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Synthesis, Characterizations and Antimicrobial Activity of Metal Complexes of 2-(2-Furanylmethylaminocarbonyl)benzoic Acid

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Abstract: The ligand, 2-(2-furanylmethylaminocarbonyl)benzoic acid (FMBA) and it's transition metal complexes have been synthesized and characterized by elemental analysis, spectral studies, magnetic moments and thermal studies. The antifungal activity of all the samples was monitored against common fungi.

Keywords: Phthalamic acid, Metal chelates, IR, NMR Spectral studies, Theromogravimetric.

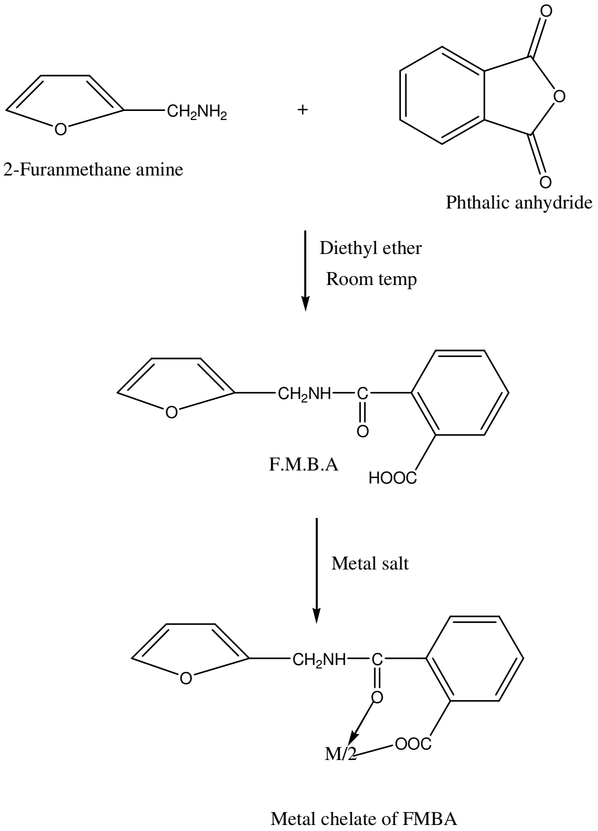
Introduction

The 2-phenylamino carbonyl benzoic acid is known as phthalamic acid containing amide group. The derivatives of phthalamic acid and bisphthalamic acid have been reported as metal complexing agent. The amide derivatives of similar type of ligands are also reported for their metal complexing study[1-7]. With this context the present work in light of complexation of 2-(2-furanlmethylcarbonylamino)benzoic acid (FMBA). Thus the present communication comprises the synthesis, characterization and microbiacidal study of FMBA and it's metal complexes. The reaction is shown in Scheme 1.

Experimental

Synthesis of ligand: 2-(2-Furanylmehtylaminocarbonyl)benzoic acid (FMBA)

2-Furarmethylamine (9 mL, 0.05 mole) and phthalic anhydride (7.49 g, 0.05 mole) were dissolved separately in diethyl ether (50 mL). Both this solutions were mixed and stirred on a magnetic stirrer till the complete formation of the product FMBA takes place. The compound was filtered, washed with ether, dried and recrystallised from ethanol. Yield was 75%, m.p. 162-3 ^{0}C uncorrected (capillary method).



Scheme 1

Analisis: $C_{13}\ H_{11}\ NO_4$ (245)

	C %	H %	N%
Cal:	63.67%	4.49 %	5.71 %
Found:	63.5%	4.30 %	5.60 %

IR: 3400 cm^{-1} (-NH)

28500, 2920, 1430 cm^{-1} ($-CH_2$)

3200 – 2600 cm^{-1} (OH of COOH)

1690 cm^{-1} (CO)

1680, 1580, 1610 cm^{-1}(-CONH)

3030 cm^{-1} (Aromatic)

^{1}H NMR: 10.6ppm (- COOH)

6.6 - 7.8 ppm (aromatic)

4.4 ppm (- NH)

2.3 ppm (- CH_2)

LCMS: M^+ m/c= 247

Acid value: 230 mg/1g of acid.

Synthesis of complexes

The ligand FMBA and metal acetate (*i.e.* Cu, Mn^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+}) were used as starting materials. The general method for synthesis of metal complexes was as follows.

The metal salt (0.01 mole) solution in ethanol- dioxane (1:1 v/v) mixture (25 mL) was added to 50 mL of solution of ligand ethanol-dioxane (1:1 v/v) (0.02 mole) with constant stirring. The reaction mixture was adjusted to pH 4-5 by addition of sodium acetate. Then it was refluxed on water bath until solid separated out. The solid were filtered, washed with solvent and then air dried.

