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SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL STUDY OF SOME TRANSITION METAL COMPLEXES OF BIDENTATE CHALCONE LIGAND

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ABSTRACT

Transition metal complexes containing bidentate O,O donar ligand, 4-hydroxy-3-[3-(3,4,5-trimethoxy phenyl)-acryloyl]-6-methyl-2H-pyran-2-one derived from 3-acetyl-6-methyl-pyran-2,4(3H)-dione (dehydroacetic acid) and 3,4,5-trimethoxy benzaldehyde, have been synthesized and characterized by elemental analysis, thermal analysis, magnetic succeptibility, UV-visible, IR, ^{1}H-NMR, Mass spectroscopy. X-ray diffraction analysis & antimicrobial activity. Analytical & spectral data, the stoichiometry of the complexes was found to be 1:2 (metal: ligand). The physic-chemical data suggest a distorted octahedral geometry for the Cu (II) complexes and an octahedral geometry for all the other complexes. The synthesized ligand and its metal complexes were screened for their in vitro antibacterial and antifungal activity against several human pathogenic bacteria and fungi. It has been found that some of the complexes were active & show higher activity than the free ligand. Metal chelation affects significantly bioactive behaviour of the organic ligands.

KEYWORDS: Dehydroacetic acid, metal complexes, chalcone, antimicrobial activity,

INTRODUCTION

Unsaturated ketones are gaining importance as reactive intermediates and are used to obtain the biologically important heterocycles.[1-6] This class of compounds exhibit wide spectrum of pharmaceutical and biological properties.[7-9] In recent years, there has been a growing interest in compounds containing a carbonyl group directly linked to an α,β-unsaturated system (chalcone) and their presumed role in the prevention of various degenerative diseases. Chalcones are important compounds because of their contribution to human health and their multiple biological effects.[10-16] Therefore one of the oxygen hetrocyclic 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[17-20] It is also a versatile starting material for the synthesis of a wide variety of hetrocyclic ring systems.[21] A search of the literature revealed that no work has been done on transition metal complexes of the chalcones derived from 3,4,5-trimethoxybenzaldehyde & dehydroacetic acid.

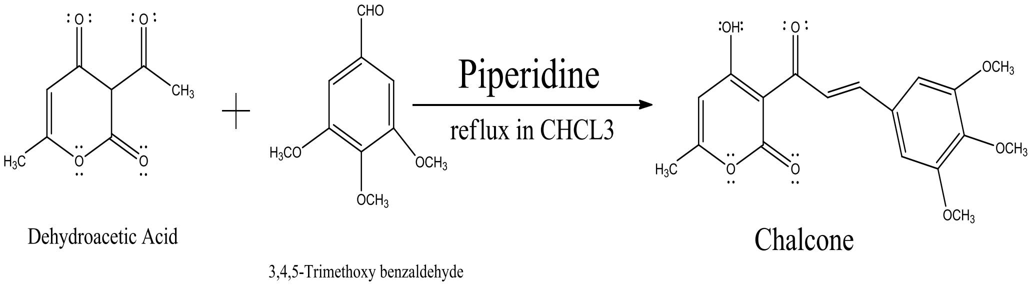
The aim of this work to is synthesis & characterize the solid complexes of a ligand containing a carbonyl group directly linked to the α,β- unsaturated system derived from DHA &3,4,5-trimethoxy benzaldehyde with Cu(II), Ni(II), Co(II), Mn(II) & Fe(III) complex to investigate their antibacterial activity towards Gram-positive Bacteria (Bacillus Cereus & Bacillus Megaterium) and Gram-negative Bacteria (Shigella boydii & Escherichia coli) and their fungicidal activity towards Saccharomyces Cerevisiae & Penicillium Notatum fungi.

