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Synthesis, Characterization and Biological Study of Ni(II) Metal Complex of Hydrazone Schiff Base Ligand

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ABSTRACT :Synthesis of Ni(II) metal complex using tridentate Schiff base ligand (*E*)-4-hydroxy-*N'*-(1-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3yl)ethylidene)benzohydrazide. Which is synthesized from reaction of 3-acetyl-4-hydroxy-1-methyl-2(*1H*)-quinolone with 4-hydroxybenzhydrazide. Ligand were subjected to elemental analysis, UV visible, magnetic susceptibility, FTIR, ¹H NMR spectra, mass spectra. The complex was subjected to elemental analysis, UV visible, magnetic susceptibility, FTIR, ¹H NMR spectra, mass spectra and antimicrobial activity. The micro analytical and physicochemical data suggested stiochitometry of the 1:2 metal to ligand. The geometry of the complex was octahedral. IR spectra indicate that free ligand exist in the hydrazone-ketone form in solid states. The ligand behaves as a neutral tridentate with coordination involving the carbonyl of 2(*1H*) quinolone, hydrazone nitrogen and keto oxygen of amide group that is ONO donor sites. The magnetic and spectral data indicate octahedral geometry for Ni(II) complex. The molar conductivity values indicating non electrolytic nature. The mass spectra and analytical data the stiochitometry of metal complex has been found to be the 2:1 ligand to metal ratio. The ligand and their metal chealts have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% against microbial strains, *E.coli*, *S. typhi*, *S. aureus*, *B. subtilis*. The antibacterial screening of ligand and it's Ni(II) complex illustrates that ligand and complex seems to be inert towards the gram positive bacteria *E. coli* and *S. typhi*. The complex show higher activity than ligand against gram negative bacteria *S. aureus* and *B. subtilis*. Antifungal activity of ligand and complex were tested *in vitro* against fungi that is *A. niger*, *P. chrysogenum*, *F. moniliforme*, *A. flavus* by poison plate method using potato dextrose agar medium at fixed (1%) concentration. Ligand does not show fungal activity but complex show better activity. It suggests that the incorporation of metal ion in the ligand results in increasing the antimicrobial activity.

Keywords :ONO donar ligand, octahedral complexes, ¹H NMR, LC-Mass, Biological activity.

I. INTRODUCTION

The development of the field of bioinorganic chemistry has increased. The coordination chemistry of hydrazones is an intensive area of study and numerous transition metal complexes. Coordination compounds derived from aroylhydrazones have been reported because of their antimicrobial[1], antitumor[2] and corrosion inhibitors. The interest in Schiff base complexes since it has been recognized that many of these complexes may serve as models for biologically important species[3]. Synthetic flexibility of these Schiff base hydrazones occupy special place because transition metal complexes of these ligands developed due to chelating capability[4]. They are versatile ligands in coordination chemistry because their wide range of applications in catalysis[5], medicine, corrosion and analytical chemistry[6,7]. In continuation of these studies[8-11] using hydrazone ligand bearing ONO donar set, here we report the synthesis, spectroscopic, thermogravimetric and p-XRD analysis of Ni(II) complex using tridentate Schiff base like hydrazone ligand (*E*)-4-hydroxy-*N'*-(1-(4-hydroxy-1-methyl-2-oxo-1,2-dihydroquinolin-3yl)ethylidene)benzohydrazide, derived from the condensation of 3-acetyl-4-hydroxy-1- methyl-2(*1H*)-quinolone and 4-hydroxybenzhydrazide

2 Experimental

All the chemical are of analytical grades. 1-methyl aniline, diethyl malonate, diphenyl ether, n-butanol, acetic acid, 4-hydroxybenzhydrazide and nickel nitrate salt. All chemicals were perched from SD fine chemicals. Solvents were dried and distilled before use according to standard methods[12]. The precursor 3-acetyl-4-hydroxy-1-methyl-2(*1H*)-quinolone was prepared by standard method [13].

2.1 Synthesis of ligand: The equimolar mixture of 3-acetyl-4-hydroxy-1-methyl-2(1*H*)-quinolone (0.01 mol) and 4-hydroxybenzhydrazide (0.01 mol) in methanol (30mL) were refluxed in the presence of catalytic amount of glacial acetic acid (5-10 drops) for 3 hours on rotaheating mantal. The reaction mixture was then cooled to room temperature and the solid compound formed was filtered. It was then washed with methanol and dried and recrystallized from mixture of ethanol-DMF. (Yield 85%, M.p. 230°C).

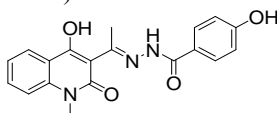


Fig. 1 structure of ligand

2.2 Synthesis of Ni(II) metal complex:

The complex was synthesized by adding drop wise hot solution of ligand in methanol (0.02 mol in 25mL) to hot methanolic solution of nickel nitrate salt (0.01 mol in 25 mL). This reaction mixture, 10% methanolic ammonia was added to adjust the pH of solution to 7.5 to 8.5. The reaction mixture stirred for 3-5 hours in warm condition on magnetic stirrer to get complex in solid form. The solid complex was filtered off, washed several times with methanol and dried in vacuum over CaCl₂.

2.3 Physical measurements

Elemental analyses (C,H,N,O) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR Spectrophotometer model RZXC Perkin Elmer in the range (400-4000 cm⁻¹), ¹H NMR spectra were recorded on Bruker Avance II at 400 MHz using tetramethyl silane as an internal standard. Electronic spectra were recorded using Shimadzu-1800 spectrophotometer using DMSO as a solvent. The LC-MS spectra were recorded on a Waters, Q-TOF Micro Mass (LC-MS) . Conductance were measured on Elico cm-180 Conductometer using 10⁻³M solution in DMSO. Room temperature magnetic data were collected on a Guoys balance using mercury (II) tetrathiocyanato cobaltacetate (II) as a calibrant. Diamagnetic contributions were estimated for each compound by using Pascal's constants.

2.4 Antimicrobial activity

The antibacterial activity were performed against microbial strains, *E.coli*, *S. typhi*, *S. aureus*, *B. subtilis* by agar-cup method at fixed concentration of 1% in DMSO. In this method test was performed on nutrient agar cup of 10 mm diameter were borered in the agar plate with sterile cork borer. All solutions were prepared in DMSO (1%) was added on cup, one cup blank DMSO and other for standard reference. The plates were incubated for 24 h at 37°C. The diameters of zones of inhibition for all test compounds were measured and the results compared with Penicillium of the same concentration as that of the test compounds under identical conditions.

Antifungal activity of the compounds was evaluated against fungi that is *A. niger*, *P. chrysogenum*, *F. moniliforme*, *A. flavus* by poison plate method using potato dextrose agar medium at fixed (1%) concentration. The plates were incubated at 37°C for 48 h. The diameters of the zone of inhibition for all the test compounds were measured and results compared with standard drug Grisofulvin of same concentration under identical conditions.

III. RESULTS AND DISCUSSION

The Schiff base is soluble in DMF, DMSO and insoluble in common organic solvents. The purity of ligand checked by elemental analysis, FT-IR, ¹HNMR and LC-Mass. The physical characteristics of the Schiff base and its metal complex is given in Table 1. The metal complex is soluble in ethanol, methanol and water. The elemental analysis data of the Schiff base and its Ni(II) metal complex are consistent with the calculated results from the empirical formula.

3.1. Conductivity measurements

The molar conductivity values for freshly prepared DMSO (10⁻³M) solutions of the complex indicate that complex is non electrolytic in nature [14].

