M-O)</th>
</tr>
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<tr>
<td>Ligand HL C₅H₄N₂O₂</td>
<td>3081 (w)</td>
<td>1725 (s)</td>
<td>1648 (m)</td>
<td>1242 (s)</td>
<td>993 (s)</td>
<td>-</td>
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<tr>
<td>Cu₃H₂FeN₂O₄</td>
<td>-</td>
<td>1703 (s)</td>
<td>1649 (s)</td>
<td>1227 (m)</td>
<td>1000 (m)</td>
<td>532 (m), 478 (m)</td>
</tr>
<tr>
<td>Cu₃H₂CuN₂O₄</td>
<td>-</td>
<td>1695 (m)</td>
<td>1653 (s)</td>
<td>1226 (s)</td>
<td>1000 (m)</td>
<td>562 (m), 479 (m)</td>
</tr>
<tr>
<td>Cu₃H₂CoN₂O₄</td>
<td>-</td>
<td>1690 (m)</td>
<td>1654 (s)</td>
<td>1225 (m)</td>
<td>999 (s)</td>
<td>542 (m), 478 (m)</td>
</tr>
<tr>
<td>Cu₃H₂MnN₂O₆</td>
<td>-</td>
<td>1697 (m)</td>
<td>1644 (m)</td>
<td>1226 (s)</td>
<td>972 (m)</td>
<td>580 (m), 525 (m)</td>
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<tr>
<td>C₄H₆N₂O₄</td>
<td>-</td>
<td>1703 (s)</td>
<td>1663 (s)</td>
<td>1226 (s)</td>
<td>1001 (w)</td>
<td>540 (s), 531 (s)</td>
</tr>
</tbody>
</table>

THERMAL ANALYSIS:-

The simultaneous TG/DT analysis of the Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) metal complexes was studied from ambient temperature to 1000°C under a nitrogen atmosphere using α-Al₂O₃ as the reference. In the TG curve of Cu(II) complex of ligand, the mass loss starts from 50°C and an inclined slope from 160-185°C with a mass loss of 6.0% (calcd., 6.10%), indicates the removal of two molecules of coordinated water, an endothermic peak in the range 150-200°C (ΔTmin=175°C) in DTA corresponds to dehydration step. The rate controlling process of dehydration is found to be random nucleation with one nucleus on each particle (F1). The mass loss continues in TG curve up to 325°C with a mass loss 26.67% (calcd., 26.67%), which is attributed to the removal of two molecules of coordinated water, an endothermic peak in the range 150-200°C (ΔTmin=165°C) in DTA corresponds to dehydration step. The anhydrous compound in second step decomposes within a short temperature range from 220-330°C with a 27.0 % mass loss (calcd., 27.52 %), an exothermic peak between 240 and 400°C with ΔTmax = 280°C in DTA. This step may be attributed to the removal of non-coordinated part of the ligand. The third step corresponds to decomposition of coordinated part of the ligand and in the range of 400-750°C with a mass loss 55.5 % (calcd., 54.01 %). The mass of the final residue corresponds to stable MnO, 11.5 % (calcd., 12.21%).

In the thermal study of Fe(III) complex of ligand show slow weight loss up to 225°C and an inclined slope from 230°C-260°C in TG curve with mass loss 10.0% (calcd., 8.92 %) indicates the removal of one molecule of water and one chloride ion, an endothermic peak in the range 180-240°C is observed in DTA (ΔTmin = 213°C). The decomposition of complex continues in between temperature 270 and 500°C with 27% mass loss (calcd., 26.67%). An exothermic peak between 250-270°C (ΔTmax = 260°C) in DTA, attributed to the removal of non-coordinating part of the ligand.

The thermal decomposition profile of Ni(II) complex of ligand show weight loss 3% (calcd., 2.98%) in the range 30-100°C indicates the removal of one physically adsorbed water molecule. An endothermic peak between 30-55°C (ΔTmin= 35°C), correspond to dehydration. The mass loss of 6.0% (calcd., 5.95%) is observed in the range 100-180°C. An endothermic peak between 120-180°C (ΔTmin= 157.5°C), correspond to loss of two coordinated water molecules. The third step decomposition is in between 250 and 425°C with 27% mass loss (calcd., 26.52%). A broad exothermic peak between 200-450°C (ΔTmax = 315.7°C) in DTA, attributed to the removal of non-coordinating part of the ligand.

