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RESEARCH ARTICLE

SYNTHESIS, SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF COPPER(II), NICKEL(II) , COBALT(II), MANGANESE(II) AND ZINK(II) COMPLEXES OF FURNA RING CONTAINING ORGANIC LIGANDS

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ABSTRACT

Background: To increase The reaction of Ethyl 5-(morpholinomethyl) furan-2-carboxylate with 4-amino salicylic acid afford a of 2-Hydroxy-4-(5-(morpholinomethyl)) furan-2-carboxamido)benzoic acid (MPFSA).. The transition metal complexes of Cu^{2+},Co^{2+} ,Ni^{2+}, Mn^{2+} and Zn^{2+} of MPFSA have been prepared. The objective of the research work is synthesis, characterization and chelating properties of furan ring containing organic ligands to monitor its antimicrobial activity. MPFSA and all the metal complexes were characterized by elemental analyses, spectral studies, magnetic moment determination, molar conductivity measurement. The free ligand and it's complexes have been tested for their antibacterial activities against two types of human pathogenic bacteria the first group is gram positive while the second group is gram negative (by using agar well diffusion method). Finally, it was found that compounds show different activity of inhibition on growth of the bacteria. The conclusion is Ni(II) Cu(II) ,Co(II) and Mn(II) complexes possess octahedral geometry around the central metal ion.

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INTRODUCTION

Literature survey point out that compounds having furan nucleus possesses some diverse biological activities and chemical applications (Vagdevi, 2001) like antimicrobial (Desai, 2014), anthelmintic (Padmashali, 2002), anti-inflammatory (Mahadevan, 2003), diuretic (Varshney, 2014), analgesic (Ravindra, 2008). The salicylic acid and its derivatives like 4-amino salicylic acid also act as good chelating agents (Mohanambal, 2014; El-Bindary, 2014), as well as potential pharmaceutical products (Ukrainczyk et al., 2014; Tilborg, 2014). The reaction between furan derivative with 4-amino salicylic acid (ASA) has not been reported so far. 4-amino salicylic acid is an excellent anti T.B agent and also acts as a chelating ligand with better microbicidal activity. Hence it was thought interesting to prepare the intermolecular ligands containing furan and salicylic acid moieties. Thus, the present communication comprises the studies on furan-salicylic acid combined molecule and its metal chelates. The obtained metal complexes were characterized by different analytical and spectral methods. The research work is illustrated in Scheme-1.

MATERIALS AND METHODS

Instrumentation: The elemental analysis for C, H and N were carried out on elemental analyzer TF-EA.1101 (Italy). IR spectra of MPFSA and its metal complexes were scanned on a Nicolet 760 FTIR spectrophotometer in KBr. The NMR spectrum of MPFSA was scanned on Brucker NMR spectrophotometer using DMSO solvent. The metal content of the metal chelates was performed by decomposing a weighed amount of each metal complexes followed by EDTA titration as reported in literature (Hong et al., 2008). Magnetic susceptibility measurement of all metal complexes were carried out at room temperature by the Gouy mehod. Mercury tetrathiocynatocobalate (II) Hg $(Co(NCS)_4)$ was used as a calibrant. The diffused reflectance spectra of solid metal complexes was recorded on a Backman DK Spectrophotometer with a sodid reflectance attachment, MgO was employed as the reflectance compound. The electrical conductivity of all the complexes was measure in acetonitrile at 10^{-3} M concentration.

Materials

Ethyl furan-2-carboxylate and p-Amino salicylic acid were obtained from local dealer. All other used chemicals were of analytical grade Ethyl 5-(morpholinomethyl) furan-2-carboxylate prepared according to literature (Hong, 2008).