Table 1 : Physical, Analytical Data of Ligand and its Metal Complexes

Compound	Mol. formula	Colour	M.P. °C	Mol. Wt.	C% Found (Calculated)	H% Found (Calculated)	N% Found (Calculated)	O% Found (Calculated)	Metal Found (Calculated)	μ_{eff} B.M.	Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
HL	(C ₁₉ H ₁₇ N ₃ O ₄)	white	230	351	64.91 (64.96)	5.58 (4.87)	10.04 (11.95)	18.04 (18.21)	--	--	---
(NiL ₂)	(C ₃₈ H ₃₄ N ₆ O ₈ Ni)	Green	>250	761	59.45 (59.94)	4.93 (4.49)	11.83 (11.03)	17.01 (16.81)	7.82 (7.70)	Diamagnetic	6.9

3.2. Magnetic and Electronic Spectral studies

The electronic spectra of ligand and Ni(II) complex was recorded in DMSO solution 10^{-3}M molar concentration. The electronic spectrum of ligand exhibits three absorption transitions at 357.5 nm (27972 cm^{-1}), 289.5 nm (34542 cm^{-1}) and 261.5 nm (38240 cm^{-1}) assigned to the $n-\pi^*$ and $\pi-\pi^*$ transitions of azomethine, 2-quinolone and 4-hydroxy group respectively.

The electronic spectrum of Ni(II) complex exhibited absorption bands at 417.5 nm (23952 cm^{-1}) and 333 nm (30030 cm^{-1}) due to ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{p})$ and charge transfer band respectively consistent with diamagnetic octahedral configuration [15]

3.3. Infrared spectra

IR spectral data of ligand and their Ni(II) metal complex is given in **Table 2**. The spectra of ligand display bands in the region 3333, 3178, 1634, 1587, 1610, 1176, 754 cm^{-1} due to enolic -OH group of 4-hydroxy-2(1H)-quinolone, -NH stretch of hydrazone, $>\text{C}=\text{O}$ (quinolone), $>\text{C}=\text{N}$ (azomethine), $>\text{C}=\text{O}$ (amide), aromatic -OH and -NH out of plane bend respectively. The careful investigation of the spectra of the complex and ligand indicate that the bands of -OH, -NH are present in the spectra of complex indicating non coordination with metal ion. They observed at lower frequency in complex may due to its presence in chelate system rather than the open system of the ligand.

Table 2
Salient Features of IR Spectral Data of Ligands.
 (Assignment of band frequencies to bond vibration modes)

Ligands /complex	$\nu(\text{OH})$ Enolic	$\nu(\text{NH})$ Hydrazone	$\nu(\text{C}=\text{O})$ Quinolone	$\nu(\text{C}=\text{N})$ Azomethine	$\nu(\text{C}=\text{O})$ amide carbonyl	$\nu(\text{NO}_2)$	$\nu(-\text{NH})$ out of plane
Ligand	3333 (b)	3178 (b)	1634 (s)	1587 (b)	1610	1176 (s)	754 (s)
NiL ₂	3348	3215	1596	1487	1556	1164	751

3.4. The ¹H-NMR Spectra of Ligand and Complex

¹H-NMR Spectra of ligand and Ni(II) complex was recorded in DMSO over the range 0-20 δ ppm. In ligand signals at 2.74 δ ppm. (s,3H, N=C-CH₃) assigned to azomethine protons, 3.53 δ ppm.(s,3H,N-CH₃), 7.20-8.14 δ ppm (m, 8H, aromatic), 10.23 δ ppm ¹H (s 1H -OH substituted on hydrazide) 11.29 δ ppm ¹H (s broad N-H), 16.76 δ ppm ¹H (broad hump, enolic-OH). In ¹H NMR spectra of Ni(II) complex indicates presence of broad signal at 10.30 δ ppm due -NH proton of hydrazone indicating non enolization of -NH with amide carbonyl in both complex. 9.04 δ ppm observed at ¹H (s 1H -OH substituted on hydrazide). There is slightly upfield shift due to change of environment of free ligand and complexation of ligand with metal. In Ni(II) complex aromatic frequency observed in the range of 8.82-6.55 δ ppm. N-CH₃ signal observed at 3.64 δ ppm., azomethine frequency observed at 2.82 δ ppm. (s,3H, N=C-CH₃) here also upfield shift in frequency observed in complex than ligand. In complex there is upfield shift in NMR frequency than free ligand indicating formation of complex takes place [16].

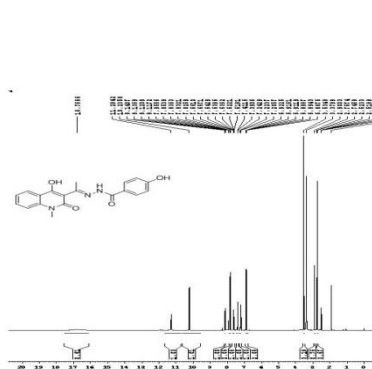


Fig.2 ¹H NMR of Ligand

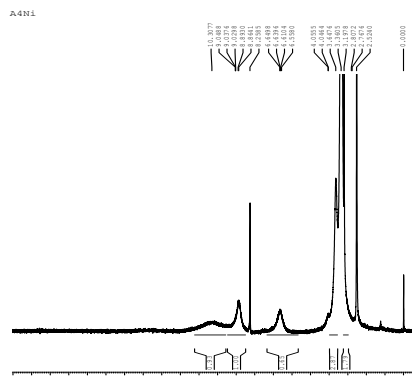


Fig.3 ¹H NMR of Ni(II) complex

3.5. Mass spectra of ligand and Ni(II) complex

Mass spectrum of the ligand and complex supports its proposed formulation. It reveals the molecular ion peak m/z at 352.2, 353.1 a.m.u. due to (M+1) and (M+2) molecular ion peak, consistent with the molecular weight of the ligand. The mass spectra of the Ni(II) complex molecular ion peak observed at 762.02 m/z which is match with their calculated mass.

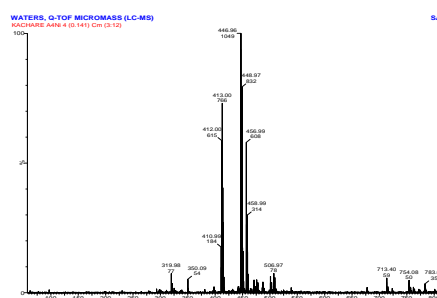


Fig.4 Mass spectra of Ni(II) complex

From above results the structure of complex is as follows

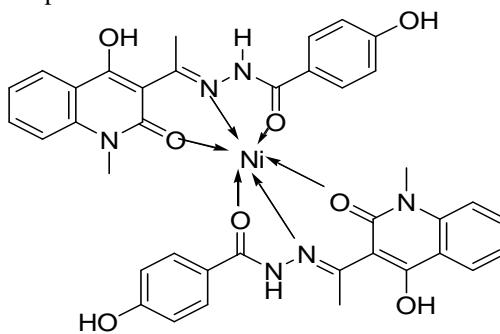


Fig.5 Structure of Ni(II) complex

IV. BIOLOGICAL ACTIVITY OF THE COMPOUNDS

4.1. In vitro antibacterial activity of the compounds

The antimicrobial activity of the ligand and complex was tested against the standard microbial strains, *Escherichia coli*, *Salmonella typhi*, *Staphylococcus aureus*, *Bacillus subtilis* by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter were borered in the agar plate with sterile cork borer. All solutions were prepared in DMSO(1%) was add on cup, One cup for DMSO as blank and other for standard reference Penicillium was also placed on the seeded nutrient agar. Then the plates were shifted to incubator at 37°C and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in **Table 4**

Inspection of the data revealed that complex and ligand lack the activity towards the Gram-negative bacteria *E. coli* and *S. typhi*. On the other hand, ligand and complex shows activity against Gram-positive bacteria *S. aureus* and *B. subtilis*. Activity of Ni(II) complex shows highest antibacterial activity than ligand.

