

SYNTHESIS, CHARACTERIZATION AND CHELATING PROPERTIES OF FURAN RING CONTAINING METAL COMPOUND

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ABSTRACT

The treatment of Ethyl 5-((diphenylamino) methyl)furan-2-yl carboxylate with 4-amino salicylic acid afford a 4-(5-((diphenylamino)methyl)furan-2-carboxamido)-2-hydroxybenzoic acid (DPFSA). The transition metal complexes of Cu^{2+} , Co^{2+} , Ni^{2+} , Mn^{2+} and Zn^{2+} of DPFSA have been prepared. DPFSA and all the metal complexes were characterized by elemental analyses, spectral studies, magnetic moment determination, molar conductivity measurement and antimicrobial activity.

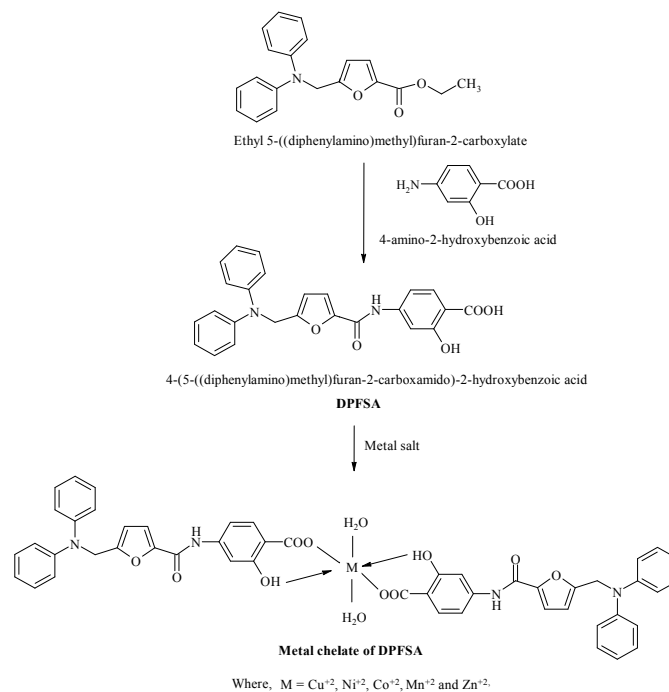
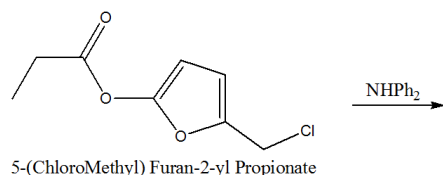
Key words:

4-(5-((diphenylamino)methyl)furan-2-yl propionate, 4-amino salicylic acid, Metal chelates, Spectral studies, Magnetic moment, Antibacterial and Antifungal activity.

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INTRODUCTION

Literature survey indicates that compounds having furan nucleus possess broad range of their diverse biological activate and chemical applications [1] like such as antimicrobial [2], anthelmintic [3], anti-inflammatory [4], diuretic [5], analgesic [6]. The salicylic acid and its derivatives like 4-amino salicylic acid also act as good chelating agents [7,8], as well as potential pharmaceutical products [9,10]. The reaction between furan derivative with 4-amino salicylic acid (ASA) has not been reported so far. Though 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 research work is illustrated in Scheme-1.



Experimental

Materials

Ethyl furan-2-carboxylate and p-Amino salicylic acid were obtained from local dealer. All other chemicals used were of analytical grade. 5-(chloromethyl)furan-2-yl propionate prepared according to literature [11].

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Synthesis of Ethyl 5-((diphenylamino)methyl)furan-2-yl carboxylate

In a 250 ml RBF, 5-(chloromethyl)furan-2-yl propionate (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 diphenyl amine (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: 70%, m.p. 118-119°C, IR, cm^{-1} (KBr): 3334 (amine), 3073 (Ar.C-H), 2925 (aliphatic C-H), 1340 (-CN), 1718 (CO). 1H NMR: δ 6.52-6.31 (2H,d,furan CH), 3.83 (2H,s,CH₂), 2.91-2.33 (6H,q,CH₂), 1.13-1.03 (9H,s,CH₃). Anal. Calcd for C₂₀H₁₉NO₃ (331.17): C,74.75; H, 5.96; N, 4.36; Found: 72.5; H, 6.1; N, 4.22.

Synthesis of 4-(5-((diethylamino)methyl)furan-2-carboxamido)-2-hydroxybenzoic acid (DPFSA)

Ethyl 5-((diphenylamino)methyl)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 DPFSA is 83% and having m.p- 205-208°C (Uncorrected).