EXPERIMENTAL

Dehydroacetic acid (purity ≥ 99%) for synthesis was obtained from Merck, Germany & used as supplied. 3,4,5-trimethoxy 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 $CDCL_3$ 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)

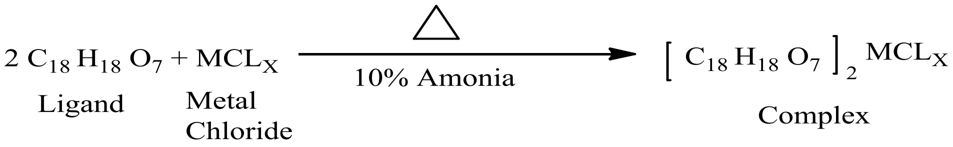
A solution of 0.01mol of dehydroacetic acid, 10 drops of piperidine & 0.01 mol of 3,4,5-trimethoxybenzaldelyde in 25 ml chloroform were refluxed for 8-10 hrs, 10 ml of the chloroform-water azeotrope mixture was separated by distillation. Crystal of product separated on slow evaporation of the remaining chloroform. The resulting precipitate was filtered, washed several times with ethanol & recrystallized from chloroform.[22-23]



Scheme: Synthesis of Ligand.

Preparation 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 vaccum desicator.



$$\underset{\text{Ligand}}{2\,C_{18}H_{18}O_{7}} + \underset{\text{Metal Chloride}}{MCL_{X}} \xrightarrow[\text{10\% Amonia}]{\triangle} \underset{\text{Complex}}{[C_{18}H_{18}O_{7}]_{2}\,MCL_{X}}$$

Scheme: Preparation of Metal Complex.

Antimicrobial Activity

The ligand and its metal complexes were screened for *in vitro* antibacterial activity against Gram-positive, *Bacillus Cereus, Bacillus Megaterium* and Gram-negative, *Shigella boydii, Escherichia Coli* by the paper disc plate method.[24] 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, 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.[25] 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 shows 1:2 (metal: ligand) stoichiometry for all the complexes (Fig.I). The analytical data of the ligand and its metal complexes corresponded well with the general formula [$M(L)_2]CL_X$, where M= Fe(III), Mn (II), Co(II), Ni(II), Cu (II), L=$C_{18}H_{18}O_7$. 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.

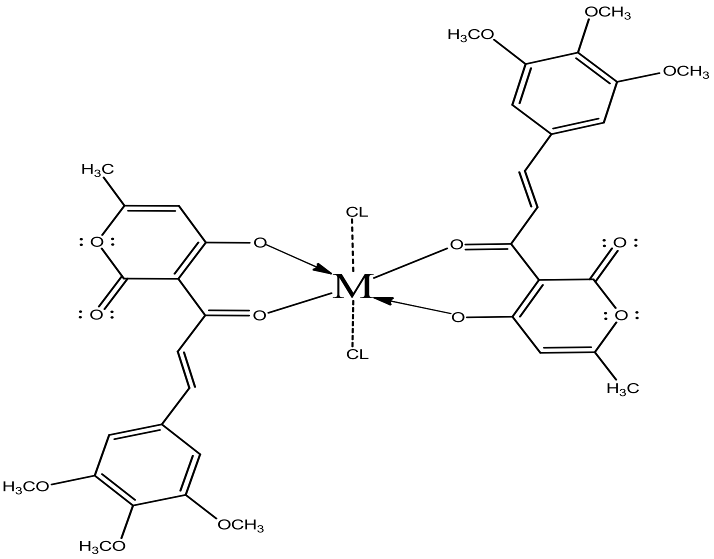


Fig I: Proposed structure of complex.

Table I: Physical Characterization and Analytical data of ligand and its metal complexes.

