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Synthesis & Spectroscopic Studies of Chalcone Ligand Chelation with Some First Transition Metal's

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Abstract

Some first transition metal [Cu(II), Ni(II), Co(II), Mn(II) and Fe(III)] chelation of 3-[3-(4-(Dimethylamino)Phenyl)acryloyl]-4-Hydroxy-6-Methyl-2H-Pyran-2-One Chalcone have been prepared and characterized by spectral and analytical technique's. The prepared Chalcone act as bidentate for the chelation reaction with Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) ions. Thermal investigations also support existence of coordinated water molecule in metal chelate. Lattice water molecules existing in a number of chelates. Powder X-ray diffraction outcomes shows that Mn(II), Fe(III), Cu(II) and Ni(II) complexes are Hexagonal with P-type, in addition to Co(II) complex is monoclinic with P-type.

Keywords :- Dehydroacetic acid, metal complexes, chalcone, ,

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.

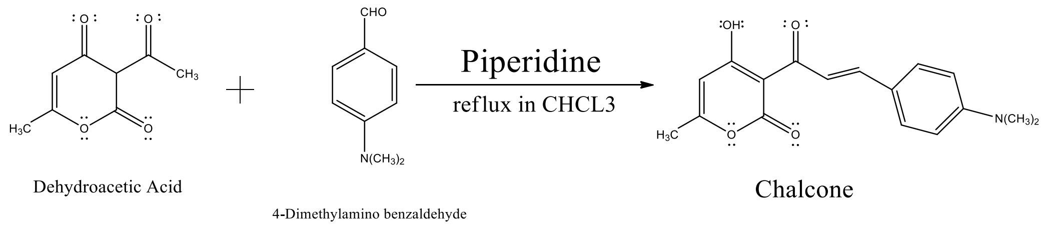
Chalcones are the condensation product of acetophenone with aromatic aldehydes in the presence of strong base. Chalcones and their metal complexes play a prominent role in modern coordination chemistry. These compounds possessing novel structural features, interesting spectral and magnetic properties, have been the subject of intensive research due to their importance in medical, agriculture, 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[1-2] mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants. For instant, 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[2]. Such unsaturated β-dicarbonyl compounds and their metal complexes possess interesting biochemical properties such as antitumour, antioxidant, antifungal and antimicrobial activities[1-14]. 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.

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 $CDCL_3$ 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 4-Dimethylaminobenzaldehyde 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[15-16].



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 vaccum desicator.

RESULTS AND DISCUSSION

The elemental analyses showed 1:2 (metal : ligand) stoichiometry for all the complexes. 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), $L=C_{17}H_{17}NO_4$. 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.