The thermal decomposition profile of Co(II) complex of ligand show no weight loss up to 150°C. The mass loss of 6.5% (calcd. 6.14%) is observed in the range 150-200°C. An endothermic peak between 140-210°C (ΔTmin = 180°C), correspond to the loss of two molecules of water. The second step decomposition is in between temperature 235 and 375°C with 28.5% mass loss (calcd. 27.33%). A broad exothermic peak between 225-375°C (ΔTmax = 320°C) in DTA, attributed to the removal of non-coordinating part of the ligand.

The mass loss continues and follows slow decomposition of remaining part of the ligand 53.5% (calcd., 53.64). The mass of the final residue corresponds to CoO, 11.5% (calcd. 12.8%).

In the TG curve of Mn(II) complex of ligand, the first step shows a steep slope between 150-200°C with a mass loss of 6.0% (calcd., 6.2%), indicates the removal of two molecules of coordinated water, an endothermic peak in the range 150-200°C (ΔTmin=165°C) in DTA corresponds to dehydration step. The anhydrous compound in second step decomposes within a short temperature range from 220-330°C with a 27.0 % mass loss (calcd., 27.52 %), an exothermic peak between 240 and 400°C with ΔTmax = 280°C in DTA. This step may be attributed to the removal of non-coordinated part of the ligand. The third step corresponds to decomposition of coordinated part of the ligand and in the range of 400-750°C with a mass loss 55.5 % (calcd., 54.01 %). The mass of the final residue corresponds to stable MnO, 11.5 % (calcd., 12.21%).

MAGNETIC MEASUREMENT AND ELECTRONIC ABSORPTION SPECTRA -:

The electronic spectra of all the complexes were recorded in DMF solution. The magnetic and electronic spectral data are given in table III. The electronic spectrum of the Mn(II) complex exhibited three bands at 12848 cm⁻¹ (ε= 26 dm³mol⁻¹cm⁻¹), 20492 cm⁻¹ (ε= 16 dm³mol⁻¹cm⁻¹) and 33113 cm⁻¹ (ε= 28 dm³mol⁻¹cm⁻¹), which are assigned to ²A₁g → ²T₁g(G), ⁴A₁g → ⁴T₂g(G) and ⁴A₁g → ²A₁g, ⁴E₁g(4G) transitions, respectively, indicating an octahedral configuration²³,²⁴ around the Mn(II) ion. The octahedral geometry of Mn(II) was further confirmed by the value of...
the magnetic moment (5.84 μB).

Three electronic transitions were observed in the electronic spectrum of the Fe(III) complex, at 14472 cm$^{-1}$ ($\epsilon= 22$ dm$^3$mol$^{-1}$cm$^{-1}$), 2132 cm$^{-1}$ ($\epsilon= 26$ dm$^3$mol$^{-1}$cm$^{-1}$) and 24272 cm$^{-1}$ ($\epsilon= 32$ dm$^3$mol$^{-1}$cm$^{-1}$), which are assigned to $^4A_{1g} \rightarrow T_{1g}(G)$, $^4A_{1g} \rightarrow T_{2g}(G)$ and $^4A_{1g} \rightarrow E_g(G)$, respectively, suggesting an octahedral complex of Fe(III), which was confirmed by the value of magnetic moment (5.69 μB) \(^{23}\).