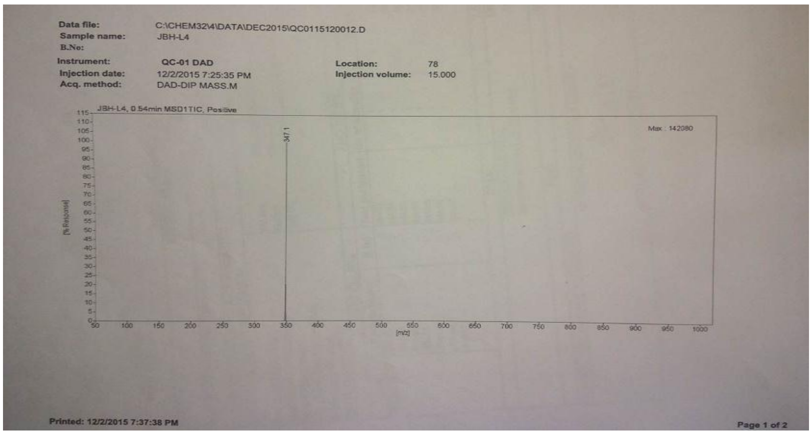
Ligand/ complexes	F.W.	M.P./ decomp. Temp.(^{0}C)	Yield %	Colour	Found (Calcd.), %			
					M	C	H	O
Ligand HL $C_{18}H_{18}O_7$	346	152	70	Red Orange	-	62.22 (62.42)	5.21 (5.24)	32.24 (32.34)
$C_{36}H_{34}FeO_{14}$	746	248	60	Brown	7.03 (7.48)	57.78 (56.92)	4.43 (4.59)	30.44 (29.01)
$C_{36}H_{34}CuO_{14}$	754	230	70	Apricot	8.96 (7.43)	57.03 (56.33)	4.37 (4.54)	29.00 (29.70)
$C_{36}H_{34}CoO_{14}$	748	238	50	Amber	7.09 (7.86)	57.91 (56.68)	4.40 (4.57)	29.13 (29.88)
$C_{36}H_{34}MnO_{14}$	745	182	42	Bronze	7.98 (6.37)	57.07 (57.99)	4.43 (4.60)	30.14 (29.04)
$C_{36}H_{34}NiO_{14}$	749	222	60	Lemon	6.55 (6.47)	57.33 (57.70)	4.40 (4.57)	29.19 (29.89)

^{1}H-NMR Spectra of ligand

The ^{1}H NMR spectra of free ligand in $CDCL_3$ at room temperature shows the following signals. δ2.30 (s, 3H, -CH_3), 3.93 (s, 9H, three –OCH_3 gr), 5.98 (s,1H, C_5-hydrogen of DHA moiety),6.92(s, 2H, Ar-H), 7.92(d,1H, olefinic proton), 8.24 (d,1H, olefinic proton) and 13.56 (s,1H, enolic OH of DHA moiety).

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 (347 m/e), this was a good agreement for the formation of the new ligand. The mass spectra giving in the following fig. II.



Data file: C:\CHEM32\4\DATA\DEC2015\QC0115120012.D
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Injection date: 12/2/2015 7:25:35 PM
Acq. method: DAD-DIP MASS.M
Location: 78
Injection volume: 15.000

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Page 1 of 2

Fig. II: Mass Spectra of Chalcone Ligand.

IRspectra of ligand

The FTIR spectrum of free ligand shows characteristic bands at 3108, 1731, 1649, 1238cm^{-1} assignable to ν (OH) of the intramolecular phenolic group of the dehydroacetic acid moiety, ν (C=O) (lactone carbonyl), ν(C=O) (acetyl carbonyl) & ν (C-O) (phenolic) stretching mode, respectively.[26] In the IR spectra of all the metal chelates, no band was observed in the region of 3200-3000cm^{-1}. Instead, in its place, a broad band characteristic of ν (OH) of coordination water was observed in the region 3570-3200cm^{-1}. The absence of ν (OH) (Phenolic) at 3100cm^{-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 ν (C-O) (phenolic)[27] by 10-45cm^{-1}. The ν (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.[26-28] The IR spectra of all the compounds showed a prominent band at ≈1377 & ≈ 970cm^{-1}, typical of ν (C-O-C) and trans –CH=CH- absorption. The presence of new bonds in the region 600-450cm^{-1} can be assigned to ν (M-O) vibration.[29] 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. I.

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

Compound	ν (OH) (dehydroacetic acid moiety)	ν (C=O) (lactone)	ν (C=O) (acetyl carbonyl)	ν (C-O) (phenolic)	ν (C=C) (trans)	ν (M-O)
Ligand HL $C_{18}H_{18}O_7$	$3108_{(m)}$	$1731_{(s)}$	$1649_{(w)}$	$1238_{(s)}$	$976_{(s)}$	-
$C_{36}H_{34}FeO_{14}$	-	$1703_{(s)}$	$1648_{(s)}$	$1255_{(m)}$	$1000_{(m)}$	$530_{(m)}$ $488_{(m)}$
$C_{36}H_{34}CuO_{14}$	-	$1715_{(s)}$	$1651_{(s)}$	$1273_{(s)}$	$998_{(s)}$	$560_{(w)}$ $480_{(m)}$
$C_{36}H_{34}CoO_{14}$	-	$1681_{(m)}$	$1649_{(s)}$	$1240_{(m)}$	$972_{(s)}$	$531_{(w)}$ $476_{(m)}$
$C_{36}H_{34}MnO_{14}$	-	$1720_{(w)}$	$1648_{(m)}$	$1278_{(s)}$	$996_{(m)}$	$585_{(w)}$ $533_{(w)}$
$C_{36}H_{34}NiO_{14}$	-	$1685_{(m)}$	$1661_{(w)}$	$1268_{(w)}$	$983_{(w)}$	$551_{(w)}$ $531_{(m)}$