Table 4: Report for Antibacterial testing.

compound	Method- Agar cup method cup size - 10 mm			
	<i>Bacillus subtilis</i> (mm)	<i>Stapylococcus aureus</i> (mm)	<i>Escherichia coli</i> (mm)	<i>Salmonella typhi</i> (mm)
Ligand(L)	14	12	--	--
(NiL ₂)	34	29	--	--
Penicillium	14 mm	20 mm	36 mm	28 mm

4.2. In vitro antifungal activity of the compounds

Compounds were screened in vitro against *Aspergillus niger*, *Penicillium chrysogenum*, *fusarium moneliforme*, *Aspergillus flavus*, by poison plate method with potato dextrose agar media. The compound [Gresiofulvin was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrome wire loop. The plates were incubated at room temperature for 48 hours. The result obtained are presented in

Table 5. Ligand does not show antifungal activity but it's Ni(II) complex shows appreciable activity. Antifungal activity of complex increased several times on being coordinated with metal ions. Ni(II) complex shows more than 90% reduction of fungal growth for all fungi.

Table 5 : Report for Antifungal testing

Compound	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium Moniliforme</i>	<i>Aspergillus flavus</i>
Ligand	+ve	+ve	+ve	+ve
(NiL ₂)	-ve	-ve	-ve	-ve
Grisefulvin	-ve	-ve	-ve	-ve

Legends- +ve - Growth -(Antifungal Activity absent)
-ve - No growth (More than 90 % reduction in growth Antifungal activity present)
RG - Reduced Growth.

V. CONCLUSION

In the light of above discussion we have proposed octahedral geometry for complex. On the basis of physicochemical and spectral data discussed above, one can assume that the ligand behaves as, ONO tridentate, coordinating via quinolone carbonyl, azomethine nitrogen and amide oxygen in both complexes. The mass spectra of ligand and its Ni(II) metal complex are in great accordance with calculated and observed. The complex is biologically active and having greater activity compared to free ligand.

VI. ACKNOWLEDGEMENTS

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Preparation and Properties of binuclear Schiff Base Complexes of Cu (II) Co(II) and Ni(II) Inter-complex Reaction

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ABSTRACT: Homo and hetero binuclear Schiff base complexes of Ni(II), Cu (II) and Co (II) were prepared by inter-complex reaction between the corresponding metal complexes of 2-hydroxy-1-naphthaldehyde and 2-amino-3-hydroxy pyridine. The complexes were characterized by elemental analysis and estimation of metals. Thermal behavior of the complexes was studied by TG-DTA analysis. Structures of the complexes were elucidated by spectroscopic methods like, infrared spectroscopy, UV-visible spectroscopy, mass spectrometry and ¹H NMR spectroscopy. The powder X-ray diffraction study suggested crystalline nature of the complexes with tetragonal geometry. Magnetic moments and electronic spectra reveal tetrahedral structure of the complexes. Antibacterial activity of complexes were studied against Gram-positive bacteria, *Staphylococcus aureus*, *Bacillus subtilis* and Gram-negative bacteria, *Salmonella typhi*, *Escherichia coli* by agar cup method. Their antifungal activity was also tested against *Aspergillus niger*, *Penicillium chrysogenum*, *Fusarium moniliforme* and *Aspergillus flavus* by poison plate method using potato dextrose agar medium at one percent concentration. All complexes show considerable antimicrobial activity.

KEYWORDS: Schiff base, inter-complex reaction, binuclear complex, biological activity

I. INTRODUCTION

Mixed metal complexes differ from traditional complexes in the sense that they are having at least two different or same metals associated with two different ligands (metal organic ligands) the presence of more than one type of ligands in a complex increases chances of variation in properties expected for the complex. This makes the researcher interested in the synthesis of mixed metal complexes with varying properties. [1] Synthesis and characterization of mixed metal complexes is gaining importance day by day. The increased interest in this research area has motivated many researchers to get involved in this field. In recent years many publications are devoted to synthesis and characterization of mixed metal as well as ligands complexes. [2-6] The Schiff base complexes were also used as drugs and they possess a wide variety of antimicrobial activity against bacteria, fungi and it also inhibits the growth of certain type of tumors. [7-8] The complexes formed by coordination with metal ions, have the tendency to coordinate further or react with other complexes, then they may act as metal organic ligand (MOL). The donor atoms are unable to coordinate with the same metal ions due to steric factors. This unutilized functionality is drawn on another metal ion forming poly nuclear complex [9-10]

Here a complex containing some unutilized functionality in ligand is considered as a ligand and named as metal organic ligand (MOL). This (MOL) when allowed to react with metal ions result in the formation of mixed metal complexes. We report here, a novel approach of synthesizing mixed metal complexes. It has been hypothesized that the coordinated ligands of two metal chelates can be reacted to obtain a new metal chelate. In the present work, we have allowed two such complexes under the conditions that permit coordinated NH₂ to react with the coordinated CHO group. Here an ionic bonds of the precursor do not dissociate and metal-ligand bonding in both the complexes remains intact [11]. Due to the reaction between coordinated amine and aldehyde groups, Schiff bases were formed. The imine nitrogen of the Schiff base was allowed to coordinate with the metal nearby while the deficiency created at the metal ion on aldehyde end was sufficed by aqua-ligands liberated during imine formation. The resultant binuclear complex thus has one of the metal ions in di aqua form. When the metal ion in the reacting complexes was different, the resultant complexes were mixed metal complexes [12].

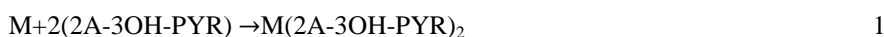
II. MATERIALS AND METHOD

Reagents: 2-amino 3-hydroxy pyridine and 3-ethoxy salicylaldehyde (>99.0%) were purchased from S.D. Fine Chemicals. Nickel acetate, copper acetate, sodium hydroxide and solvents (>99.0%) were purchased from E-Merck Ltd, Mumbai (India). The purification was done according to the needs through known procedures.

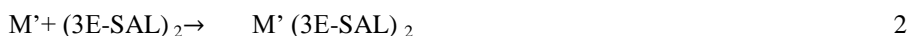
Measurements: Elemental analysis (C, H, N & O) was done using Perkin Elmer, series II, 2400 CHNS/O Analyzer. The metal content of the complexes were determined by EDTA titration method after decomposition of the metal complexes with an acid mixture of HClO_4 , H_2SO_4 and HNO_3 (1:1.5:2.5) in case of $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$. The amount of Fe(II) from homo binuclear complex of Fe(II) viz $\text{Fe}_2(\text{SB})_2(\text{H}_2\text{O})_2$ was determined by EDTA titration method. $\text{FeZn}(\text{SB})_2(\text{H}_2\text{O})_2$ was done by separating the iron from zinc. Solution containing a mixture of metal ions, before precipitating iron as hydroxide, add 5grms of NH_4Cl to retain zinc in the solution. Now estimate the iron as iron oxide gravimetrically. Reserve the filtrate and washings for volumetric estimation of zinc by titrating against standard EDTA solution volumetrically. In the same manner separation and estimation metals of $\text{FeMn}(\text{SB})_2(\text{H}_2\text{O})_2$ can be done by separating iron as iron oxide gravimetrically and Mn(II) volumetrically by titrating against standard EDTA solution volumetrically. All chemicals used were of analytical grade and used without purification. All metal salts were purchased from SD fine chemicals. Elemental analysis (C, H, N, O) were performed on Perkin Elmer-2400. IR spectra were recorded on FTIR spectrophotometer model RZXC Perkin-Elmer in the range (4000-400 cm^{-1}), ^1H NMR spectra were recorded on Bruker Avance II at 400 MHz using tetramethylsilane as an internal standard. Electronic spectra was recorded on the Shimadzu 1800 spectrophotometer using DMSO as a solvent. Mass spectra were recorded on Waters, Q-TOF Micro Mass (LC-MS). Magnetic data at room temperature were collected on Gouy balance. Mercury (II) tetrathiocyanate cobalt acetate was used as a calibrant. Diamagnetic contributions were calculated for each compound by Pascal's constants. TGA/DTA analysis was performed in an inert nitrogen atmosphere on Perkin Elmer STA 6000. Heating rate was $10^\circ/\text{min}$. x-ray diffractogram was scanned on Bruker AXS D_s.

