

Study of Newly Synthesised Pyrazolone and It's Metal Complexes

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ABSTRACT: Pyrazolone Ligand plays very vital role in many biological and chemical reactions due to the imine linkage. Various references suggested that the present work on 1,3,4-substituted Pyrazol-5-one having importance due to β -diketo (beta-diketo) moiety with pyrazolone ring.

The keto group at the 4th position on the pyrazolone ring is treated with chemically and biologically important acetohydrazide of indene which contains fluorine to yield new Ligand. This Ligand has been employed for the synthesis of the metal complexes with different metal salts. Present work deals with characterization of Ligand and it's metal complexes which are further screened for their antimicrobial activity.

KEYWORDS: Pyrazolone, metal complexes.

I. INTRODUCTION

1,3,4-substituted pyrazol-5-one is one of the excellent chelating agent[1]. Fluorine substituted organic molecules are familiar for a wide range of biological functions[2-4]. Pyrazolones and its derivatives show good antibacterial or antifungal activity by this information we synthesise fluorine substituted derivative which could possibly show enhanced biological activity. In the present paper the 4-(3-fluorobenzoyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one is derivatised into its imino derivative with 2-(5-fluoro-2-methyl-1H-inden-3-yl)acetohydrazide[5-8] which can act as a polydentate ligand..

II. MATERIALS AND METHODS

A. R. grade or purified L. R. grade chemicals were used for the synthesis of 2-(5-fluoro-2-methyl-1H-inden-3-yl)-N'-((3-fluorophenyl)(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)acetohydrazide and the metal complexes.

Synthesis of ligand:-

2-(5-fluoro-2-methyl-1H-inden-3-yl)-N'-((3-fluorophenyl)(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)acetohydrazide i.e . FI3FMPPHAs 4-(3-fluorobenzoyl)-5-methyl-2-phenyl-2,4-dihydro-3H-pyrazol-3-one (0.01 mole) and 2-(5-fluoro-2-methyl-1H-inden-3-yl)acetohydrazide (0.01 mole) were taken in a round bottom flask. Then the entire mixture was dissolve in minimum quantity of alcohol and the mixture was kept for reflux 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 recrystallised from 50% of alcohol. The yield of FI3FMPPH was about 80%.

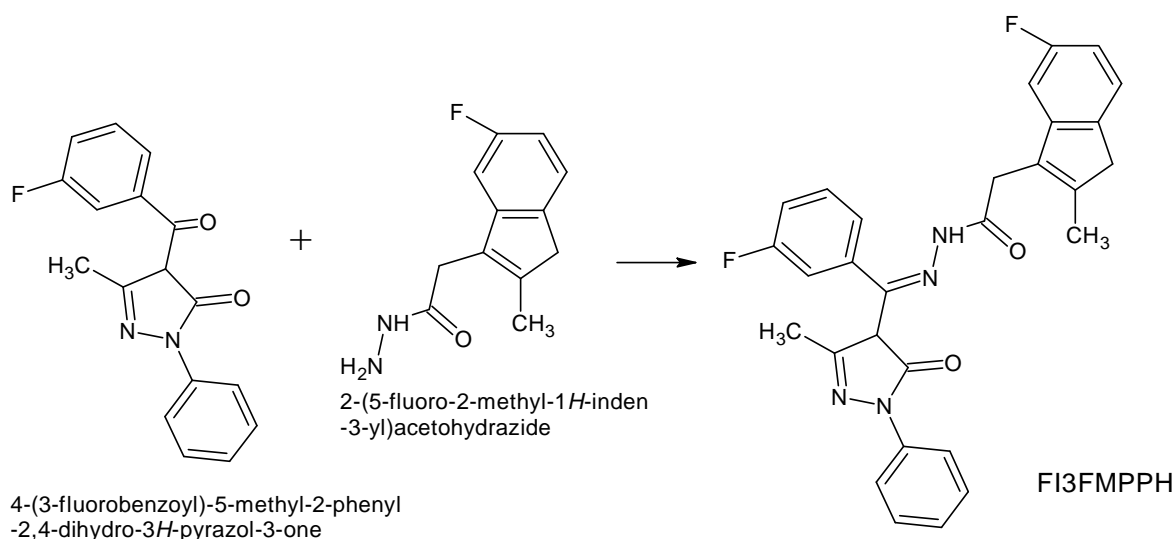


Diagram 1:- Synthesis of Ligand FI3FMPPH

Synthesis of metal complexes of ligand FI3FMPPH:-

The weighed ligand FI3FMPPH was dissolved in the minimum quantity of alcohol. Then equimolar quantities of divalent metal salts and FI3FMPPH were mixed and the reaction mixture was heated on water bath for an 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 FI3FMPPH with divalent metal chlorides $MCl_2 \cdot xH_2O$, where $M = Co(II), Ni(II)$ and $Zn(II)$.

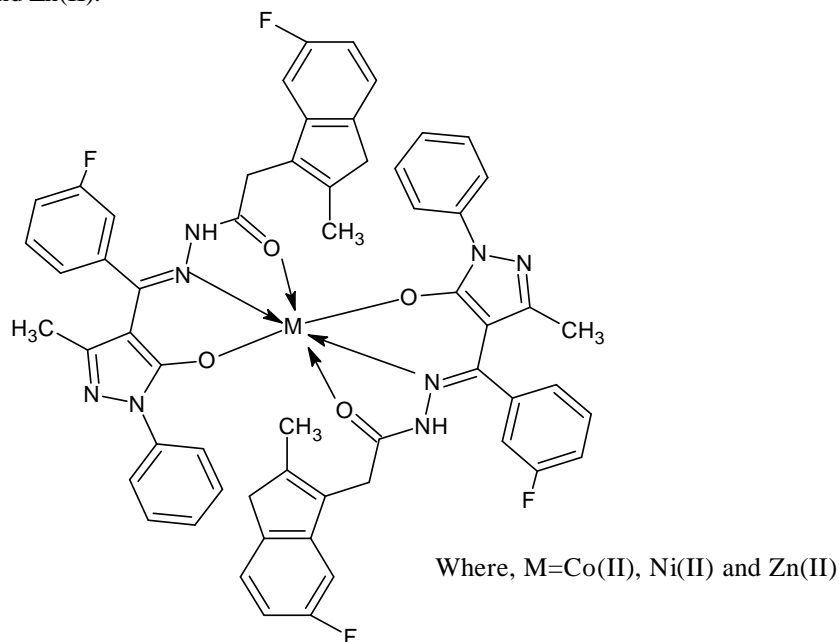


Diagram 2:- General structure for metal complex of FI3FMPPH

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III.RESULTS AND DISCUSSIONS

The newly synthesized ligand have been characterized by elemental analysis, IR, NMR and Mass spectra. The newly synthesized complexes of this ligand are nonhygroscopic, coloured solids insoluble in water but soluble in polar solvents like chloroform, methanol, ethylacetate, dimethylformamide and dimethylsulphoxide. 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 Co and Ni complexes show presence of unpaired electrons of complexes exhibit paramagnetic. The infrared spectral studies of the metal complexes reveals that the metal-ligand bonding is through azomethine nitrogen in the 4th position and through donor in 5th 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 newly synthesised compounds are characterised by various methods as follows.

Table 1: Physicochemical properties and Elemental analysis of Ligand FI3FMPPH

Ligand	Colour	Yield	M.P.	Molecular formula Molecular weight	Observed/ (Calculated)			
					C%	H%	N%	F%
FI3FMPPH	Light Lemon Yellow	80%	203- 204 ^o C	C ₂₉ H ₂₄ F ₂ N ₄ O ₂ 498.52	69.84 (69.87)	4.83 (4.85)	11.21 (11.24)	7.61 (7.62)

Table 2: Colour, Decomposition temperature, Elemental analysis data and Magnetic moment (B.M.) of the Metal Complexes of Ligand FI3FMPPH

Complexes	Colour	Decomposition temp.	Observed/ (Calculated)					μ_{eff} B.M.
			M%	C%	H%	F%	N%	
(FI3FMPPH) ₂ Co	Light Orange	315 ^o C	5.55 (5.59)	66.06 (66.10)	4.33 (4.40)	7.18 (7.21)	10.53 (10.63)	4.89
(FI3FMPPH) ₂ Ni	Light Green	300 ^o C	5.54 (5.57)	66.07 (66.11)	4.36 (4.40)	7.18 (7.21)	10.55 (10.63)	3.18
(FI3FMPPH) ₂ Zn	Cream	220 ^o C	6.11 (6.17)	65.66 (65.69)	4.33 (4.37)	7.14 (7.17)	10.49 (10.57)	Diamagnetic

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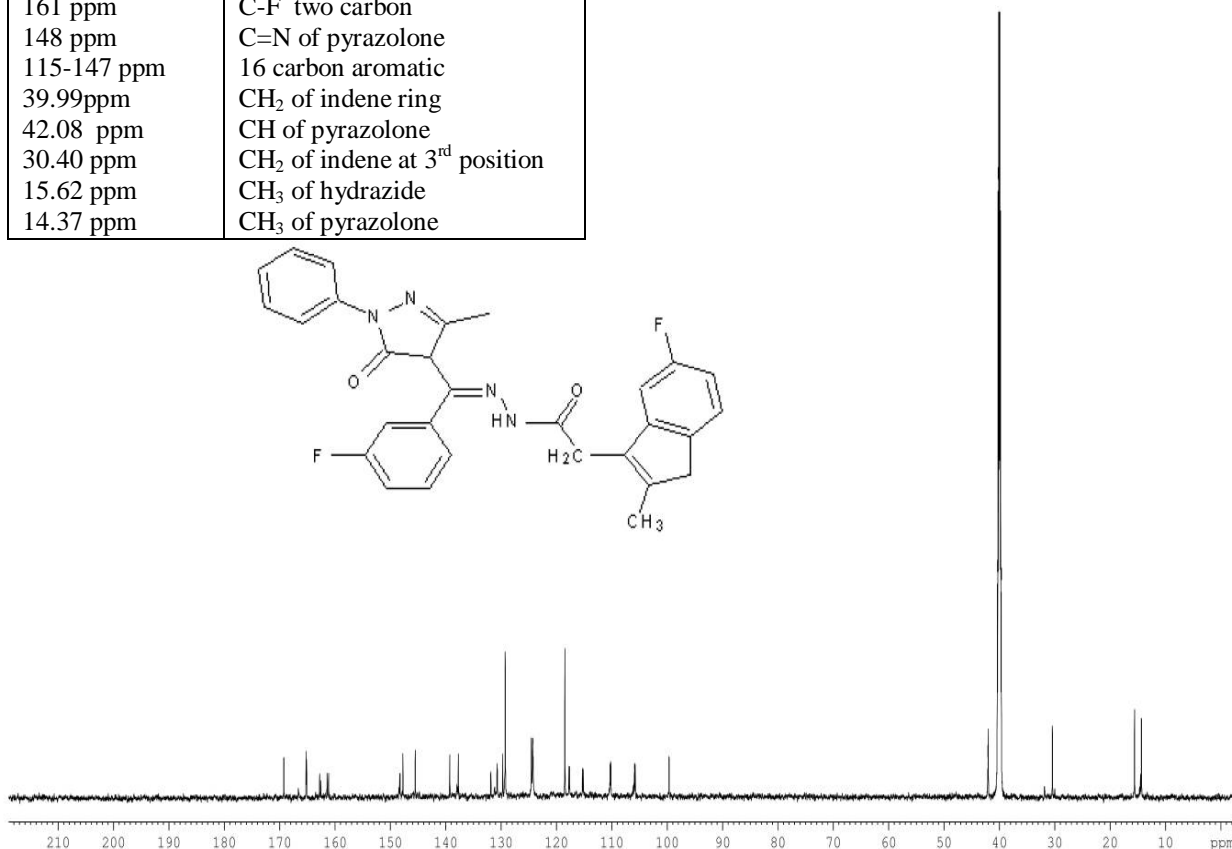
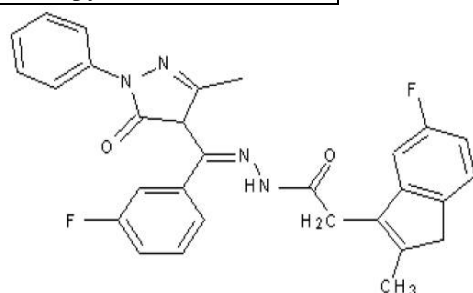
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Table 3: Assignments of Some Important FT-IR Bands for ligand FI3FMPPH and their Metal Complexes

Complex	νNH (cm^{-1})	$\nu\text{C=O}$ indene (cm^{-1})	$\nu\text{C=N}$ (cm^{-1})	$\nu\text{C=O}$ pyrazolone (cm^{-1})	$\nu\text{C=N}$ pyrazolone ring (cm^{-1})	$\nu\text{C-F}$ (cm^{-1})	$\nu\text{N-N}$ (cm^{-1})	$\nu\text{M-O}$ (cm^{-1})	$\nu\text{M-N}$ (cm^{-1})
FI3FMPPH	3255	1620	1580	1677	1593	1165	911	--	--
(FI3FMPPH) ₂ Co	3346	1624	1539	--	1588	1166	913	565	517
(FI3FMPPH) ₂ Ni	3347	1625	1544	--	1589	1166	913	564	511
(FI3FMPPH) ₂ Zn	3347	1633	1542	--	1589	1166	913	565	512

Table 4: ¹³C NMR of Ligand FI3FMPPH

¹³ C NMR	Assignments
169 ppm	-C=O of hydrazide
165 ppm	-C=O of pyrazolone
162 ppm	C=N hydrazide
161 ppm	C-F two carbon
148 ppm	C=N of pyrazolone
115-147 ppm	16 carbon aromatic
39.99 ppm	CH ₂ of indene ring
42.08 ppm	CH of pyrazolone
30.40 ppm	CH ₂ of indene at 3 rd position
15.62 ppm	CH ₃ of hydrazide
14.37 ppm	CH ₃ of pyrazolone