Thermal Analysis

The simultaneous TG/DT analysis of the Co(II), Cu(II), Ni(II), and Mn(II) metal complexes was studied from ambient temperature to 1000^0C under a nitrogen atmosphere using α-Al_2O_3

as the reference. The TG curve of the Cu(II) and Ni(II) complexes exhibited no mass loss up to 285^0C, indicating the absence of coordinated water[30] and the high thermal stability of the complexes. On the TG curve of Cu(II) complex, the first step of decomposition from 295 to 352 °C, with a mass loss 21.75 % (calcd. 22.83 %), accompanied by an exothermic peak with t_{max}= 309 °C on the DTA curve, may be attributed to the removal of the non-coordinated part of the ligand. The second step, from 485 to 650 °C with mass loss 49.30 % (calcd. 49.10 %), corresponds to the decomposition of the coordinated part of the ligand. An exothermic peak with t_{max}= 505.7 °C on the DTA curve was observed for this step. The mass of the final residue corresponded to stable CuO, 20.85 % (calcd. 18.37 %).

The TG curve of the Ni(II) complex shows a two-step decomposition. The first step from 360 to 410 °C with a mass loss of 24.50 % (calcd. 23.08%), accompanied by an endothermic peak with t_{max}= 319 °C on the DTA curve, may be attributed to the decomposition of the non-coordinated part of the ligand. The second step, from 460 to 835 °C with a mass loss of 50.24 % (calcd. 49.43 %), corresponds to the removal of the coordinated part of the ligand. For this step, a broad endothermic peak in the DTA was observed. The mass of the final residue 12 % (calcd. 17.05 %) does not correspond to any stoichiometry of the end product, as the residue obtained is not close to that expected for metal oxide.

The TG curve of the Mn(II) complex showed a rapid first step decomposition between 240–350 °C with 48 % mass loss (calcd. 48.14 %), associated with an exothermic peak on the DTA curve (ΔT_{max}= 247.38 °C), indicating the loss of two coordinated DMF molecules and the non-coordinated part of the complex, aromatic ring with a beta carbon.[31] The complex did not remain stable at higher temperatures and exhibited a slow second step decomposition in the temperature range 360–950 °C with a mass loss of 42 % (calcd. 42.22 %). The broad endothermic peak for this step on the DTA curve corresponds to the oxidative degradation of the coordinated part of the ligand. The decomposition was completed at ≈950 °C leading to the formation of the stable metal oxide MnO (observed 10 %, calcd. 9.54 %).

The Co(II) complex decomposed in two successive steps in the temperature range of 300–850 °C. Two coordinated DMF molecules and the non-coordinated part of the ligand were removed in the first step at 300–400 °C with a mass loss 47.5 % (calcd. 47.88 %). A broad exothermic peak was observed between 200–400 °C (ΔT_{max}= 338.12 °C). The complex finally decomposed to CoO with the removal of the coordinated part of the ligand (observed 42 %, calcd. 42 %) in the temperature range 400–850 °C.

The thermal study of the Fe(III) complex shows stability up to 325 °C. The first step showed a rapid decomposition between 340 –400 °C with a 45 % mass loss (calcd. 45.3 %). A broad exotherm was observedin the DTA (ΔT_{max}= 366.1 °C). This step may be attributed to the removal of one coordinated DMF molecule, one chloride ion (may be oxidized as Cl_2) and the non-coordinated part of the ligand.The complex continued slow decomposition of the remaining part of the ligand with a mass loss of 44 % (calcd. 44.42 %) in the temperature range 400–900°C. A broad endotherm was observed for this step in the DTA. The mass of the final residue corresponds to the stable FeO (observed 11 %, calcd. 10.2 %).