Synthesis of Metal Complexes:

The method used in the synthesis of metal complexes consists of following three steps. In the first step, 2-amino-3-hydroxy pyridine (2A-3OH-PYR), (0.404gm) in absolute alcohol (~20mL) was prepared and a solution of Copper /Cobalt / Nickel acetates (0.497g/0.399g) in rectified spirit (20mL), were mixed, stirred for an hour to obtain a four coordinated complex, $\text{M}(2\text{A}-3\text{OH}-\text{PYR})_2$ in solution as shown in equation-1,



In the second step, 3-ethoxy salicylaldehyde (3E-SAL), (0.665 g) in absolute alcohol (~20ml) was prepared and a solution of Nickel/Copper /Cobalt acetates (0.5g, 0.1m) in rectified spirit (~20ml), were mixed and stirred for an hour to obtain a four coordinated complex, $\text{M}'(3\text{E}-\text{SAL})_2$ in solution. The reaction is shown in equation 2.



In third step, a solution of $\text{M}(2\text{A}-3\text{OH}-\text{PYR})_2$ was added to the refluxing solution of $\text{M}'(3\text{E}-\text{SAL})_2$. The reaction mixture was refluxed for 6-hours in a water bath to obtain the product under slightly alkaline condition created by sodium hydroxide. The precipitate was then filtered, washed with ethanol and dried over fused CaCl_2 . The third step of the reaction is depicted in equation 3.



All complexes were prepared by the above discussed method. The heterodinuclear complex, whereas homobinuclear complex, $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$, $\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$ and $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$ were obtained when $\text{M}=\text{Cu}$ and $\text{M}'=\text{Co}$ (II), Ni(II) respectively in heterodinuclear complexes and $\text{M} \& \text{M}'=\text{Cu}$ in mononuclear complex. The melting points of all the complexes were found to be higher than 300°C .

III. RESULTS AND DISCUSSION

IR Spectra : The IR Spectra of reactant complexes and dinuclear complexes displayed some similarities and dissimilarities, Significant IR bands are shown in Table 1. The spectra of the reactant complex $\text{M}(2\text{H}-3\text{AP})_2$ showed a strong absorption at 1551 cm^{-1} frequency¹ which was assigned to coupled vibrations of NH_2 bending and stretching



[13] absorptions at 3330 cm^{-1} were attributed to NH_2 asymmetric and symmetric stretching frequency respectively. A weak band at 556 cm^{-1} was observed in the complex which was assigned to the M-N stretching .

IR spectra of reactant complex $\text{M}^+(3\text{E-S})_2$ exhibited a broad band and strong peak at 1530 cm^{-1} which was assigned to C=O stretching in the complex. A weak band at 456 cm^{-1} observed in the spectra was due to M-O stretching frequency. Both the complexes showed a band in the region of 3330 cm^{-1} & 3365 cm^{-1} arising due to aromatic ring vibrations the spectra of both the reactant complexes did not show a broad band in the region of 3400 cm^{-1} which indicated the absence of any coordinated water molecule.

In the spectra of resulting binuclear complexes viz $\text{MM}^+(\text{SB})_2(\text{H}_2\text{O})_2$ peak due to C=O stretching (1530 cm^{-1}) NH_2 bending and NH_2 stretching (1551 cm^{-1}) was found to be absent .New stronger bonds appearing at $547\text{-}582\text{ cm}^{-1}$ and $401\text{-}460\text{ cm}^{-1}$ were assigned to M-O and M-N stretching frequencies. A broad band in the region 3400 shows presence of two coordinated water molecules and a sharp and strong peak between $1600\text{-}1597\text{ cm}^{-1}$ which may be attributed to C=N stretching was in accordance with the proposed structure of the complex.

Table 1: FT-IR Spectral frequencies of Complexes

System	VC=N cm^{-1}	VO-H cm^{-1}	VM-O cm^{-1}	VM-N cm^{-1}
$\text{M}^+(3\text{E-S})_2$			556	
$\text{M}(3\text{H-2AP})_2$			594	418
$\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$	1608	3411	539	466
$\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$	1608	3456	539	468
$\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$	1608	3434	540	418