The electronic spectrum of the Co(II) complex exhibited three bands at 92392 cm$^{-1}$ ($\epsilon= 17$ dm$^3$mol$^{-1}$cm$^{-1}$), 18726 cm$^{-1}$ ($\epsilon= 59$ dm$^3$mol$^{-1}$cm$^{-1}$) and 23923 cm$^{-1}$ ($\epsilon= 98$ dm$^3$mol$^{-1}$cm$^{-1}$), which are assigned to $^3T_{2g}(F) \rightarrow ^3T_{2g}(F)$, $^3T_{1g}(F) \rightarrow ^3A_{2g}(F)$ and $^3T_{1g}(F) \rightarrow ^3T_{1g}(F)$, respectively, indicating octahedral configuration around the Co(II) ion. The magnetic moment of the Co(II) complex was 4.92 μB. The calculated spectral parameters $\nu_2/\nu_1$, 10Dq, B, $\beta$ and the ligand field stabilizing energy (LFSE) have the values 1.96, 9169 cm$^{-1}$, 783.1 cm$^{-1}$, 0.81 and 26.20 kcal mol$^{-1}$, respectively, which are in good agreement with the reported values of an octahedral Co(II) complex \(^{23}\).

The electronic spectrum of the Ni(II) complex exhibited three bands at 9671 cm$^{-1}$ ($\epsilon= 34$ dm$^3$mol$^{-1}$cm$^{-1}$), 14880 cm$^{-1}$ ($\epsilon= 67$ dm$^3$mol$^{-1}$cm$^{-1}$) and 25125 cm$^{-1}$ ($\epsilon= 188$ dm$^3$mol$^{-1}$cm$^{-1}$), which are assigned to $^3A_{2g} \rightarrow ^3T_{2g}(F)$, $^3A_{2g} \rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \rightarrow ^3T_{1g}(F)$, respectively. The ligand field parameters $\nu_2/\nu_1$, 10Dq, B, $\beta$ and the LFSE have the values 1.68, 9345 cm$^{-1}$, 675.6 cm$^{-1}$, 0.63 and 26.69 kcal mol$^{-1}$, respectively. These values, as well as the magnetic moment value (2.99 μB), support an octahedral geometry of the Ni(II) complex \(^{23}\).

The spectrum of the Cu(II) complex consisted of a broad band at 15083 cm$^{-1}$ ($\epsilon= 94$ dm$^3$mol$^{-1}$cm$^{-1}$), assigned to the $^2E_g \rightarrow ^2T_{2g}$ transition of a distorted octahedral geometry \(^{24}\). In addition to this band, the band observed at 24937 cm$^{-1}$ ($\epsilon= 1143$ dm$^3$mol$^{-1}$cm$^{-1}$) arises from intra ligand charge transfer. The LFSE value of the Cu(II) complex is 42.64 kcal mol$^{-1}$. The obtained values of LFSE determine the stability of the complexes and follows the order in terms of metal ions Cu(II)>Ni(II)>Co(II).

### POWDER X-RAY DIFFRACTION ANALYSIS -

The Cu(II), Ni(II) and Co(II) complexes of ligand were subjected to X-ray powder diffraction studies. The X-ray powder diffraction pattern of Cu(II) complex is presented in (Fig. IV). X-ray powder data of all the main peaks having relative intensity greater than 10% have been indexed by using computer software independently by trial and error method. The indexed powder diffraction data, the unit cell data and crystal lattice parameters of complex are presented in following Table. The diffractogram of Cu(II) complex had ten reflection with maximum reflection at $2\theta = 23.92^\circ$ corresponding to the value of d = 11.6810 Å. The crystal volume is obtained from indexing of the diffraction pattern. The Z (number of molecules per unit cell) values were calculated and rounded up to the nearest whole number. The porosity percentage was calculated from the observed and calculated densities. The density calculated from diffraction data and the observed density was found to be very close to each other indicating the perfection in indexing. Such refined parameters were also used for finding out probable space group. All these values are given in Table.

The crystallographic data of the complexes fit perfectly in orthorhombic for Cu-complex with 2 molecules each per unit cell.

The Ni(II) complexes of diffractogram of Ni(II) complex of Ligand had eleven reflection with maximum reflection at $2\theta = 25.7^\circ$ corresponding to the value of d = 3.4636 Å. The crystallographic data of the complexes fit perfectly in monoclinic system for Ni complex 2 molecule per unit cell of ligand. The probable space group is P 2/m for all the Ni(II) complex under investigation.