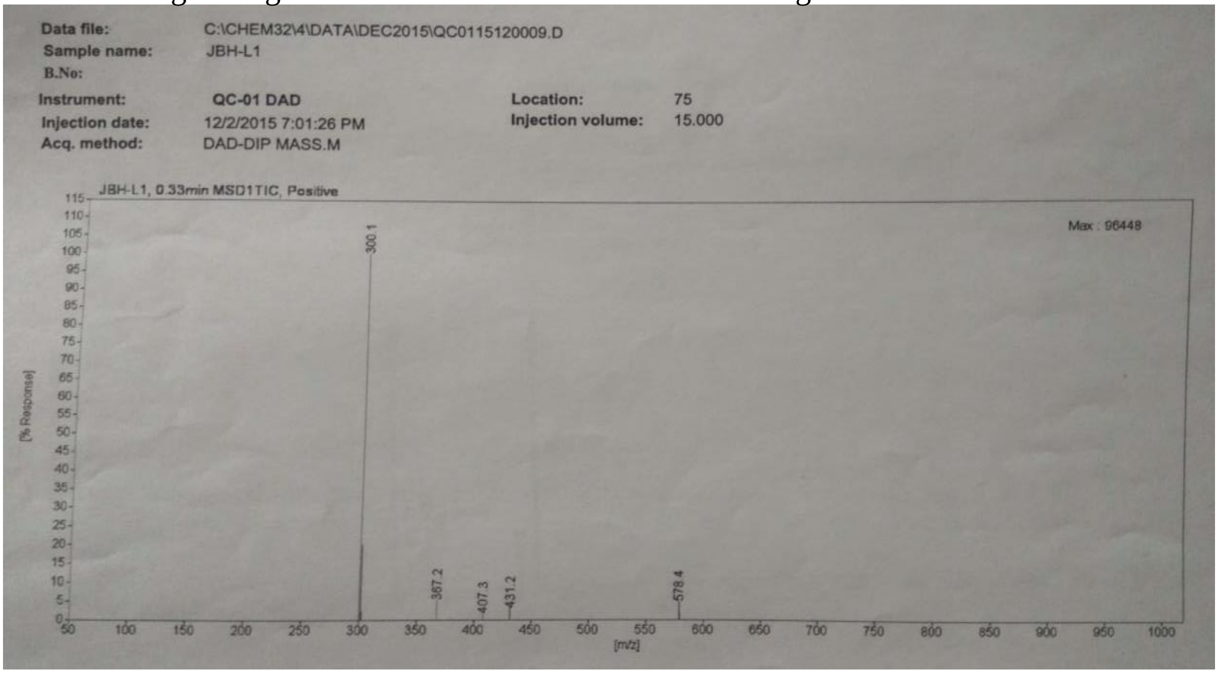
Ligand/ complexes	F.W.	M.P./decomp. Temp.(^{0}C)	Yield %	Colour	Found (Calcd.), %			
					M	C	H	N
Ligand HL $C_{17}H_{17}NO_4$	299	225	70	Yellow	-	68.18 (68.21)	5.70 (5.72)	-
$C_{34}H_{32}FeN_2O_8$	652	248	60	Brown	8.51 (8.56)	62.55 (62.59)	4.89 (4.94)	4.20 (4.29)
$C_{34}H_{32}CuN_2O_8$	654	298	80	Apricot	9.60 (9.63)	61.82 (61.86)	4.85 (4.89)	4.22 (4.24)
$C_{34}H_{32}CoN_2O_8$	655	300<	80	Amber	8.95 (8.99)	62.22 (62.29)	4.86 (4.92)	4.20 (4.27)
$C_{34}H_{32}MnN_2O_8$	651	264	65	Bronze	8.41 (8.43)	62.51 (62.67)	4.90 (4.95)	4.25 (4.30)
$C_{34}H_{32}NiN_2O_8$	655	282	90	Lemon	8.86 (8.96)	62.31 (62.32)	4.91 (4.92)	4.17 (4.27)

^{1}H-NMR Spectra of ligand :-

The ^{1}H NMR spectra of free 3-[3-(4-(Dimethylamino)Phenyl)acryloyl]-4-Hydroxy-6-Methyl-2H-Pyran-2-One in $CDCL_3$ at room temperature shows the following signals. δ2.27 (s, 3H, $-CH_3$), 3.09 (s, 6H, two N–$(CH_3)_2$ gr), 5.92 (s,1H, C_5-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).

Mass Spectra 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.



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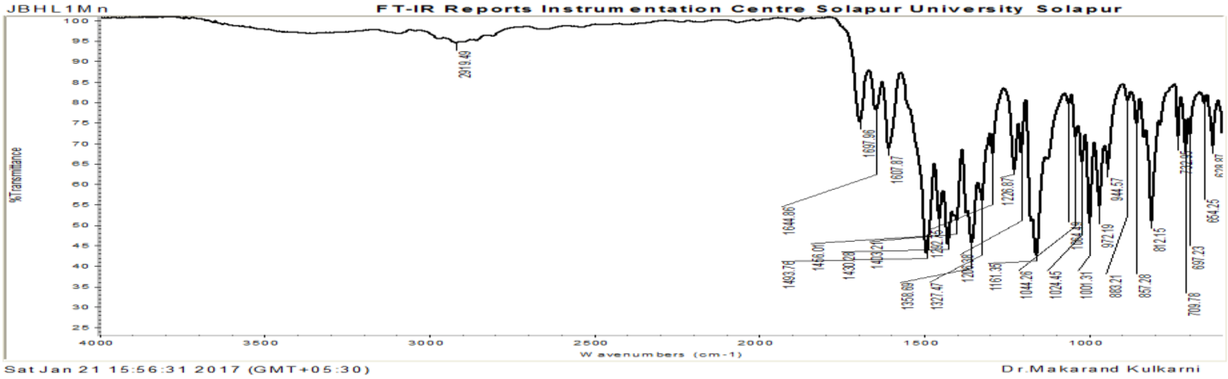
Injection volume: 15.000
Acq. method: DAD-DIP MASS.M