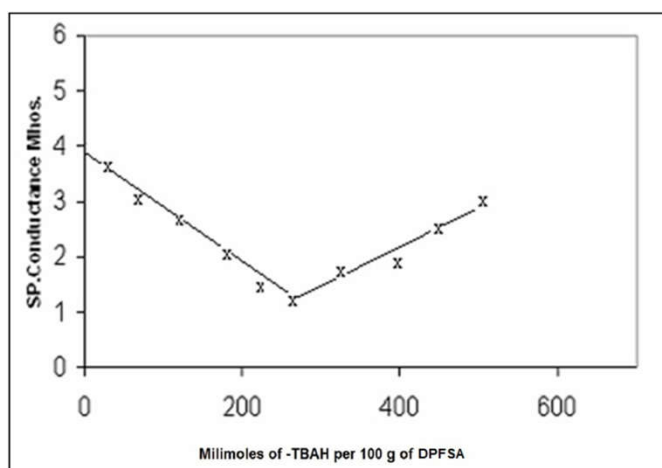
Elemental Analysis: C₂₅H₂₀N₂O₅ (428.44)

	C%	H%	N%
Calculated:	70.02	4.67	6.53
Found :	70.00	4.60	6.50

Acid value of ligand

mg of TBAH / 1 gm of ligand =807

Number of COOH group=1.02



plot of conductometric titration of DPFSA

IR Features	3035, 1540, 1660 cm^{-1}	Aromatic
	1675 cm^{-1}	CO
	2900-3350 cm^{-1}	OH
	3420 cm^{-1}	Sec.NH
	2850, 2920 cm^{-1}	CH ₂ , CH ₃
NMR (DMSO)	δ ppm	

δ ppm	Protons	Nature	Assignment
7.63 to 7.91	15H	Multiplet	Aromatic
12.92	1H	Singlet	-COOH
5.10	1H	Singlet	-OH
8.5	1H	Singlet	-CONH-
4.38	2H	Singlet	-N-CH ₂

Thermogravimetric analysis data of Ligands

Wt loss at 1st stage of degradation.=10.30 mg

Calculated value of decarboxylation=10.27 mg

Synthesis of metal chelates of DPFSA

The Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺ metal chelates of DPFSA have been prepared in a similar manner. The general procedure is as follow.

To a solution of DPFSA (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 DPFSA) 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 on 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 detail are given in Table-1.

Table 1 Analytical Data of the Metal Chelates of DPFSA

Empirical Formula	Yield (%)	Elemental Analysis							
		C%		H%		N%		M%	
		Cal.	Found	Cal.	Found	Cal.	Found	Cal.	Found
DPFSA	83	70.02	70.00	4.67	4.60	6.3	6.50	-	-
DPFSA Cu ²⁺ 2H ₂ O	68	57.86	57.80	4.58	4.60	6.75	6.70	7.65	7.60
DPFSA Co ²⁺ 2H ₂ O	64	55.47	55.50	4.62	4.60	6.81	6.80	7.18	7.20
DPFSA Mn ²⁺ 2H ₂ O	62	58.48	58.50	4.63	4.60	6.82	6.80	6.70	6.70
DPFSA Ni ²⁺ 2H ₂ O	70	58.20	58.20	5.34	5.30	6.79	6.80	7.12	7.10
DPFSA Zn ²⁺ 2H ₂ O	61	57.94	58.00	4.59	4.60	6.75	6.70	7.90	7.90

Measurements

The elemental analysis for C, H and N were carried out on elemental analyzer TF-EA.1101 (Italy). IR spectra of DPFSA and its metal complexes were scanned on a Nicolet 760 FTIR spectrophotometer in KBr. The NMR spectrum of DPFSA was scanned on Bruker NMR spectrophotometer using DMSO solvent. The metal content of the metal chelate were 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 method. Mercury tetrathiocyanatocobalate (II) Hg [Co(NCS)₄] was used as a calibrant. The diffused reflectance spectra of solid metal complex were recorded on a Beckman DK Spectrophotometer with a solid 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.

Table 2 Magnetic Moment and Reflectance Spectral data of Metal Chelates of DPFSA ligand

Metal chelate	Magnetic Moment μ_{eff} (B.M.)	Molar Conductivity $\Omega\text{m ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$	Absorption band (cm^{-1})	Transitions
Cu-DPFSA	1.48	8.88	24497	C.T.
			15758	${}^2B_{1g} \rightarrow {}^2A_{1g}$
Ni-DPFSA	3.49	8.22	22490	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)
			13114	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)
Co-DPFSA	1.52	8.88	22978	${}^4T_{1g}$ (F)
			19048	$\rightarrow {}^6T_{2g}(\square_1)$
			8543	${}^4T_{1g}$ (F)
				$\rightarrow {}^4A_{2g}(\square_2)$
Mn-DPFSA	3.59	8.22	23405	${}^6A_{1g} \rightarrow {}^6A_{1g}({}^4E_g)$
			18583	${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$
			16120	$\rightarrow {}^4T_{1g}$ (P)
				${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$

Zn²⁺ Diamagnetic in Nature.