Measurements

The elemental contents of C, H and N were determined by Thermofinigon Flash 1101 EA (Italy). The metals were determined volumetrically by Vogel's method[8]. To a 100 mg chelate sample, each 1 mL of HCl, H_2SO_4 and $HClO_4$ were added and then 1 g of $NaClO_4$ were added. The mixture was evaporated to dryness and the resulting salt was dissolved in double distilled water and diluted to mark. From this solution the metal content was determined by filtration with standard EDTA solution. Infrared spectra of the synthesized compounds were recorded on Nicolet. 760 FT - IR spectrometers, NMR spectrum of FMBA was recorded on 60 MHZ NMR spectrophotometer. Magnetic susceptibility measurement of the complexes was carried out on Gouy balance at room temperature. The electronic spectra of complexes in solid were recorded at room temperature. MgO was used as reference. Thermogravimetric analysis (TGA) of FMBA sample was carried out and antifungal activity of all the samples was monitored against various fungi, following the method reported in literature[9]

Results and Discussion

The elemental content and IR - NMR spectral data and LCMS of FMBA ligands are almost consistent with the predicted structure. The thermogram (Figure 1) of FMBA indicate that the initial weight loss is about 17.78%. This is due to decarboxylation of FMBA in air. The value is quite consistent with the calculated value (17.95%). All these facts confirm the structure of FMBA. The metal complexes were stable at room temperature even though in humid atmosphere. The analytical data of all the complexes are shown in Table 1. The elemental contents of complexes are consistent with the predicted structure.

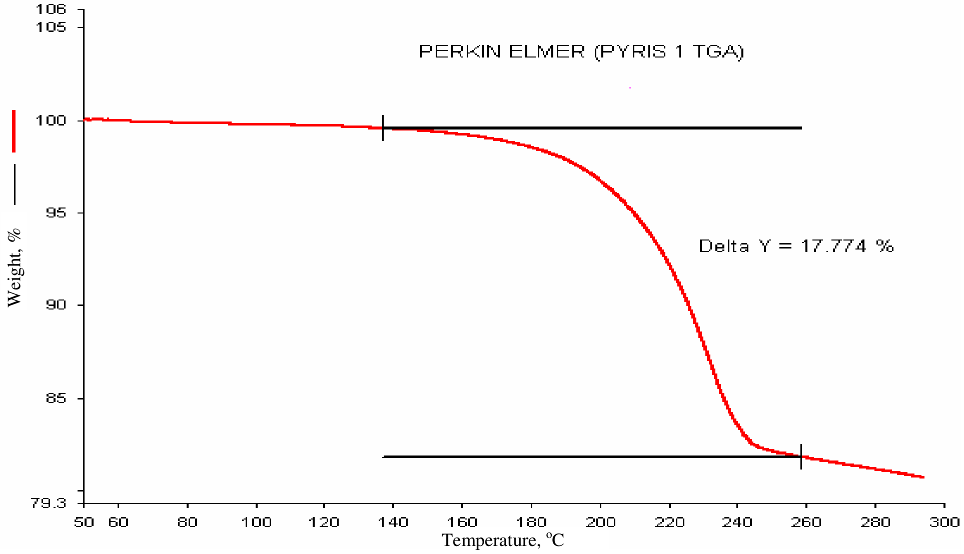


Figure 1. Thermogram of FMBA

Table 1. Analysis of FMBA - metal complexes

Metal complex	Mol.Wt	Yield %	Elemental analysis, % C % Calcd.	C % Found	H % Calcd.	H % Found	N % Calcd.	N % Found	Metal % Calcd.	Metal % Found
$C_{26}H_{20}N_2O_8\,Cu^{2+}\cdot 2H_2O$	587.54	80	53.10	53.0	4.08	4.0	4.16	4.7	10.81	10.7
$C_{26}H_{20}\,N_2O_8\,Ni^{2+}\cdot 2H_2O$	582.71	85	53.54	53.4	3.43	9.3	4.80	4.7	10.70	10.0
$C_{26}H_{20}N_2O_8\,Co^{2+}\cdot 2H_2O$	582.93	82	53.52	53.4	3.43	3.3	4.80	4.7	10.05	10.0
$C_{26}H_{20}\,N_2O_8\,Zn^{2+}\cdot 2H_2O$	588.39	80	53.02	52.9	3.40	3.3	4.75	4.6	11.08	11.0
$C_{26}H_{20}\,N_2O_8\,Mn^{2+}\cdot 2H_2O$	578.93	79	53.89	53.7	4.14	4.1	4.83	4.7	9.48	9.4

The metal complexes showed the slightly less broad band between 3600-3200 cm^{-1} compared to that of ligand FMBA. This might be due to presence of coordinated water molecule. The bands due to amide $\upsilon_{C=0}$ mode around 1650 cm^{-1} for the free ligands are shifted to higher frequency in all the complexes indicating involvement of the carbonyl oxygen of the amide group in coordination and non involvement of the amide nitrogen[10,11]. The absorption band around 1700 cm^{-1} and 1300 cm^{-1} in the free ligands attributed to $\upsilon_{C=o}$ and $\upsilon_{C\text{-}OH}$ of the carbonyl group[12]. They are replaced by two bands in the region of 1540-1590 cm^{-1} and 1340-1380 cm^{-1} corresponding to υ_{C00} (assymm.) and $\upsilon_{C.0}$ (symm.) in all the complexes.