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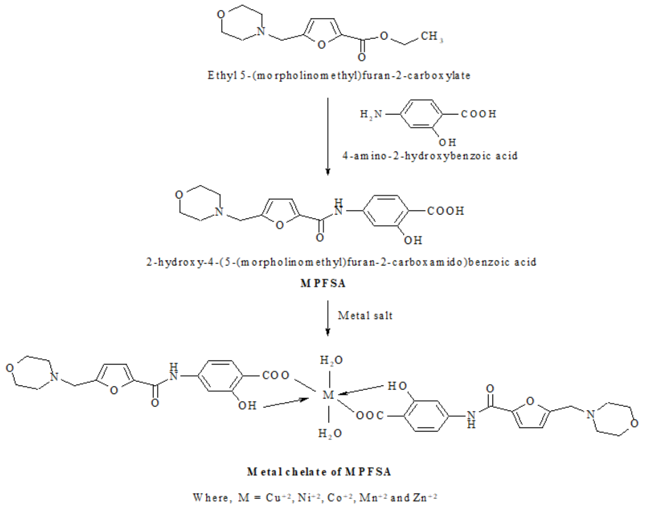

Figure 1.

Synthesis of Ethyl 5-(morpholinomethyl)furan-2-carboxylate: In a 250 ml RBF, Ethyl 5-(piperidin-1-yl-methyl)furan-2-carboxylate (0.01mole) and K_2CO_3 (0.02mole) were stirred at room temperature in DMF(20 ml) for 1.5hrs and pinch of KI was added. After that piperidine (0.015mole) was added to reaction mixture which was refluxed for 6 hrs. The reaction mixture was poured into water (20 ml) and the mixture was extracted with diethyl ether. The organic extracts were washed with water, dried over anhydrous sodium sulphate and concentrated to obtain crude product. The residue was recrystallized ethyl acetate from to give pure compound. Yield: 63 %, m.p. 112-116°C,IR,cm^{-1}(KBr): 3324 (amine), 3071 (Ar.C-H), 2926 (aliphatic C-H), 1345 (-CN), 1716 (CO). ^1H NMR: δ 6.55-6.33 (2H,d,furan CH), 3.81 (2H,s,CH_2), 2.94-2.31 (6H,q,CH_2), 1.14-1.04 (9H,s,CH_3). Anal. Calcd for $C_{12}H_{17}O_4N$ (239.27): C,60.64; H, 7.16; N, 5.85;O,26.75 Found: C,63.5; H, 7.85; N, 5.65;O,26.95

Preparation of 2-Hydroxy-4-(5-(morpholinomethyl)) furan-2-carboxamido)benzoic acid (MPFSA).): Ethyl 5-(Morpholinomethyl)Furan-2-carboxylate(0.01 mole) and 4-amino salicylic acid (0.01 mole) in 1,4-dioxane (50 ml) were charged into round bottom flask. To this mixture sodium methanolate (0.05 mole) was added and mixture was refluxed on oil bath for 8 hours. Finally the mixture was neutralized by acid or base. The product in form of Buffy precipitate was collected, washed and air dried. Yield of the ligand compound MPFSA is 72% and having m.p- 182-185°C (Uncorrected).

ELEMENTAL ANALYSIS: $C_{17}H_{18}N_2O_6$ (346.33)

Table 1.

	C%	H%	N%
Calculated	58.96	5.24	8.09
Found	59.05	5.20	8.10

Acid value of ligand

mg of TBAH / 1 gm of ligand =667
Number of COOH group=1.01

Thermo gravimetric analysis data of Ligands

Wt loss at 1st stage of degradation.=12.70 mg
Calculated value of decarboxylation=12.72 mg

Table 2. IR Features

Wave length (cm^{-1})	Group
3033, 1540,1660 cm^{-1}	Aromatic
1676 cm^{-1}	CO
2900-3350 cm^{-1}	OH
3425 cm^{-1}	Sec.NH
3425 cm^{-1}	Sec.NH
2853, 2925 cm^{-1}	CH_2 , CH_3

Table 3. NMR (DMSO)

δ ppm	Protons	Nature	Assignment
7.62 to 7.94	5H	Multiplet	Aromatic
12.94	1H	Singlet	-COOH
5.12	1H	Singlet	-OH
8.51	1H	Singlet	-CONH-
4.37	2H	Singlet	-N-CH_2
2.86, 3.66	8H	Multiplet	Morpholine