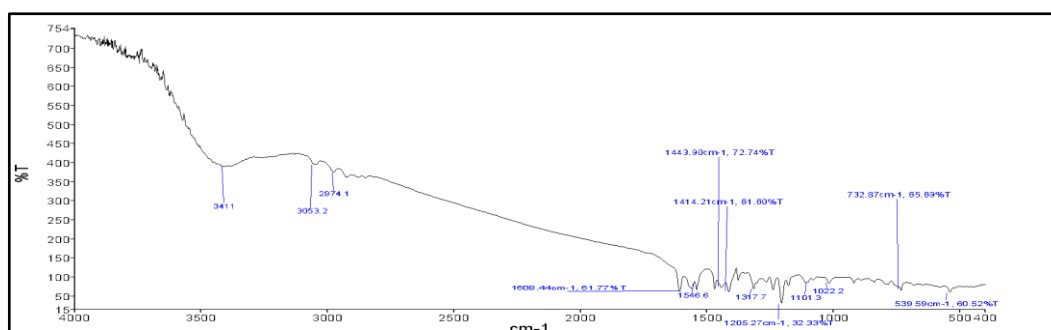


Fig : $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$

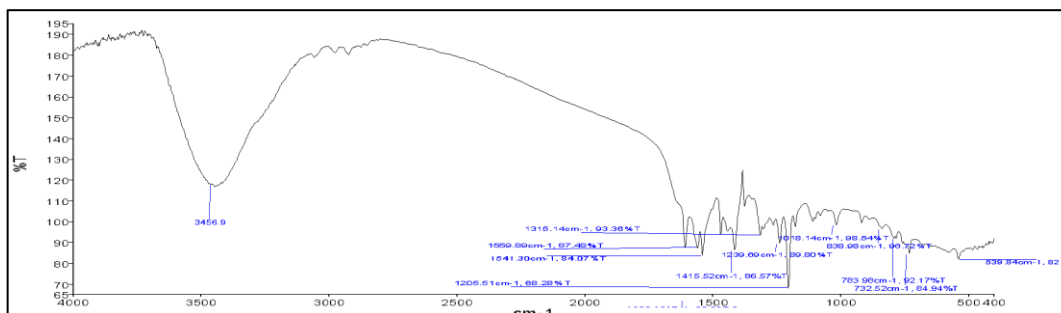


Fig : $\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$

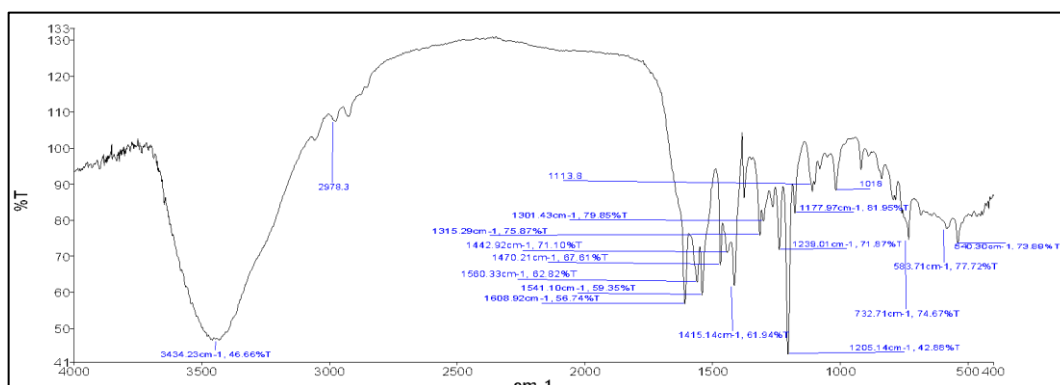


Fig : CuNi (SB)₂(H₂O)₂

Electronic Spectra and Magnetic Studies

All the complexes showed absorption peaks in the near UV region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand. The spectra of the homodinuclear complex Cu₂(SB)₂(H₂O)₂ is characterized by two weak bands at region, 22222 cm⁻¹ & 24509 cm⁻¹ assigned to 5T_{2g}→3T_{1g}, 4A_{2g}→4T_{1g} transitions respectively. The effective magnetic moment at room temperature for Cu₂(SB)(H₂O)₂ was found to be 2.21BM for each Cu(II) ion that was slightly higher than the suggested magnetic moments for the tetrahedral geometry of Copper[14]. The spectra of Hetero nuclear complexes complex CuCo(SB)₂(H₂O)₂ is characterized by two weak bands at region, 13,114 cm⁻¹ (762nm), 24,301 cm⁻¹ (411nm) assigned 3T_{2g}(F) →3T_{2g}(F), 6A_{1g}→4A_{1g}Eg (G) transitions respectively and charge transfer transitions indicating tetrahedral geometry around the metal ions. In the present investigation electronic spectra of the complex shows absorption peaks in the near ultra-violet region and these high intensity bands were due to $\pi \rightarrow \pi^*$ transition in the aromatic group of ligand [15]. The electronic absorption spectra of CuNi (SB)₂(H₂O)₂ complex, bands observed at 15,337 cm⁻¹ (652nm), 21,032 cm⁻¹ (475nm), assigned to 3T_{2g} →3T_{1g}, 3T_{2g}(F)→3T_{1g}(p), 4A_{2g}→4T_{1g} and charge transfer transition indicating tetrahedral geometry around the metal ions. The higher value of the effective magnetic moment suggests the presence of some ferromagnetic interaction at room temperature. On the basis of physico-chemical and spectral study, Following structure may be proposed for the complexes.

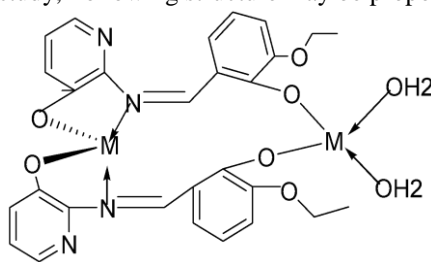


Fig-1 Proposed structure for the complexes

Table2: Physicochemical and analytical data of metal complexes

System	Mol. Wt g/mole	Color	% Yield	μ_{eff} per ion B.M.	Elemental Analysis % Found (Calculated)						
					C	H	N	O	Cu (II)	Ni (II)	Co (II)
Cu ₂ (SB) ₂ (H ₂ O) ₂	664	Dark brown	80	2.29	41.00 (41.15)	2.20 (2.21)	6.66 (6.71)	17.60 (17.64)	17.50 (17.68)	18.64 (18.87)	
CuNi(SB) ₂ (H ₂ O) ₂	663	Yellowish Green	74	*	50.20 (50.30)	3.20 (3.29)	8.29 (8.37)	9.49 (9.57)	9.48 (9.51)	8.89 (8.87)	



$\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$	668	brown	72	*	49.49 (49.50)	2.80 (2.75)	8.00 (7.89)	9.50 (9.57)	8.79 (8.81)		9.45 (9.50)
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Mass and ¹H-NMR Spectra of the Complexes:

Mass Spectra

The molecular weights of all the binuclear complexes are exactly equal to that calculated theoretically from the proposed structures. These results are further supported by the conclusions drawn from the elemental analysis which agree with the molecular formula assigned to these complexes.

Formation of binuclear metal complexes and their structure is confirmed by ¹HNMR spectral study of representative metal complexes. The result obtained was used to interpret the proton environment and number of protons present in the sample. The ¹HNMR spectra of complex is presented in Fig 2 where as the characterization of particular protons are presented in Table 3

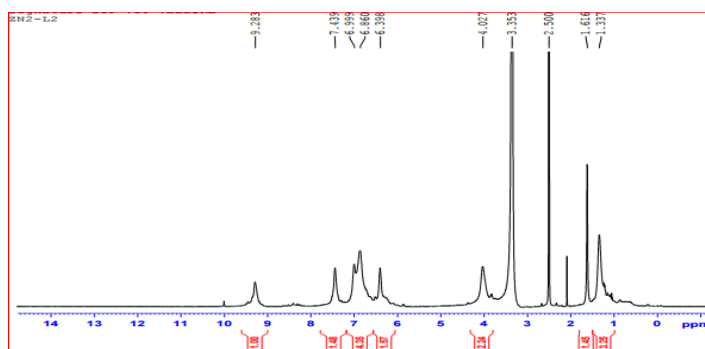


Fig:2 ¹HNMR Spectrum of $\text{Ni}_2(\text{SB})_2(\text{H}_2\text{O})_2$

Table 3

Chemical Shift 'δ'ppm	Numbers of Protons	Multiplicity (Splitting)	Assignment
1.337	3H	S	Methyl hydrogen of Ethoxy group
4.027	2H	S	Methylene hydrogen of Ethoxy group
6.398-7.439	12H	M	Hydrogen of aromatic ring and heterocyclic pyridine
9.283	1H	S	Imine proton

The thermogram of $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$ complex is presented in (Fig.4). The curve reveals that there is presence of lattice as well as coordinated water molecules in the complex.

TG curve of $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$ complex (Fig4) shows mass loss within temperature range 50-150°C due to one lattice water molecule. An endothermic peak observed in DTA at 100 °C supports it. The second step of decomposition up to 300°C with mass loss 6.9% (calc. 7%) corresponds to elimination of two coordinated water molecules. An endothermic peak in the range 280°C was observed in the DTA curve which supports it and is attributed to the removal of two coordinated water molecules. The third step decomposition takes place up to 500°C. This decomposition suggests



removal of the organic part of the complex as four molecules of benzene ring fragments which is confirmed by an endothermic peak at 350°C and 450°C in the DTA curve.

In the fourth step sudden decomposition within temp range 500°C-700°C with weight loss of 28.5% (calc.28.9%) corresponds to decomposition of actual coordinated part of the complex above which is residue attains constant weight corresponding to metal oxide as a final product.

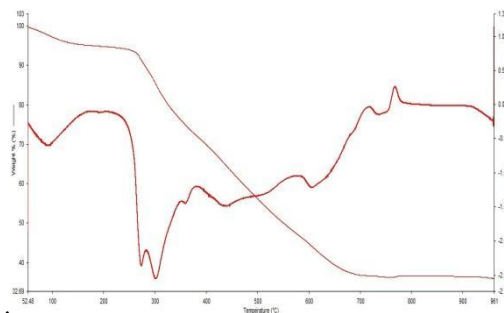


Fig:5 CuNi(SB)₂(H₂O)₂

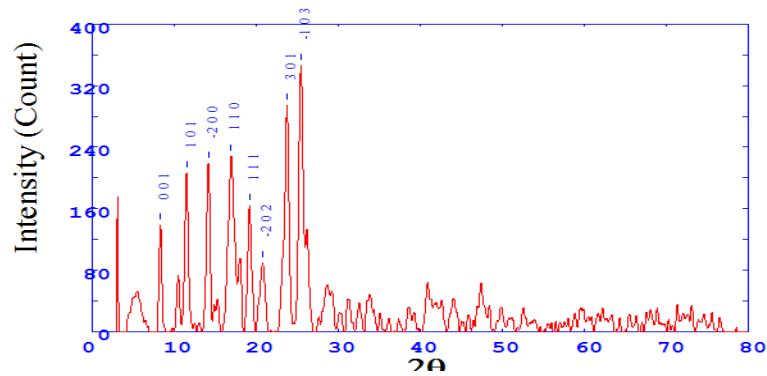
Table:4 Thermodynamic and Kinetic Parameters

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol ⁻¹)	ΔS(KJ mol ⁻¹)	ΔG(KJ mol ⁻¹)	Zx10 ⁻⁴ (S ⁻¹)	Correlation Coefficient(r)
CuNi(SB) ₂ (H ₂ O) ₂	H-M	I	769	0.99	67.33	154.669983	78.3660297	10.337266	0.999
	C-R				64.76	152.351811	75.6254401	13.660574	0.999
	H-M	II	820	0.99	28.39	161.103398	42.0112433	5.6536042	0.999
	C-R				2912	101.550337	37.7107456	72.848973	0.999

Powder X-ray diffraction data.