Mass Spectra of ligand

IR Spectra of ligand and its complexes :-



Infra-Red Spectra of Mn Complex

The FTIR spectrum of free ligand shows characteristic bands at 3081, 1725, 1648, 1456, 1242cm^{-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-N) (P-substituted emine gr) & ν (C-O) (phenolic) stretching mode, respectively[19]. 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) [20] 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 [19-21]. 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[22]. Important spectral bands for the ligand and its metal complexes are presented in Table II.

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 $C_{17}H_{17}NO_4$	$3081_{(m)}$	$1725_{(s)}$	$1648_{(w)}$	$1242_{(s)}$	$993_{(s)}$	-
$C_{34}H_{32}FeN_2O_8$	-	$1703_{(s)}$	$1649_{(s)}$	$1227_{(m)}$	$1000_{(m)}$	$532_{(m)}$ $478_{(s)}$
$C_{34}H_{32}CuN_2O_8$	-	$1695_{(s)}$	$1653_{(s)}$	$1226_{(s)}$	$1000_{(s)}$	$562_{(s)}$ $479_{(m)}$
$C_{34}H_{32}CoN_2O_8$	-	$1690_{(m)}$	$1654_{(s)}$	$1225_{(m)}$	$999_{(s)}$	$542_{(w)}$ $478_{(s)}$
$C_{34}H_{32}MnN_2O_8$	-	$1697_{(s)}$	$1644_{(m)}$	$1226_{(s)}$	$972_{(m)}$	$580_{(s)}$ $525_{(w)}$
$C_{34}H_{32}NiN_2O_8$	-	$1703_{(s)}$	$1663_{(s)}$	$1226_{(w)}$	$1001_{(w)}$	$540_{(s)}$ $531_{(m)}$

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^{0}C under a nitrogen atmosphere using α-Al_2O_3 as the reference. In the TG curve of Cu(II) complex of ligand, the mass loss starts from 50^{o}C and an inclined slope from 160-185^{o}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^{o}C(ΔTmin=175^{o}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 upto 325^{o}C with a mass loss 26.5 % (calcd., 27.1%), an exothermic peak ΔTmax = 280^{o}C in DTA 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 in the range of 350-900°C with a mass loss 54.5 % (calcd., 53.22%). A broad endotherm is observed for this step. The mass of the final residue corresponds to stable CuO, 13.0 % (calcd.,13.48%).

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.

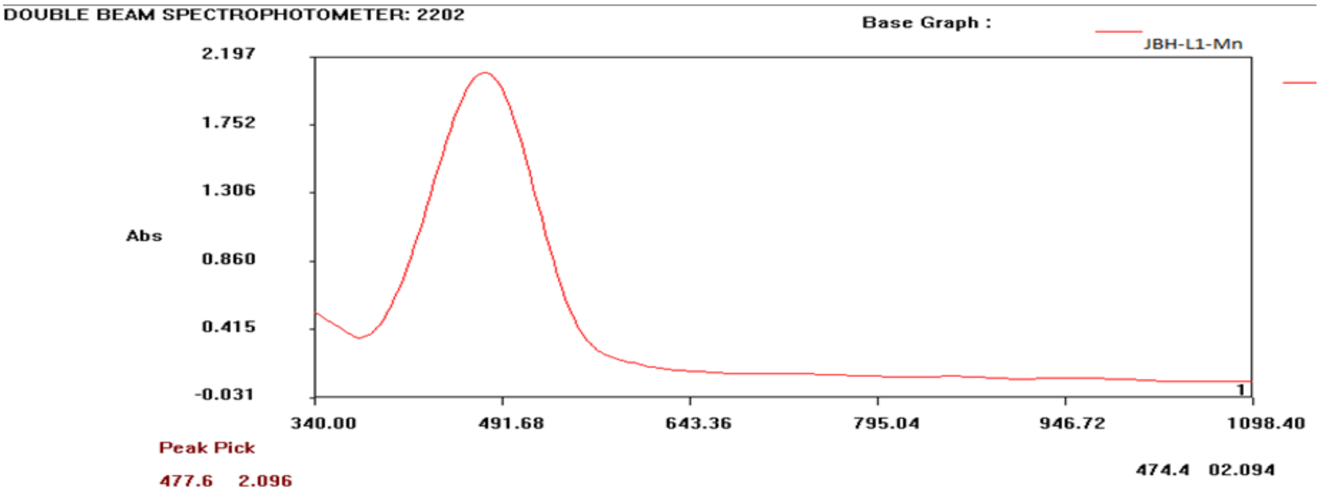
The thermal decomposition profile of Co(II) complex of ligand show no weight loss up to 150°C. The mass loss of 6.5% (calcd. 6.14%) is observed in the range 150-200°C. An endothermic peak between 140-210°C (ΔTmin = 180°C), correspond to the loss of two molecules of water. The second step decomposition 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 exotherm 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 upto 225°C and an inclined slope from 230°-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.