Synthesis of metal chelates of MPFSA: The Cu^{2+},Co^{2+}, Ni^{2+}, $Mn^{2+}$and Zn^{2+} metal chelates of MPFSA have been prepared in a similar manner. The general procedure is as follow. To a solution of MPFSA (33.2g, 0.1 mole) in ethanol-acetone (1:1v/v) mixture (150 ml), 0.1N KOH solution was added dropwise with stirring. The pasty precipitates were obtained at neutral pH. These were dissolved by addition of water up to clear solution. It was diluted to 250 ml. by water and was known as stock solution. 25 ml of the stock solution (which contains 0.01 mole MPFSA) was added drop wise to the solution of metal salt (0.005 mole for divalent metal ions) in water at room temperature. Sodium acetate or ammonia was added up to complete precipitation. The precipitates were digested by water bath at 80° C for 2h. The digested precipitates of chelates were filtered washed with water and air dried. It was amorphous powder. Yield was almost quantitative. The details are given in Table-4 and Table-5.

Study of Antifungal activity: The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro plant pathogenic organisms listed in Table-6. The antifungal activities of all the samples were measured by cup plate method (Baily, 1966). Each of the plant pathogenic strains on potato dextrose agar (PDA) medium and that PDA medium contained potato 200 gms, dextrose 20gms, agar 20gms and water 1 litre. 5 days old cultures were employed. The compounds to be tested were suspended (1000ppm) in PDA medium and autoclaved at 120° C for 15 min. at 15 atm pressure. These mediums were poured into sterile Petri plate and the organisms were inoculated after cooling the Petri plate. The percentage inhabitation for fungi was calculated after 5 days using the formula given below.

Percentage of inhibition $= \frac{100\ (X-Y)}{X}$

Where, X: Area of colony in control plate
Y: Area of colony in test plate
The fungicidal activity of all compounds is shown in **Table-6**.

RESULTS AND DISCUSSION

All the complexes are stable and non-hygroscopic. The metal complexes are insoluble in most organic solvents.The parent ligand MPFSA was an amorphous brown powder, soluble in solvents like dioxane, DMSO and DMF. The results of elemental analysis of the ligand are reported in experimental part. They are consistent with the predicted structure as shown in Scheme-1.

Table 4. Analytical Data of the Metal Chelates of MPFSA

Empirical Formula	Yield (%)	Elemental Analysis							
		C%		H%		N%		M%	
		Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
MPFSA	64	62.73	62.70	5.81	5.80	8.13	8.10	--	--
MPFSA Cu^{2+} 2H$_2$O	70	52.71	53.00	5.37	5.40	6.83	7.00	7.75	7.70
MPFSA Co^{2+} 2H$_2$O	69	53.20	53.20	5.41	5.40	6.90	7.00	7.26	7.30
MPFSA Mn^{2+} 2H$_2$O	64	53.28	53.30	5.42	5.40	6.90	6.90	6.78	6.80
MPFSA Ni^{2+} 2H$_2$O	71	53.02	53.00	5.40	5.40	6.87	6.90	7.21	7.20
MPFSA Zn^{2+} 2H$_2$O	64	52.78	52.70	5.38	5.40	6.84	52.78	8.00	8.00

Table 5. Magnetic Moment and Reflectance Spectral data of Metal Chelates of MPFSA ligand

Metal chelate	Magnetic Moment μ_{eff} (B.M.)	Molar Conductivity Ωm ohm^{-1} cm^2 mol^{-1}	Absorption band (cm^{-1})	Transitions
Cu-MPFSA	1.98	7.68	23981	C.T.
			15511	$^2B_{1g} \rightarrow {}^2A_{1g}$
Ni-MPFSA	4.23	9.79	23120	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)
			15768	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
Co-MPFSA	2.05	7.68	24110	$^4T_{1g}(F) \rightarrow {}^6T_{2g}(v_1)$
			19882	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$
			9826	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
Mn-MPFSA	4.28	9.79	22115	$^6A_{1g} \rightarrow {}^6A_{1g}({}^4E_g)$
			18520	$^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$
			16110	$^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$

Zn^{2+} Diamagnetic in Nature.

Table 6. Antifungal Activity of Ligand MPFSA$_1$ and its metal chelates.