Where as the diffractogram of Co(II) had eleven reflection with maximum reflection at $2\theta = 13.5^\circ$ corresponding to the value of d = 6.548 Å. The crystallographic data of the Co complexes fit perfectly in monoclinic system for Co complex with 4 molecules per unit cell. The probable space group is P 2/m for Co(II) complexes under investigation.

### TABLE III. Magnetic And electronic absorption spectral data (in DMSO) of the compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{eff}/\mu_B$</th>
<th>$\nu$ cm$^{-1}$</th>
<th>Band assignment</th>
<th>Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ligand HL, CuH$_2$N$_2$O$_2$</td>
<td>-</td>
<td>32442</td>
<td>INCT$^a$</td>
<td>-</td>
</tr>
<tr>
<td>Cu$_3$H$_2$FeN$_2$O$_5$</td>
<td>5.74</td>
<td>15924</td>
<td>$^4A_{1g} \rightarrow ^4T_{1g}(G)$</td>
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<tr>
<td>Cu$_3$H$_2$CuN$_2$O$_5$</td>
<td>1.95</td>
<td>15083</td>
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<td>4.92</td>
<td>9794</td>
<td>$^3T_{1g}(F) \rightarrow ^3T_{2g}(F)$</td>
<td>Octahedral</td>
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<tr>
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<td>5.69</td>
<td>18248</td>
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<td>9671</td>
<td>$^3A_{2g} \rightarrow ^3T_{1g}(F)$</td>
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</table>
Figure IV: X-ray Diffractogram of Cu-Complex

Table: XRD data of Cu-Complex

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<th>L</th>
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<th>sin²θ-CALC</th>
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Crystal System: **Orthorhombic**

\[
a = 16.7968 \pm 0.02166 \, \text{Å} \\
b = 11.6965 \pm 0.00936 \, \text{Å} \\
c = 7.4843 \pm 0.00708 \, \text{Å}
\]

\[
\alpha = 90.00 \pm 0.000 \, \text{DEG} \\
\beta = 90.00 \pm 0.000 \, \text{DEG} \\
\gamma = 90.00 \pm 0.000 \, \text{DEG}
\]

Density (pobs) = 1.3853 g cm\(^{-3}\) 
Density (pcal) = 1.3922 g cm\(^{-3}\)

Porosity % = 0.4935 
Particle size = 87.81 Å

Porosity % = 0.4935

Z = 2

Volume = 1470.41 Å\(^3\)
ANTIMICROBIAL ACTIVITY:

The synthesized Ligand and their complexes were screened for antibacterial activity against four pathogenic organisms: Shigella Boydii, Bacillus Cereus, Bacillus Megaterium and Escherichia Coli and antifungal activity against three organisms: Saccharomyces Cerevisiae, Penicillium Noatakum and Aspergillus Oryzce (Table 2). The paper disc diffusion method and mycelia dry weight method with glucose nitrate media were used for antibacterial and antifungal activities respectively. The tested compounds were dissolved in N,Ndimethylformamide (DMF) to get a solution of 1 mg/ml. The inhibition zones were measured in millimeters at the end of an incubation period of 48 hrs at (35±2)°C. DMF alone showed no inhibition. Commercial antibacterial Ciprofloxacin and antifungal Griseofulvin were also tested under similar conditions for comparison.

It is observed that the metal complexes show enhanced antimicrobial activity as compared to the ligand. This is because of chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to delocalization of p electrons over whole chelate ring. Thus chelation increase lipophilic character in the complexes and results in the enhancement of activity. The inhibition by metal complexes has been increased by 30-65% and 40-70% for 125 and 250 ppm concentration respectively.

CONCLUSION:

On the basis of present investigation metal complexes are biologically active and show enhanced antimicrobial activities compared to free ligand. Based on the physicochemical and spectral data discussed above, a distorted octahedral geometry for the Cu(II) complex and an octahedral geometry for the Mn(II), Fe(III), Co(II) and Ni(II) complexes are proposed.

A thermal study revealed that the complexes are thermally stable. An XRD study suggested the monoclinic crystal system for the Co(II), Ni(II) and Orthorhombic crystal system for the Cu(II) complexes.

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REFERENCES: