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Synthesis, Characterisation and Antimicrobial Activity of New Complexing Agent of 1-Phenyl-3-Methyl-4-Benzoylpyrazol-5-One and its Metal Complexes

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ABSTRACT: A new multidentate ligand 2-(5-fluoro-2-methyl-lH-inden-3-yl)-*N*'-((3-methyl-5-oxo-l-phenyl-4,5dihydro-lH-pyrazol-4- yl)(phenyl) methylene)acetohydrazide i.e. FIMPPH have been derived in good yield by the reaction of 4-benzoyl-3-methyl-l-phenylpyrazol-5- one with 2-(5-fluoro-2-methyl-l*H*-inden-3-yl)acetohydrazide. It has been employed for the synthesis of the metal complexes with the transition metal ions viz. Fe^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+}. Both the ligand FIMPPH and its metal complexes are studied for the antimicrobial activity.

KEYWORDS: Acetohydrazide, pyrazolone, metal complexes, antimicrobial activity.

I. INTRODUCTION

The literature survey evidences the importance of 4-benzoyl-3-methyl-l-phenylpyrazol-5-one as an excellent chelating agent[1,2] as well as it exhibits biological activity[3]. The Fluorinated organic molecules are known to perform a wide range of biological functions[4-6].In the present paper the heterocycle, 4-benzoyl-3-methyl-l-phenylpyrazol-5-one is derivatised into its imino derivative with hydrazide of 5-fluoro-2-methyl indene-3-acetic acid which can act as polydentate ligand.

II. MATERIALS AND METHODS

A. R. grade or purified L. R. grade chemicals were used for the synthesis of the substituted pyrazolones, 2-(5-fluoro-2- methyl-1H-inden-3-yl)acetohydrazide, 2-chloro phenylglycine methyl ester and the metal complexes.

Synthesis of ligand, FIMPPH: 2-(5-fluoro-2-methyl -1H- inden-3-yl)-N'-((3-methyl-5-oxo-l-phenyl-4,5dihydro-lH-pyrazol-4-yl)(phenyl) methylene)acetohydrazide i.e. FIMPPH was prepared as 4-benzoyl-3-methyl-l-phenylpyrazol-5-one (2.8g i.e. 0.0lmole) and 2-(5-fluoro-2- methyl-l*H*-inden-3-yl)acetohydrazide (2.2g i.e. 0.0lmole) was taken in a round bottom flask. Then the entire mixture was dissolved in minimum quantity of alcohol and the mixture was refluxed for 90 minutes. The resulting mixture was added to a beaker containing crushed ice. The solid obtained was filtered by suction, washed several times with water and dried at room temperature and then recrystallised from 70% of alcohol. The yield of FIMPPH was about 85%.

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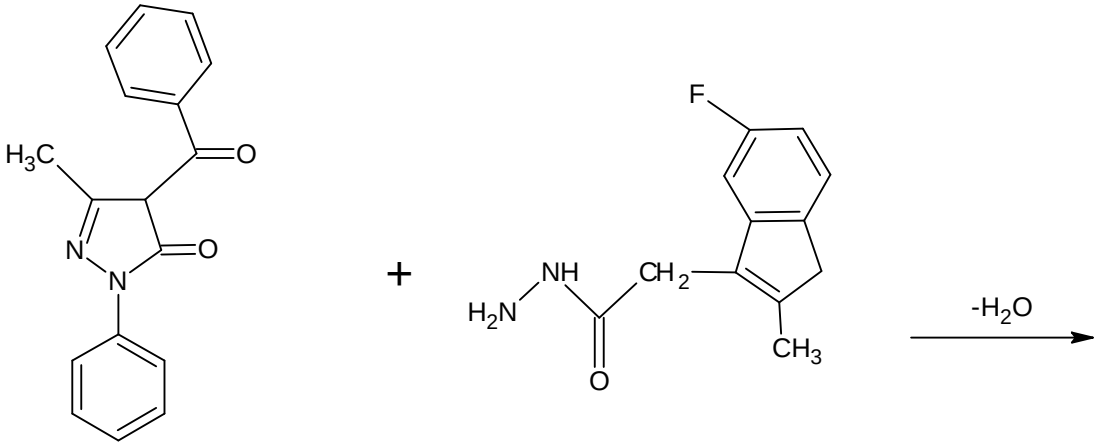
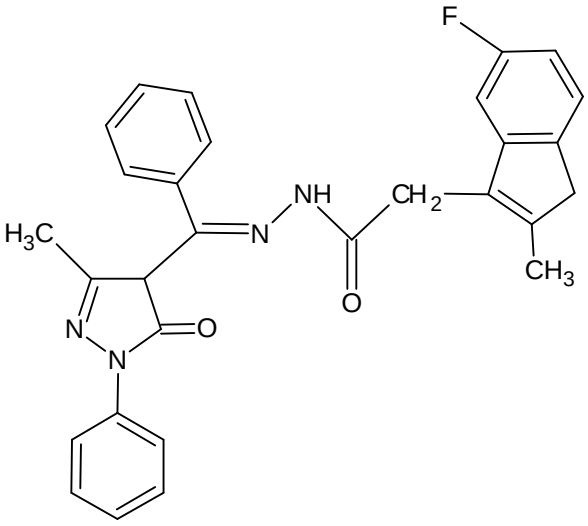


4-benzoyl-3-methyl-1-phenyl pyrazol-5-one

2-(5-fluoro-2-methyl-1H-inden -3-yl)acetohydrazide



2-(5-fluoro-2-methyl-1H-inden-3-yl)-N'-((3-methyl-5-oxo-1-phenyl -4,5dihydro-1H-pyrazol-4-yl)(phenyl)methylene)acetohydrazide

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Synthesis of Metal Complexes of FIMPPH: First the weighed ligand FIMPPH was dissolved in the alcohol. Then equimolar quantities of divalent metal salt and FIMPPH were mixed and the reaction mixture was heated on water bath for one hour. It was then cooled when coloured solid separated out which was washed with water and dried in vacuum. This is the general method for the synthesis of metal complexes of FIMPPH with divalent metal chlorides $MC1_2.xH_20$, where M= Co(II), Ni(II) and Zn(II) and $FeS0_47H_2O$ for Fe(II).

III. RESULTS AND DISCUSSIONS

The newly synthesized polydentate ligand have been characterized by elemental analysis, IR, and nmr spectra. The newly synthesized complexes of this polydentate ligand are nonhygroscopic, coloured solids, insoluble in water but soluble in solvents like chloroform, methanol, ethylacetate, dimethylformamide and dimethylsulphoxide. They exhibit nonelectrolytic nature in dimethylformamide. Their high decomposition temperatures suggest strong metal- ligand bonding in the complexes. The elemental analysis data of the complexes conform to 1:2 metal- ligand stoichiometry. The room temperature magnetic susceptibility measurements of complexes show presence of unpaired electrons of complexes exhibit paramagnetic moments except Zn(II) complex which is diamagnetic in nature. The infrared spectral studies of the metal complexes reveal that the metal-ligand bonding is through azomethine nitrogen in the 4^{th} position and through donor in 5^{th} position of the pyrazolone ring. Some important bands in the infrared spectra of the complexes have been identified and assigned to provide evidences of the bonding sites in the metal complexes. The structures of these metal complexes have been investigated by various physicochemical techniques *viz.* elemental analysis, electrical conductance measurements, uv-visible, IR, nmr, room temperature magnetic susceptibility measurements and thermal analysis as applicable (Table No.1 - 6) .

Antimicrobial studies: The metal complexes along with ligands were screened for their anti-microbial activities such as anti-bacterial and anti-fungal activity against selected microorganisms such as *S.typhi, S. aures, C. albicans* and *Penicillum* and minimum inhibitory concentration (MIC) values were ascertained(Table No.7 -10).

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Table :1 Physicochemical properties and elemental analysis of FIMPPH

Ligand	Colour	Yield %	M.P. °C	Molecular formula Molecular weight	Observed/ (Calculated)			
					%C	%H	%N	%F
FIMPPH	Lemon Yellow	85	193-194	$C_{29}H_{25}FN_40_2$ 480.5	72.4 (72.48)	5.2 (5.24)	11.5 (11.66)	3.9 (3.95)

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Table:2 Colour, Decomposition temperature, analytical Data, Molar conductance and Magnetic moment (B.M.) of the Metal Complexes of FIMPPH

Complexes	Colour	Decompo-sition temp. °C	Observed/ (Calculated)					Molar Conductance $\Omega^{-1}cm^2mole^{-1}$	μ_{eff} B.M.
			%M	%C	%N	%H	%F		
$Fe(FIMPPH)_2$	Dark Chocolate	313 °C	5.49 (5.50)	68.62 (68.64)	11.02 (11.04)	4.71 (4.77)	3.72 (3.74)	42.9	5.02
$Co(FIMPPH)_2$	Light Orange	301°C	5.78 (5.79)	68.39 (68.43)	10.95 (11.01)	4.71 (4.75)	3.73 (3.73)	43.8	3.90
$Ni(FIMPPH)_2$	Light Green	308°C	5.74 (5.77)	68.44 (68.45)	11.00 (11.01)	4.71 (4.75)	3.73 (3.73)	44.0	2.81
$Zn(FIMPPH)_2$	Off White	286°C	6.33 (6.38)	68.01 (68.00)	10.93 (10.94)	4.67 (4.72)	3.69 (3.71)	43.5	Diamagnetic

Table:3 Assignments of Some Important FT-IR Bands for ligand FIMPPH and Metal Complexes of FIMPPH

Complex	νNH (cm^{-1})	νC=0 indene (cm^{-1})	νC=N (cm^{-1})	νC=0 pyrazolone (cm^{-1})	νC=N pyrazolone ring (cm^{-1})	νC-F (cm^{-1})	νN-N (cm^{-1})	νM-0 (cm^{-1})	νM-N (cm^{-1})
FIMPPH	3267	1670	1616	1633	1591	1168	909	-	-
$Fe(FIMPPH)_2$	3333	1618	1560	1601	1591	1166	912	509	429
$Co(FIMPPH)_2$	3337	1624	1567	1601	1590	1166	913	511	430
$Ni(FIMPPH)_2$	3346	1623	1571	1602	1589	1166	913	512	430
$Zn(FIMPPH)_2$	3344	1630	1572	1602	1589	1165	913	511	429

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Table:4 ^{13}C NMR of Ligand FIMPPH

^{13}C NMR	Assignments
168 ppm	-C=0 of hydrazide
166 ppm	-C=0 of pyrazolone
164 ppm	C-F of indene
162 ppm	C=N hydrazide
160 ppm	C=N of pyrazolone
117-147 ppm	16 carbon aromatic
41.59 ppm	CH_2 of indene ring
41.4 ppm	CH of pyrazolone
29.8ppm	CH_2 of indene at 3rd position
15.2 ppm	CH_3 of hydrazide
13.9ppm	CH_3 of pyrazolone

Table:5 Proton Magnetic Resonance Shifts (values) of Schiff Base Ligand FIMPPH and their Assignments

FIMPPH / Proton Magnetic Resonance	Assignments
10.58 ppm	-NH
6.718-7.977 ppm	Multiplet of aromatic protons
3.218 ppm	CH_2 on 1st position in indene ring
3.189 ppm	CH2 on 3rd position of indene ring
2.059 ppm	CH of 4th position of pyrazolone ring
1.869 ppm	CH_3 on 2nd position of indene ring
1.356 ppm	CH3 on 3rd position of pyrazolone ring

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Table:6 Proton Magnetic Resonance Shifts (values) of metal complex with FIMPPH and their Assignments

Ligand/ Complex	NH proton ppm	Multiplet of aromatic protons ppm	CH_2 on 1st position in indene ring ppm	CH_2 on 3rd position of indene ring ppm	CH of 4th position of pyrazolone ring ppm	CH_3 on 2nd position of indene ring ppm	CH_3 on 3rd position of pyrazolone ring ppm
FIMPPH	10.58	6.718-7.977	3.218	3.189	2.058	1.869	1.356
$Fe(FIMPPH)_2$	-	6.808-7.612	3.341	3.259	2.384	1.856	1.196
$Co(FIMPPH)_2$	-	6.879-7.798	3.321	3.210	2.225	1.906	1.358
$Ni(FIMPPH)_2$	-	6.796-7.687	3.051	3.009	2.237	2.094	1.293
$Zn(FIMPPH)_2$	-	6.798-7.645	3.317	3.285	2.254	1.834	1.192

Table:7 MIC Value of FIMPPH and its metal complex for Salmonella typhii (S.typhii)

	Concentration in ppm					
	1000 ppm	500 ppm	200 ppm	100 ppm	50 ppm	20 ppm
FIMPPH	X	X	X	X	X	X
$Fe(FIMPPH)_2$	√	√	X	X	X	X
$Co(FIMPPH)_2$	√	√	√	√	√	√
$Ni(FIMPPH)_2$	√	√	√	√	√	√
$Zn(FIMPPH)_2$	X	X	X	X	X	X

Table:8 MIC Value of FIMPPH and its metal complex for Staphylococcus aureus(S. aureus)

	Concentration in ppm					
	1000 ppm	500 ppm	200 ppm	100 ppm	50 ppm	20 ppm
FIMPPH	X	X	X	X	X	X
$Fe(FIMPPH)_2$	√	√	√	√	√	√
$Co(FIMPPH)_2$	√	√	√	√	√	√
$Ni(FIMPPH)_2$	X	X	X	X	X	X
$Zn(FIMPPH)_2$	√	√	√	√	√	√

Table:9 MIC Value of FIMPPH and its metal complex for Candida albicans (C. albicans)

	Concentration in ppm					
	1000 ppm	500 ppm	200 ppm	100 ppm	50 ppm	20 ppm
FIMPPH	√	√	√	√	√	√
$Fe(FIMPPH)_2$	X	X	X	X	X	X
$Co(FIMPPH)_2$	X	X	X	X	X	X
$Ni(FIMPPH)_2$	X	X	X	X	X	X
$Zn(FIMPPH)_2$	√	√	√	√	√	X

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Table:10 MIC Values of FIMPPH and its metal complex for Penicillium

	Concentration in ppm					
	1000 ppm	500 ppm	200 ppm	100 ppm	50 ppm	20 ppm
FIMPPH	X	X	X	X	X	X
$Fe(FIMPPH)_2$	X	X	X	X	X	X
$Co(FIMPPH)_2$	X	X	X	X	X	X
$Ni(FIMPPH)_2$	X	X	X	X	X	X
$Zn(FIMPPH)_2$	X	X	X	X	X	X

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