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 18345 cm^{-1}(ε= 26 $dm^3mol^{-1}cm^{-1}$), 19763 cm^{-1}(ε= 16 $dm^3mol^{-1}cm^{-1}$) and 23154 cm^{-1}(ε= 28 $dm^3mol^{-1}cm^{-1}$), which are assigned to $^6A_{1g} \rightarrow ^4T_{1g}(G)$, $^6A_{1g} \rightarrow ^4T_{2g}(G)$ and $^6A_{1g} \rightarrow ^4A_{1g}$, $^4E_{1g}(4G)$ transitions, respectively, indicating an octahedral configuration[32,33] 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 cm^{-1}(ε= 22 $dm^3mol^{-1}cm^{-1}$), 21322 cm^{-1}(ε= 26 $dm^3mol^{-1}cm^{-1}$) and 24272 cm^{-1}(ε= 32 $dm^3mol^{-1}cm^{-1}$), which are assigned to $^6A_{1g} \rightarrow ^4T_{1g}(G)$, $^6A_{1g} \rightarrow ^4T_{2g}(G)$ and $^6A_{1g} \rightarrow ^4E_g(G)$, respectively, suggesting an octahedral complex of Fe(III),which was confirmed by the value of magnetic moment (5.93 $_{\mu B}$).[32]

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

Compound	**μ_{eff}/μ_B**	**ν /cm^{-1}**	**Band assignment**	**Geometry**
Ligand HL $C_{18}H_{18}O_4$	-	32442 40545	INCT^a INCT	-
$C_{36}H_{34}FeO_{14}$	5.93	14472 21322 24272	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4E_g(G)$	Octahedral
$C_{36}H_{34}CuO_{14}$		14225 25316	$^2E_g \rightarrow {}^2T_{2g}$ INCT	Distorted Octahedral
$C_{36}H_{34}CoO_{14}$	4.54	9487 18656 21551	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
$C_{36}H_{34}MnO_{14}$	5.84	18345 19763 23154	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}$	Octahedral
$C_{36}H_{34}NiO_{14}$	3.13	9345 15698 22471	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral

The electronic spectrum of the Co(II) complex exhibited three bands at 9487 cm^{-1}(ε= 17 dm^{3}mol^{-1}cm^{-1}), 18656 cm^{-1}(ε= 59 dm^{3}mol^{-1}cm^{-1}) and 21551 cm^{-1}(ε= 98 dm^{3}mol^{-1}cm^{-1}), which are assigned 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 ν2/ν1, 10Dq, B, βand 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.[32]

The electronic spectrum of the Ni(II) complex exhibited three bands at 9345 cm^{-1}(ε= 34 dm^{3}mol^{-1}cm^{-1}), 15698 cm^{-1}(ε= 67 dm^{3}mol^{-1}cm^{-1}) and 22471 cm^{-1}(ε= 188 dm^{3}mol^{-1}cm^{-1}), which are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, respectively. The ligand field parameters ν2/ν1, 10Dq, B, βand the LFSE have the values 1.68, 9345 cm^{-1}, 675.6 cm^{-1}, 0.65 and 26.69 $_{kcal}$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.[32]