CuCo(SB)₂(H₂O)₂ complex was used to study the X-ray powder diffraction. Diffractogram is presented in Fig. 6 The standard deviation observed is within the permissible limit. The observed density for Cu₂(SB)₂(H₂O)₂ complex is 0.5gcm⁻³ while calculated density from Z value and unit cell volume for complexes is 0.50439 gcm⁻³ respectively. The porosity percentage calculated from the observed and calculated densities was found to 0.87035%. The crystal system was found to be tetrahedral with probable space group P. The lattice parameters reported are a = 13.48451 Å, b = 7.404824Å, c = 8.986458Å α= γ= 90° and β = 92.72° [17-18]

CuNi(SB)₂(H₂O)₂ complex was used to study the X-ray powder diffraction. Diffractogram is presented in Fig.7. The standard deviation observed is within the permissible limit. The observed density for CuNi(SB)₂(H₂O)₂ complex is 1gcm⁻³ 0.50439 g cm⁻³ while calculated density from Z value and unit cell volume for complexes is 0.50439 g cm⁻³ respectively. The porosity percentage calculated from the observed and calculated densities was found to 87.31%. The crystal system was found to be tetrahedral with probable space group P. The lattice parameters reported are a = 9.854336 Å, b = 7.1256431Å, c = 7.069273Å α= γ= 90° and β = 96.18°



: Fig 6: $\text{CuCo(SB)}_2(\text{H}_2\text{O})_2$

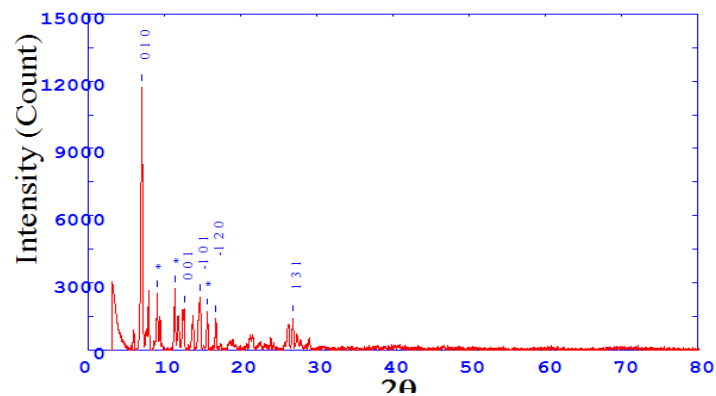


Fig.7: $\text{CuNi(SB)}_2(\text{H}_2\text{O})_2$

Table 5: Report for Antibacterial Testing.

Medium-Nutrient Agar
Method –Agar cup method

Dose of compound -1%
cup size-10mm

Sr. No.	Test Compound	Inhibition Zone (nm)			
		<i>Escherishia coli</i>	<i>Salmonella typhi</i>	<i>Staphylococcus aureus</i>	<i>Bacillus subtilis</i>
	Penicillin	14 mm	20 mm	36 mm	28 mm
1	$\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$	16	-ve	20	-ve
2	$\text{CuCo(SB)}_2(\text{H}_2\text{O})_2$	-ve	-ve	20	20
3	$\text{CuNi(SB)}_2(\text{H}_2\text{O})_2$	-ve	20	20	20

Table 6: Report for Antifungal Testing

Test compound	Inhibit			
	<i>Aspergillus niger</i>	<i>Penicillium chrysogenum</i>	<i>Fusarium moniliforme</i>	<i>Aspergillus flavus</i>
Grisofulvin	-ve	-ve	-ve	-ve
1 $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$	-ve	+ve	-ve	-ve
2 $\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$	RG	RG	-ve	RG
3 $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$	RG	-ve	-ve	RG

Complex: +ve growth = Antifungal activity absent -ve growth = Antifungal activity present
RG = reduced growth (more than 50% reduction in growth observed)

Antimicrobial activity of the complexes:

The antibacterial activity of the complexes were tested against the standard microbial strains.

Escherichia coli, *Salmonella typhi*, *Staphylococcus aureus* and *Bacillus subtilis* by agar cup method at fixed concentration of 1% [19] and compared with known antibiotic viz *Penicillium* (Table 5). For fungicidal activity, compounds were screened in Vitro against *Aspergillus niger*, *penicillium chrysogenum*, *Fusarium moniliforme*, *Aspergillus flavus* by poison plate method with potato dextrose agar media. The complexes were tested at 1% concentration in DMSO and compared with control (Table 6)

The complexes individually show varying degrees of inhibiting effects on the growth of the bacterial species. Some complexes show activity against Gram-negative *Escherichia coli*, *Salmonella typhi* & *Bacillus subtilis*. The some complexes show activity against Gram-positive bacteria *Escherichia coli* & *Bacillus subtilis*. The metal complex $\text{Cu}_2(\text{SB})_2(\text{H}_2\text{O})_2$ shows better activity for *Escherichia coli* however the activity of these complexes is higher than that of standard drugs. Also these complexes show better activity against *Staphylococcus aureus* but the activity is less than the standard drug. The complex $\text{CuCo}(\text{SB})_2(\text{H}_2\text{O})_2$ is found to be active against *Staphylococcus aureus*, *Bacillus subtilis* bacterium. However the activity of these complexes is less than that of standard drugs. The complex $\text{CuNi}(\text{SB})_2(\text{H}_2\text{O})_2$ is found to be active against *Salmonella typhi*. However the activity of these complexes is exactly equal to that of standard drugs. *Staphylococcus aureus*, *Bacillus subtilis*. However the activity of these complexes is less than that of standard drugs. Results of antifungal testing indicate that all the bimetallic complexes show moderate to high antifungal activity.

IV. CONCLUSION

The preparation of binuclear complexes by a novel synthetic route is strongly supported by analytical data. The formation of precursor complex as well as imines in binuclear complexes confirmed by existent and missing peaks in infrared spectra. The effective magnetic moment and electronic spectral data supported the tetrahedral environment in the metal ion. The presence of two coordinated water molecules was detected both from elemental analysis and thermo gravimetric analysis. The molecular ion peak in the mass spectra also supported the formation of binuclear complexes. Finally; the molecular mechanical method used for energy minimization corroborated the proposed structure of the complexes. The novel method to synthesize the binuclear complexes is capable of opening a new area in the preparation of complexes with a lot more variations.

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Synthesis, Characterization and Antimicrobial study of Manganese (II) Complex of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one

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ABSTRACT

The synthesis of Manganese (II) metal complex **1** has been synthesized by using novel (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one ligand. The ligand was prepared by the Claisen-Schmidt condensation method of 2,6-dihydroxy acetophenone and 2-furaldehyde. The structure of the complex has been characterized by the analytical data, conductivity measurement, magnetic moment, UV-Vis spectra, and thermal studies. Analytical data shows 1:2 stoichiometry and the magnetic moment, TG-DTA suggests that Mn(II) complex has octahedral geometry. The presence of coordinated water molecules in Mn (II) complex **1** is confirmed by thermal studies. The conductivity data reveals that the complex is non electrolyte. Antimicrobial study of complex with selected bacterial strain and fungal strain carried out and the results have been compared with commercial standards. The Mn (II) complex **1** shows moderate to good Antibacterial and Antifungal activity.

Keywords: Antimicrobial activities, TG-DTA study, Physico-chemical property, Magnetic Susceptibility and Conductivity.

I. INTRODUCTION

Chalcones and their metal complexes play an important role in modern coordination chemistry. These compounds possessing novel structural features, interesting spectral and magnetic properties, have been observed 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 bonded to olefinic linkage 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[1-3].