The infrared spectra of all the complexes are identical and suggest the formation of the entire metalocyclic compound by the absence of band characteristic of free -OH group of parent FMBA. The other bands are almost at their respectable positions as appeared in the spectrum of parent-FMBA ligand. However, the band due to (M-O) band could not be detected as it may be appeared below the range of instrument used. The important IR spectral data are shown in Table 2.

Magnetic moments of metal complexes are given in Table 2. The diffuse electronic spectrum of Cu^{2+} chelate show two broad bands around 13000 and 23000 cm^{-1}. The first band may be due to a $^2B_{1g}$ - $^2A_{1g}$ transition, while the second band may be due to charge transfer. The first band shows structures suggesting a distorted octahedral structure for the Cu^{2+} metal chelates[13,14] .The higher value of the magnetic moment of the Cu^{2+} chelate supports the same. The Co^{2+} metal chelate gives rise to two absorption bands at 23800 and 19040 CMT, which can be assigned $^4T_{1g}$ - $^4T_{1g}$ - $^4T_{1g}$ (P) transitions respectively[15,16].

The spectrum of Mn^{2+} polymeric complex comprised two bands at 19010 cm^{-1} and 23300 cm^{-1}. The latter does not have a very long tail. These bands may be assigned to $^6A_{1g}$ - 4_{2g}(G) and $^6A_{1g}$ - $^4A_{2g}$(G) transitions, respectively. The high intensity of the bands suggests that they may have some charge transfer character. The magnetic moment is found to be lower than normal range. In the absence of low temperature measurement of magnetic moment it is difficult to attach any significance to this. As the spectrum of the metal chelate of Ni^{2+} has two distinct bands at 11960 - 11450 and 17700-17400 cm^{-1} which are assigned as $^3A_{2g}$ (F) - $^3T_{1g}$ (F) and A_{2g} (F) - $^3T_{1g}$ (F) transitions, respectively suggested the octahedral environment for Ni$^{2+.}$ The observed μ_{eff} values are in the range 3.01 - 3.2 moiety[14,15].

The examination of antifungal activity of FMBA ligand and its all complexes (Table 3) reveals that the ligand is moderately toxic against fungi, while all the chelates are more toxic than ligand. Among all the chelates, the Cu^{2+} complex is more toxic against fungi.

Table 2. Spectral features and magnetic moment of FMBA - metal chelates

Metal chelates	μ_{eff} (BM)	Electronic spectral data, cm^{-1}	Transition	IR spectral feature common for all (CMT)
FMBA-Cu^{2+}	2.13	23245 15775	Charge Transfer $^2B_{1g}$ - $^2A_{1g}$	1100 C-O-M & 500 O-M bands.
FMBA-Ni^{2+}	3.32	22575 15400	$^3A_{1g}$ - $^3T_{1g}$ (P) $^3A_{1g}$ - $^3T_{1g}$ (F)	
FMBA-Co^{2+}	4.54	22721 15255 8930	$^4T_{1g}$(F) - $^4T_{2g}$ (F) $^4T_{1g}$(F) - $^4T_{2g}$ $^4T_{1g}$(F) - $^4T_{2g}$(P)	
FMBA-Mn^{2+}	5.45	23865 18340 16815	$^6A_{1g}$ - $^4A_{2g}$ ^4E_g $^6A_{1g}$ - $^4T_{2g}$ (4G) $^6A_{1g}$ - $^4T_{1g}$ (PG)	
FMBA-Zn^{2+}		D	D	

D=Diamagnetic*

Table 3. Antifungal actvity of FMBA ligand and its metal celates

Sample	Zone of inhibition of fungal at 1000 ppm (%)				
	PE	*AS*	*F*	*AP*	*TS*
FMBA	54	51	60	66	68
FMBA-Cu^{2+}	88	88	89	86	89
FMBA-Zn^{2+}	72	60	75	82	86
FMBA-Ni^{2+}	80	72	73	78	79
FMBA-Co^{2+}	65	73	70	78	83
FMBA-Mn^{2+}	75	72	70	75	80

PE = *Penicillium Expansum;* AS = *Alternaria solani;* F= *F.Udum;* AP = *Agpergillus pisi;* TS=*Trichoderma* sp.

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