The spectrum of the Cu(II) complex consisted of a broad band at 14225 cm^{-1}(ε= 94 dm^{3}mol^{-1}cm^{-1}), assigned to the $^2E_g \rightarrow {}^2T_{2g}$transition of a distorted octahedral geometry.[33] In addition to this band, the band observed at 25316 cm–1 (ε= 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 X-ray diffractograms of the Co(II), Mn(II) and Fe(III) complexes were scanned in the range 5–100° at a wavelength of 1.543 Å. The diffractograms and associated data depict the 2θvalue for each peak, the relative intensity and inter-planar spacing (d-values). The X-ray diffraction pattern of these complexes with respect to major peaks of relative intensity greater than 10 % were indexed using a computer programme.[34] This indexing method also yields the Miller indices (h, k, l), the unit cell parameters and the unit cell volume. The unit cell of Co(II) complex yielded values of lattice constants: a= 8.9706 Å, b= 8.6441 Å and c= 4.7755 Å, and a unit cell volume V= 369.2291 Å3. The unit cell of the Mn(II) complex yielded values of lattice constants: a= 24.5882 Å, b= 4.4656 Å, c= 5.8676 Å, and a unit cell volume V= 627.2087Å3. The unit cell of the Fe(III) complex yielded values of lattice constants: a= 7.0696 Å, b= 14.8954 Å, c= 5.3504 Å, and a unit cell volume V= 830.4539 Å3. In concurrence with these cell parameters, conditions such as a ≠ b ≠ cand α= γ= 90° ≠ βrequired for a monoclinic sample were tested and found to be satisfactory. Hence, it can be concluded that the Co(II), Mn(II) and Fe(III) complexes were monoclinic crystal systems. The experimental density values ofthe complexes were determined using the specific gravity method[35] and found to be 2.1908, 2.5002, and 2.0522 g cm–3 for the Co(II), Mn(II) and Fe(III) complexes, respectively. Using the experimental density values, ρ, the molecular weight of the complexes, M, Avogadro’s number, N, and the volume of the unit cell, V, the number of molecules per unit cell, n, were calculated using the equation ρ= nM/NV and they were found to be one for Co(II) and two for the Mn(II) and Fe(III) complexes. With these values, the theoretical densities were computed and found to be 2.1824, 2.4637 and 2.0645 g cm–3for the respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits of experimental error.[36]

Antimicrobial Activity

The results of the antimicrobial activity of ligand and metal complexes were tested *in vitro* against bacteria *Shigella Boydii, Bacillus Cereus, Bacillus Megaterium and Escherichia Coli* by paper disc plate method.[37] The compounds were tested at the concentration 1 mg ml^{-1} in DMF and compared with known antibiotics *viz Ciprofloxacin* (Table IV). 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[38] with glucose nitrate media, are given in (Table V), in which the results of the control were also presented from table IV and V, it was clear that the inhibition by the metal chelates was higher than that of the free ligand and results are in good agreement with earlier reported literature.[39]

Table IV: Antibacterial activity of HL and its metal complexes.

Test Compound	**Inhibition zone diameter (mm)**			
	Shigella Boydii	***Bacillus Cereus***	***Bacillus Megaterium***	***Escherichia Coli***
	Concentration, 1mg ml^{-1}	**Concentration, 1mg ml^{-1}**	**Concentration, 1mg ml^{-1}**	**Concentration, 1mg ml^{-1}**
Ciprofloxacin	30	54	36	32
Ligand HL $C_{18}H_{18}O_4$	10	09	08	09
$C_{36}H_{34}FeO_{14}$	22	20	19	19
$C_{36}H_{34}CuO_{14}$	14	16	24	24
$C_{36}H_{34}CoO_{14}$	24	21	22	22
$C_{36}H_{34}MnO_{14}$	21	20	20	18
$C_{36}H_{34}NiO_{14}$	20	19	13	16

Table V: Antifungal activity of HL and its metal complexes.

Test Compound	**Inhibition zone diameter (mm)**		
	Saccharomyces Cerevisiae	***Penicillium Natatum***	***Aspergillus Oryzae***
	Concentration, 0.5mg ml^{-1}	**Concentration, 0.5mg ml^{-1}**	**Concentration, 0.5mg ml^{-1}**
Griseofulvin	40	34	42
Ligand HL $C_{18}H_{18}O_4$	02	02	02
$C_{36}H_{34}FeO_{14}$	20	22	23
$C_{36}H_{34}CuO_{14}$	14	21	22
$C_{36}H_{34}CoO_{14}$	12	20	16
$C_{36}H_{34}MnO_{14}$	12	16	14
$C_{36}H_{34}NiO_{14}$	11	10	02

The increased activity of the chelates can be explained on the basis of the overtone concept and the Tweedy Chelation Theory[40]. The increase in activity with concentration is due to the effect of metal ions on the normal metabolic function of the cell. The action of compounds may involve the formation of hydrogen bonds with the active centre of cell constituents, resulting in interference with the normal function of the cell.[41]

CONCLUSION

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. The ligand behaves as bidentate, coordinating 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 in agriculture could lead to interesting results.

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