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 18248 cm^{-1}(ε= 26 $dm^3mol^{-1}cm^{-1}$), 20492 cm^{-1}(ε= 16 $dm^3mol^{-1}cm^{-1}$) and 33113 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[23,24] around the Mn(II) ion. The octahedral geometry of Mn(II) was further confirmed by the value of the magnetic moment (5.84 $_{\mu B}$).



Ultra-Violet Visible Spectra of Mn Complex

Three electronic transitions were observed in the electronic spectrum of the Fe(III) complex, at 14472 cm^{-1}(ε= 22 dm^{3}mol^{-1}cm^{-1}), 21322 cm^{-1}(ε= 26 dm^{3}mol^{-1}cm^{-1}) and 24272 cm^{-1}(ε= 32 dm^{3}mol^{-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 (5.69$_{\mu B}$) [23].

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 $C_{17}H_{17}NO_4$	-	32442 40545	INCT^a INCT	-
$C_{34}H_{32}FeN_2O_8$	5.74	15924 21598 24331	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4E_g(G)$	Octahedral
$C_{34}H_{32}CuN_2O_8$	1.95	15083 24937	$^2E_g \rightarrow {}^2T_{2g}$ INCT	Distorted Octahedral
$C_{34}H_{32}CoN_2O_8$	4.92	9794 18726 23923	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	Octahedral
$C_{34}H_{32}MnN_2O_8$	5.69	18248 20492 33113	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ $^6A_{1g} \rightarrow {}^4A_{1g}$	Octahedral
$C_{34}H_{32}NiN_2O_8$	2.99	9671 14880 25125	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	Octahedral

The electronic spectrum of the Co(II) complex exhibited three bands at 9794 cm^{-1}(ε= 17 dm^{3}mol^{-1}cm^{-1}), 18726 cm^{-1}(ε= 59 dm^{3}mol^{-1}cm^{-1}) and 23923 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 4.92 $_{\mu B}$. The calculated spectral parameters ν2/ν1, 10Dq, B, β 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}(ε= 34 $dm^3mol^{-1}cm^{-1}$), 14880 cm^{-1}(ε= 67 $dm^3mol^{-1}cm^{-1}$) and 25125 cm^{-1}(ε= 188 $dm^3mol^{-1}cm^{-1}$), 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 (2.99 $_{\mu B}$), 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}(ε= 94 $dm^3mol^{-1}cm^{-1}$), 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 (ε= 1143 $dm^3mol^{-1}cm^{-1}$) 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 diffractograms of Cu(II) complex are presented in (Fig. IV). X-ray powder data of all the main peaks having relative intensity greater then 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 $2\theta = 7.562^o$ corresponding to the value of d = 11.6810Å. 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 this 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 $2\theta = 25.7^o$ corresponding to the value of d = 3.4636Å. 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 2θ =

13.510^{o} 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.

Conclusion :-

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. 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.

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