Sample	Diameter of Zone of Inhibition (In mm)				
	B. Subtilis	S.aureus	E.Coli	P.aeruginosa	C.albicans
MPFSA	08	08	11	11	08
Cu-MPFSA	12	16	10	14	09
Ni-MPFSA	06	10	16	11	18
Co-MPFSA	12	16	10	14	09
Mn-MPFSA	07	12	17	10	17
Zn-MPFSA	11	06	09	14	09
Amoxicillin	15	16	17	18	12
Ampicillin	13	12	14	10	11

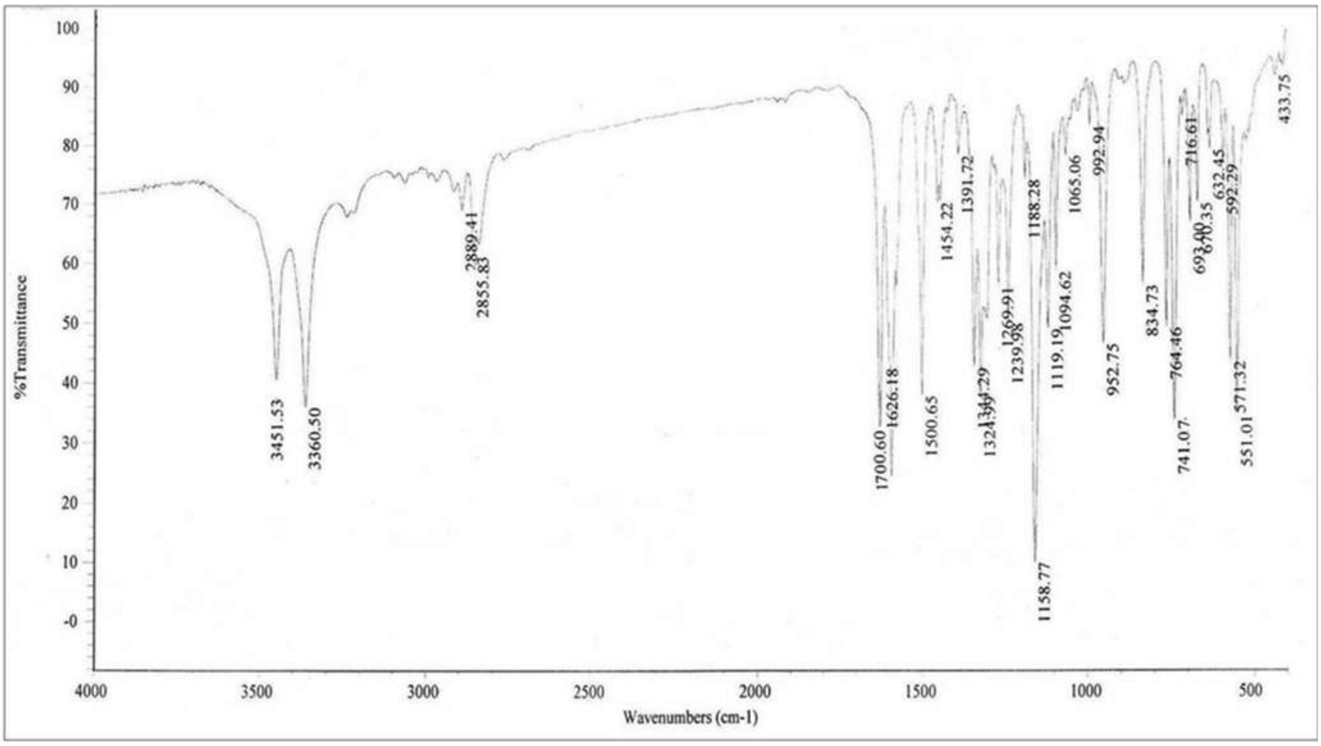

Figure 2. IR Scan of MPFSA sample

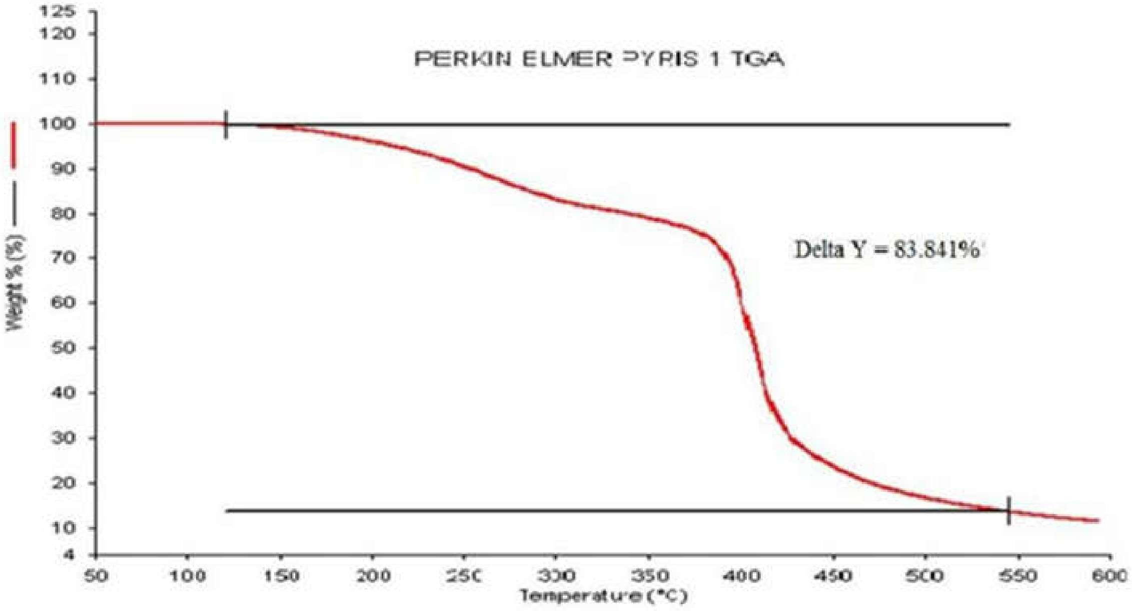

Figure 3. TGA Thermo gram of (MPFSA)Mn^{2+} complex

Table 7. TGA of Matel chelates

Empirical Formula	%Wt loss at temperature			
	250	300	350	400
(MPFSA)Cu^{2+}	6.30	8.80	19.02	70.00
(MPFSA)Ni^{2+}	6.70	22.20	67.00	75.08
(MPFSA)Co^{2+}	7.32	16.21	24.05	75.12
(MPFSA)Mn^{2+}	8.42	22.54	64.41	83.84
(MPFSA) Zn^{2+}	7.25	16.18	24.02	75.02

IR spectra: Examination of IR spectrum (not shown) of MPFSA reveals that broad band of phenolic hydroxyl stretching is observed at 2900-3350 cm^{-1} as well as additional absorption bands at 3035, 1540,1660 are characteristics of the salicylic acid (Bhatt et al., 2003). The strong bands at 1675 for C=O and band at 3420 for sec. NH. The NMR data (shown in experimental part) also confirm the structure of MPFSA. The Metal chelate of MPFSA with ions Cu^{2+},Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} vary in colours. On the basis of the proposed structure as shown in Scheme-1, the molecular formula of the MPFSA ligand is $C_{17}H_{18}N_2O_6$ (346.33). The complex coordinates with one central metal atom at four coordination sites and with two water molecules. Therefore the general molecular formula of the resulting metal chelate is $(C_{17}H_{18}N_2O_6)_2$ M.$2H_2O$ for divalent metal ions. This has been confirmed by results of elemental analysis reported in Table-4. The data are in agreement with the calculated values.

Inspection of the IR Spectra (not shown) of metal chelates reveals that all the spectra are identical in all respects. The comparison of IR spectrum of the parent ligand MPFSA with that of its each metal chelates has revealed certain characteristics differences. One of the significant differences to be expected between the IR spectrum of the parent ligand and its metal chelates is the presence of more broadened bands in the region of 3200-3600 cm^{-1} (Silverstein, 1991; Kemp, 1998) for the metal chelates as the oxygen of the O-H group of the ligands forms a coordination bond with the metal ions (Nakamoto, 1970; Lever, 1968). This is explained by the fact that water molecule might have strongly absorbed to the metal chelates samples during their formation. Another noticeable difference is that the bands due to the CO at 1730 cm^{-1} in the IR spectrum of the each metal chelates.