Graph 1: Carbon NMR of Ligand FI3FMPPH

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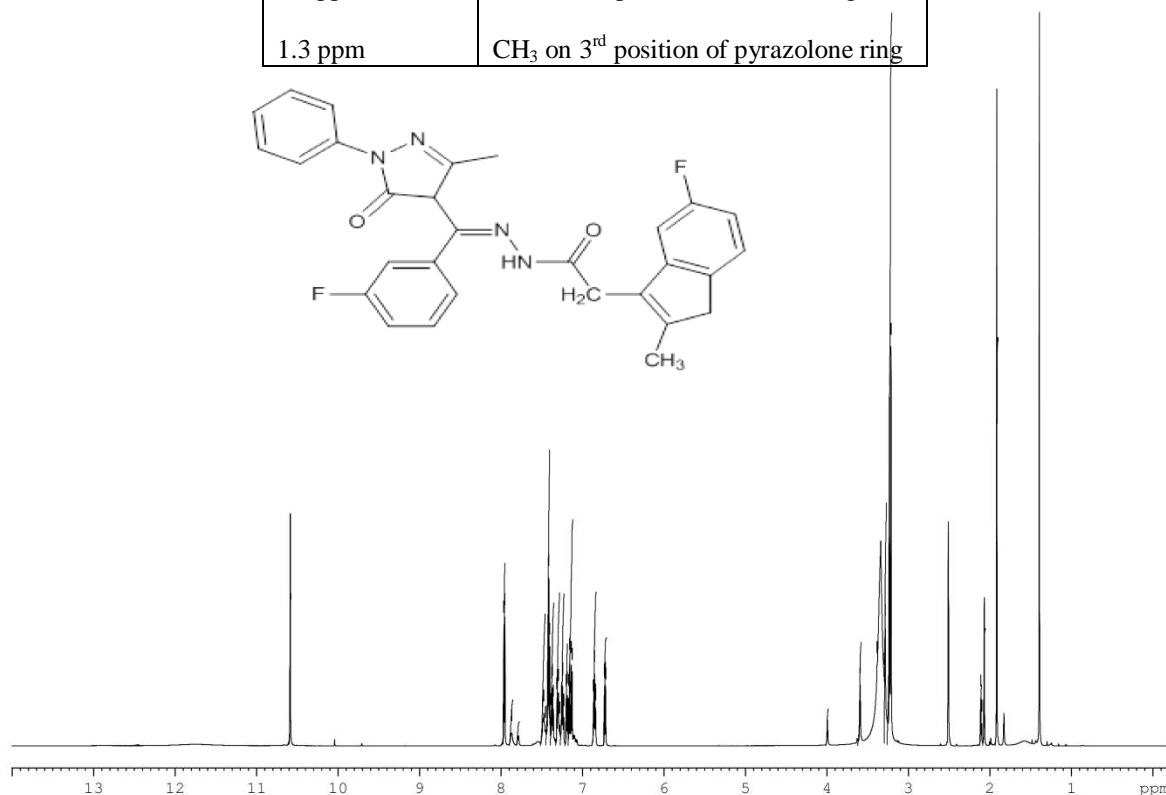
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Table 5: Proton Magnetic Resonance Shifts (δ values) of Schiff Base Ligand FI3FMPPH and their Assignments

Proton Magnetic resonance	Assignments
10.5 ppm	-NH
6.7-7.9 ppm	Multiplet of aromatic protons
3.3 ppm	CH ₂ on 1 st position in indene ring
3.2 ppm	CH ₂ on 3 rd position of indene ring
2.1 ppm	CH of 4 th position of pyrazolone ring
1.9 ppm	CH ₃ on 2 nd position of indene ring
1.3 ppm	CH ₃ on 3 rd position of pyrazolone ring



Graph 2: Proton NMR of Ligand FI3FMPPH

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ANTIMICROBIAL STUDIES:

The ligand FI3FMPPH and their Metal Complexes were screened for their anti-bacterial and anti-fungal activity against E. coli and Rhizopus and minimum inhibitory concentration (MIC) values were ascertained by disc diffusion method[9]. The zone of inhibition recorded in mili meter (mm).

Table 6: Zone of inhibition in mm of ligand FI3FMPPH and their Metal Complexes

Sr. No.	Sample name	Zone of inhibition (mm) of ligand FI3FMPPH and their Metal Complexes against following strains							
		Test Bacteria:- E. coli				Test Fungi:- Rhizopus			
		25 ppm	50 ppm	100 ppm	200 ppm	25 ppm	50 ppm	100 ppm	200 ppm
1	FI3FMPPH	--	--	9	10	--	--	--	--
2	(FI3FMPPH) ₂ Co	11	8	--	9	8	7	7	8
3	(FI3FMPPH) ₂ Ni	8	10	8	8	7	7	6	8
4	(FI3FMPPH) ₂ Zn	9	8	9	10	--	6	6	--

IV. CONCLUSION

New 2-(5-fluoro-2-methyl-1H-inden-3-yl)-N'-((3-fluorophenyl)(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)acetohydrazide i.e . FI3FMPPH ligand and their metal complexes are successfully formed namely (FI3FMPPH)₂Co, (FI3FMPPH)₂Ni and (FI3FMPPH)₂Zn. New compounds analytical and spectroscopic data suggest formation of ligand and their metal complexes using green solvents like primary alcohols which further show good antimicrobial activity.

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