Chalcones constitute an important group of natural products, which has two aromatic rings joined by α, β unsaturated carbonyl system. The name chalcone is given by Kostanecki and Tambar [4]. The metal complexes

possess interesting biochemical properties, such as antitumor, antioxidant, and antimicrobial, anti-fungal and antimicrobial activities [5]. The magnetic moment, TG-DTA supports the octahedral geometry of the metal complex of chalcone.

II. MATERIALS AND METHODS

2.1. Synthesis of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one ligand:

The reagents used for preparation of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl) prop-2-en-1-one are of A.R. grade. A mixture of 2,6-dihydroxy acetophenone (0.01 mol) and 2-furaldehyde (0.01 mol) are dissolved in ethanol (20 mL) and then solution of potassium hydroxide 10 mL (15%) were added to it. The mixture was stirred for overnight. The progress of the reaction was monitored by TLC. It was then poured on ice cold water and acidified with dilute HCl. The coffee brown solid was precipitates, filtered and washed with water and recrystallized from ethanol to give the chalcone [6].

2.2. Synthesis of Metal Complex:

The solution of 0.02 mole of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was taken in round bottom flask containing 30 ml of anhydrous methanolic solution and boiled for 10 minutes. A hot solution of 0.01 mole, of Manganese Acetate in 20 ml of methanol was added drop wise to the solution of the chalcone of 5-methylfurfural to this reaction mixture, 10% alcoholic ammonia was added up to slightly alkaline pH. The complex was precipitated at 8 pH range. The pH 8-10 range was definite for these complexes [7]. The content was stirred on magnetic stirrer for one hour. The solid metal complex separated out and washed with methanol three to four times. The melting point of the complex was determined by Thiele's melting apparatus. The reactions of formation of Mn (II) complex 1 is shown in **Figure-1**.

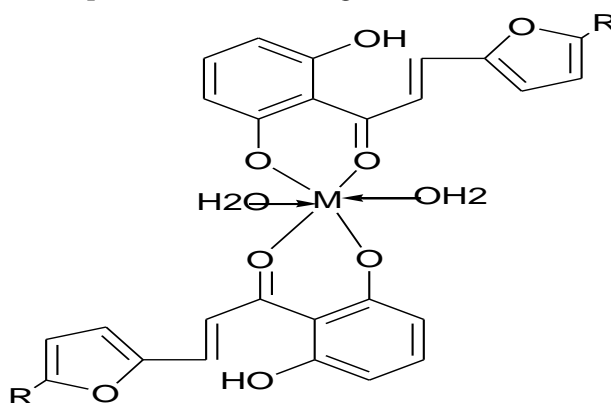


Figure-1: Metal complex 1 of Manganese (II) with (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one
R= -H, M= Mn(II)

III. RESULTS AND DISCUSSION

3.1. Physical parameters:

Metal complex 1 of Manganese (II) with (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was brown in color. The complex was precipitated at 8 pH range, having Melting point 320°C. The complex is insoluble in water and soluble in DMSO, DMF [8].

3.2. CHO analysis:

The carbon, hydrogen, oxygen, Manganese metal percentage in Mn (II) complex **1** of chalcone measured at SAIF Cochin, Kerala. The calculated and measured values of CHO analysis are matching and are given in the Table-1.

Table-1: Study CHO analysis of synthesized Mn (II) complex **1**

Metal complex	Chemical formula	Mol. Wt.	Elemental analysis : % found (calculated)						
			C	H	N	O	S	X(Br)	M
Mn (II) Complex	[C ₂₆ H ₂₂ O ₁₀ Mn]	549	56.84 (64.33)	4.03 (4.57)	-	29.12 (19.78)	-	-	9.99 (11.32)

3.3. Magnetic susceptibility, solution conductivity and electronic absorption spectral data Magnetic susceptibility:

The magnetic moment of Mn (II) complex **1** in the present investigation are in the range which is almost close to the spin only value of 5.92 B.M. These values are in good agreement with the moment reported for mononuclear high spin octahedral Mn (II) complex **1** by earlier workers [9].

Table-2: Study magnetic susceptibility, solution conductivity and electronic absorption of synthesized Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Mn(II) Complex	Molar Conductance Ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} (B.M.)	Absorption Maxima cm ⁻¹ (nm)		
			⁶ A _{1g} → ⁴ T _{2g} (G)	⁶ A _{1g} → ⁴ A _{1g} (G), ⁴ E _g	Charge Transfer
1	2.12	5.86	24937(401)	28571(350)	32154(311)

Solution conductivity and electronic absorption spectral data:

The solution conductivities of 10⁻³ M solution of metal complex in DMSO were measured on EQUIPTRONICS digital conductivity meter EQ - 660 with 20 μΩ to 200 μΩ at 298K temperature. They are insoluble in water and soluble in DMSO, DMF. The low solution conductivity of 10⁻³ M solutions of Mn (II) complex **1** in DMSO indicates their non-electrolytic nature.

Figure-2.



Figure-2: Electronic absorption spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

The electronic absorption spectra of Mn(II) complex **1** were showed three bands at 19,120 to 25000 cm⁻¹, 25125 to 27700 cm⁻¹, and 28993 to 30581 cm⁻¹ assignable to ⁶A_{1g}→⁴T_{2g}(G), ⁶A_{1g}→⁴E_{1g} or ⁶A_{1g}→⁴T_{1g}(G) and charge transfer indicating octahedral geometry around the metal ion [10-11].

3.4. Infra-red spectrum:

The IR spectrum of α, β-unsaturated carbonyl group has characteristic bands of chalcone at prominent bands between 1625 to 1650 cm⁻¹. The characteristic peaks in infra red spectrum give the presence of particular functional group. The region at which other absorption bands appear depends on the type of aromatic / hetero-aromatic rings as well as the substituent present on these rings. The infrared spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was recorded on a Perkin- Elmer Spectrum RX-IFTIR Spectrophotometer in the range 4000-400 cm⁻¹ (Table-2) using potassium bromide pellet at CIL, Chandigarh, Punjab. The stretching frequency of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one is represented in table number (2) and the IR spectrum in Figure-3.

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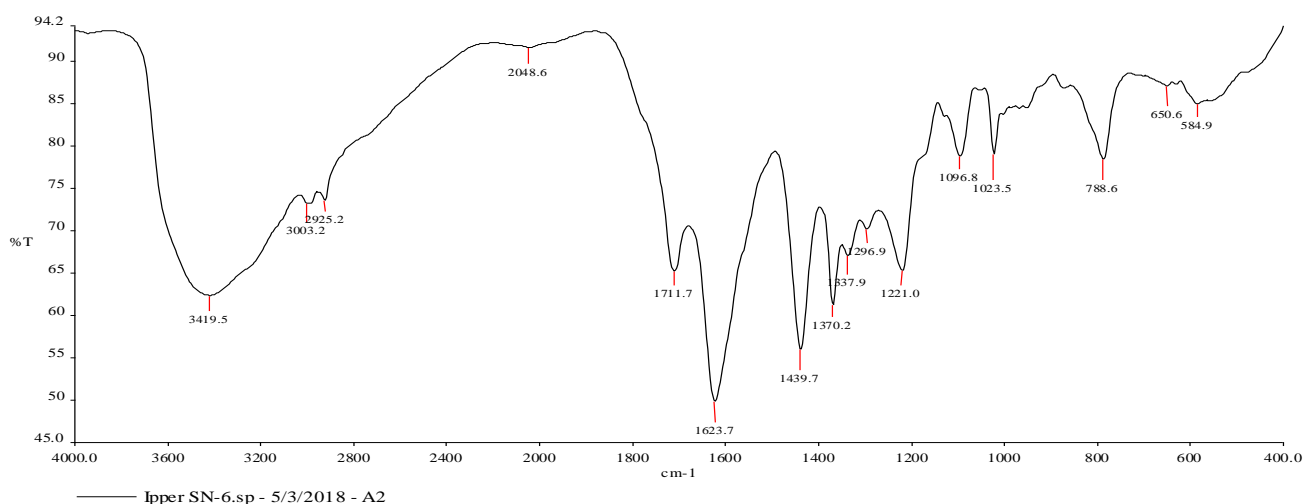


Figure-3: IR spectrum of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Table-3: IR spectral data of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Molecule	$\nu(\text{OH})$ (Enolic)	(-CO-CH=CH-) α,β -unsaturated carbonyl group	Carbon yl group (-C=O in pyron ring)	(C-O-C) Stretching Frequency	(C=C) Stretching Frequency	Aromatic Ring (C=C) Stretching Frequency	Ar-H Stretching Frequency	-NO ₂ stretching frequency
Ligand	3420	1652	-	1096	1575	1457	2920	-

3.5. Thermal analysis Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

The simultaneous thermo gravimetric, differential thermal analysis of Mn (II) complex **1** of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one was performed in an inert nitrogen atmosphere on Perkin Elmer STA

6000 at SAIF, Cochin, Kerala. The heating rate was 10°/min and flow rate of nitrogen 50 ml/min. The reference substance used was α Al₂O₃ in platinum crucible and sample weighted in the range of 4-12 mg. The thermogram of Mn (II) complex (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one is presented in figure-2. This curve reveals that there is presence of lattice as well as coordinated water in the complex.