Antifungal activity

The fungicidal activity of all the compounds was studied at 1000 ppm concentration in vitro plant pathogenic organisms listed in Table-3. The antifungal activities of all the samples were measured by cup plate method [12]. Each of the plant pathogenic strains on potato dextrose agar (PDA) medium. Such a 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 a PDA medium and autoclaved at 120° C for 15 min. at 15 atm pressure. These medium 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.

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

Where, X: Area of colony in control plate
Y: Area of colony in test plate

The fungicidal activity all compound are shown in Table-3.

Table 3 Antifungal Activity of Ligand DPFSA₁ and its metal chelates

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

RESULTS AND DISCUSSION

The parent ligand DPFSA was an amorphous brown powder, soluble in various 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.

Examination of IR spectrum (not shown) of DPFSA 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 [13]. 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 DPFSA.

The Metal chelate of DPFSA with ions Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺ and Zn²⁺ vary in colours. On the basis of the proposed structure as shown in Scheme-1, the molecular formula of the DPFSA ligand is C₂₅H₂₀N₂O₅. Which upon complexation 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 [C₂₅H₂₀N₂O₅]₂ M.2H₂O for divalent metal ions. This has been confirmed by results of elemental analysis reported in Table-1. 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 DPFSA 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} [14,15] for the metal chelates as the oxygen of the O-H group of the ligands forms a coordination bond with the metal ions [16,17]. 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 DPFSA ligand assigned to inplane OH determination [14-17] is shifted towards higher frequency in the spectra of confirmed by a weak bands at 1095 cm^{-1} corresponding to C-O-M stretching [14-17]. Thus all of these characteristics features of the IR studies suggested the structure of the metal chelates as shown in Study of the TGA curves of ligand showing that each ligand degrades in two steps. The first degradation observed up to 200° to 240°C in all ligands indicates the weight loss in the range at 14.0 to 18.0% percentages. This is depending up on the molecular weight of sample. The IInd stage at degradation of all the ligands beyond 200°C is rapid and loss about 70% to 90% at 300°C depending upon the nature of ligand. All the ligands containing one – COOH groups. Hence the TGA of ligands in air may decarboxylation [73,74]. The calculated value of CO₂ of each ligands and % loss of 1st stage degradation of each ligands are presented in Tables 3.8. Examination of these data reveals that the decarboxylation of each ligand consistent with the calculated values. All these facts confirm the structure of ligands. Inspection of all TG thermograms reveals that each ligand degrades in two step. The initial degradation might be due to decarboxylation of each ligand. The calculated and estimated loss of CO₂ gas. Values are shown in table -4 this confirm the structure of all the ligands.

Scheme

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-2. Examination of these data reveals that all chelates other than that of Zn²⁺, are Para magnetic while those of Zn²⁺ are diamagnetic.

The diffuse electronic spectrum of the [CuDPFSA(H₂O)₂] metal complex shows broad bands at 24497 and 15758 cm^{-1}

due to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition [18] and charge transfer, respectively suggesting a distorted octahedral structure [19-21] for the $[CuDPFSA(H_2O)_2]$ complex. Which is further confirmed by the higher value of μ_{eff} of the $[CuDPFSA(H_2O)_2]$ complex. The $[NiDPFSA(H_2O)_2]$ and $[CuDPFSA(H_2O)_2]$ complex gave two absorption bands respectively at 22490, 13114 and 24497, 15758 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 $[NiDPFSA(H_2O)_2]$ and $[CuDPFSA(H_2O)_2]$ complex [22]. The spectra of $[MnDPFSA(H_2O)_2]$ shows weak bands at 23405, 18583 and 16120 cm^{-1} assigned to the transitions ${}^6A_{1g} \rightarrow {}^6A_{1g}({}^4E_g)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, respectively suggesting an octahedral structure for the $[MnDPFSA(H_2O)_2]$ chelate. 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 $[ZnDPFSA(H_2O)_2]$ polymer is not well resolved, it is not interpreted but it is μ_{eff} value shows that it is diamagnetic as expected.

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 $Ohm^{-1} Cm^{-1}$.

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 72%. Hence produced metal chelates can be employed as garden fungicides. Further work in the direction is in progress.

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