The band at 1400 cm^{-1} in the IR Spectrum of MPFSA ligand assigned to inplane OH determination (Silverstein, 1991; Kemp, 1998; Nakamoto, 1968; Lever, 1968) is shifted towards higher frequency in the spectra of confirmed by a week bands at 1095 cm^{-1} corresponding to C-O-M starching (Silverstein, 1991; Kemp, 1998; Nakamoto, 1970; Lever, 1968). Thus all of these characteristics features of the IR studies suggested the structure of the metal chelates as shown in Figure 1.

Electronic Absorption Spectra and Magnetic Moment: Examination of data of the metal content in each compound revealed a 1:2 metal: ligand (M: L) stoichiometry in all of the chelate of divalent metal ions. Magnetic moment (μ_{eff}) of each of the metal chelates is given in Table-5. Examination of these data reveals that all chelates other than that of Zn^{2+}, are Para magnetic while those of Zn^{2+} are diamagnetic.

Copper and Nickel Complexes: The diffuse electronic spectrum of the ($CuMPFSA(H_2O)_2$) metal complex shows broad bands at 15511 and 23981 cm^{-1} due to the $^2B_{1g} \rightarrow ^2A_{1g}$ transition (Figgis, 1976) and charge transfer, respectively suggesting a distorted octahedral structure (Carlin, 1997; Patel, 2012; Kettle, 1975) for the ($CuMPFSA(H_2O)_2$) complex. Which is further confirmed by the higher value of μ_{eff} of the ($CuMPFSA(H_2O)_2$) complex. The ($NiMPFSA(H_2O)_2$) and ($CuMPFSA(H_2O)_2$) complex gave two absorption bands respectively at 15768, 23120 and 15511, 23981 cm^{-1} corresponding to $^3A_{2g} \rightarrow ^3T_{1g}$ (P) and $^3T_{1g}$ (F)transitions. Thus absorption bands at the diffuse reflectance spectra and the value of the magnetic moments μ_{eff} indicate and octahedral configuration for the ($NiMPFSA(H_2O)_2$) and ($CuMPFSA(H_2O)_2$) complex (Patel et al., 2014).

Cobalt, Manganese and Zink Complexes: The ($CoMPFSA(H_2O)_2$) and ($MnMPFSA(H_2O)_2$) complex gave two absorption bands respectively at 24110,19882, 9826 and 22115,18520,16110 cm^{-1} corresponding to

${}^4T_{1g}(F) \rightarrow {}^6T_{2g}(v_1)$,${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(v_2)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and ${}^6A_{1g} \rightarrow {}^6A_{1g}({}^4E_g)$,${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$,

${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$ transitions. Thus absorption bands at the diffuse reflectance spectra and the value of the magnetic moments μ_{eff} indicate and octahedral configuration for the ($CoMPFSA(H_2O)_2$) and ($MnMPFSA(H_2O)_2$) complex (22). The high intensities of the bands suggests that they might be charge transfer in origin μ_{eff} is found to be lower than normal range. In the absence of low temperature moments it is difficult to give any significance. As the spectrum of the ($ZnPFSA(H_2O)_2$) polymer is not well resolved, it is not interpreted but it is μ_{eff} value shows that it is diamagnetic as expected.

Molar Conductance Measurements: Conductivities of all the complexes were measured in acetonitrile solvent and all the complexes were found to be electrolytic (15) in nature of 1:2 type and molar conductivity values are in the range of 32.3-36.7 Ohm^{-1} Cm^{-1}.

Antifungal activity: The antifungal activity of all the compounds measured for various plant pathogens. Inspection of the result shown in Table-3 indicates that all compounds are good toxic for fungi. Out of all the compounds copper chelates is more toxic than other. These compounds almost inhibit the fungi about 73%. Hence produced metal chelates can be employed as garden fungicides. Further work in the direction is in progress.

Conclusion

Metal complexes of MPFSA ligands derived from Ethyl 5-(morpholinomethyl)furan-2-carboxylate, 4-amino salicylic acid and 2-Hydroxy-4-(5-(morpholinomethyl)) furan-2-carboxamido)benzoic acid (MPFSA) were prepared and characterized by elemental analysis, FTIR and UV-Vis. Spectra, conductivity measurements and magnetic susceptibilities. The Ni(II) Cu(II) ,Co(II) and Mn(II) complexes possess octahedral geometry around the central metal ion.

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