The thermogram of Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one shows first weight loss at 60°C indicating presence of lattice water. The second loss due to the coordinated water molecule liberated, from the complex. The anhydrous compound undergoes four step decomposition. In the first two steps, decomposition occurs due to loss of non-coordinated part of ligand. The first step shows decomposition within a temperature of range from 240-330°C with mass loss of 39.29%, which is supported by a sharp endothermic peak at 259°C in DTA curve. It may be due to half decomposition of non-coordinated part of ligand. In the second step, decomposition observed at about 350-400°C with the weight loss of 33.78% in TG curve. This is supported by an endothermic peak at 380°C. This may be due to decomposition of remaining coordinated part of ligand. Beyond 600°C there is a formation of MnO as indicated by constant weight loss of in TG-DTA curve.

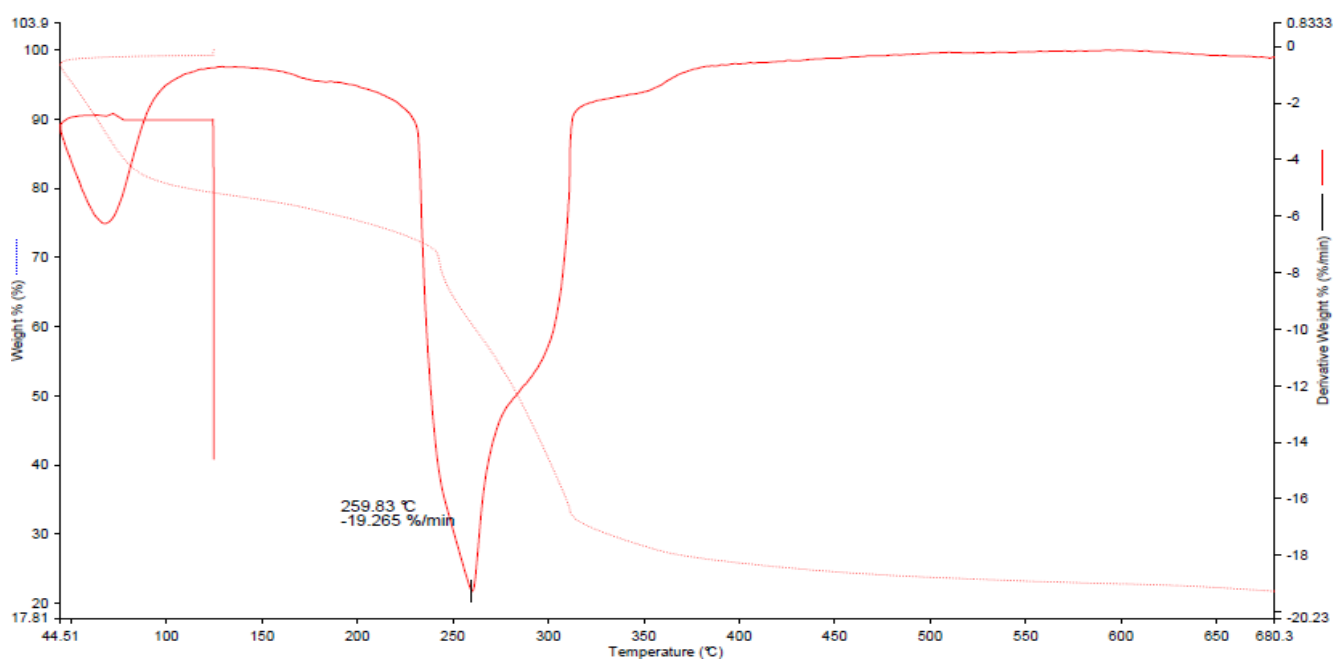


Figure-4: TG-DTA curve of Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

3.6. Thermodynamic and Kinetic Parameters

Akahira [12], first introduced that decomposition and kinetic studies of thermal reactions are useful in determining thermodynamic and kinetic parameters like free energy, entropy change, activation energy, pre-exponential factor. Thermal decomposition studies of materials are useful in predicting thermal stability (**Table-3**).

The negative values of the entropy of activation (ΔS) indicate that the metal complex is thermally stable. ΔG is positive for the complexes revealing that the free energy of the final residue is higher than that of the initial complex, and all decomposition steps are non-spontaneous processes. Also, the value of free energy of activation, ΔG increases significantly for the subsequent decomposition stages of a given complex [13]

Table-3: Thermodynamic and Kinetic Parameters of Mn (II) complex 1 of (E)-3-(furan-2-yl)-1-(2,6-dihydroxyphenyl)prop-2-en-1-one

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol ⁻¹)	ΔS(KJ mol ⁻¹)	ΔG(KJ mol ⁻¹)	Z (S ⁻¹)	Correlation Coefficient (r)
Mn (II) complex	H-M C-R	I	300	0.5	26.84 21.75	- 153.91 -97.64	37.80 28.70	112973.9 98100737	0.907 0.989
	H-M C-R	II	450	0.5	6.73 4.09	- 172.89 -83.66	19.06 9.96	11545.4 527754555.2	0.999 0.997

3.7. Antimicrobial activity:

Antimicrobial activity was assayed by cup plate agar diffusion method by measuring inhibition zones in mm. In vitro antimicrobial activity of all synthesized compounds and standard have been evaluated against strains of The fungal toxicity of Mn (II) complex 1 was studied *in vitro* against *Aspergillus niger* ATCC 16404, *Saccharomyces cerevisiae* ATCC 9763, *Candida albicans* ATCC10231 fungal pathogens at fixed 1% concentration.

The antibacterial activity of Mn (II) complex 1 was studied, for evaluating antibacterial activity Gram positive and Gram negative bacterial pathogens were used. *Staphylococcus aureus* ATCC 6538, *Bacillus megaterium* ATCC 2326, *Bacillus subtilis* ATCC 6633 were Gram positive pathogens used in this study. *Escherichia coli* ATCC8739, *Salmonella typhi* ATCC9207, *Shigella boydii* ATCC 12034, *Enterobacter aerogenes* ATCC13048, *Pseudomonas aerogenosa* ATCC9027, *Salmonella abony* NCTC6017 were the Gram-negative pathogens used in this study.

From the results of antimicrobial activity of ligands and complex it is clear that the complex shows enhanced activity than ligand. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligands [14].

IV. CONCLUSION

The Mn (II) complex 1 was colored, soluble in most of the organic solvent. The stoichiometry ratios of the metal complexes are obtained has been found to be 1:2. Solution conductivity of this metal complex reveals non-electrolytic nature. The electronic spectral data, magnetic moment, TG-DTA suggests that Mn (II) has Octahedral geometry. The CHO analysis gives C, H, and O percentage in the metal complex. From the antimicrobial activity of ligand and complex it is clear that the complex shows enhanced antimicrobial activity than ligand.

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