ISSN (Online) 2456 -1304

International Journal of Science, Engineering and Management (IJSEM)
Vol 2, Issue 3, March 2017

Studies on Biologically Potent Ligands and Their Manganese(II) Complexes Synthesized Through Green Chemical Approach

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***Abstract*- This paper incorporates the preparation, characterization and biochemical screening of the biologically potent ligands and their complexes with manganese(II). The ligands used in these studies are hydrazinecarboxamides and hydrazinecarbothioamides. These ligands and their corresponding metal complexes were synthesized by two synthetic procedures, i.e., microwave as well as the conventional heating. A comparison has been made between these two synthetic methods on the basis of the yield of the products, refluxing time and the solvent consumed. The structural deductions were made on the basis of magnetic measurements, electronic, infrared, ESR, and NMR spectral studies. The complexes of manganese(II)with hydrazincarboxamides have been synthesized.The bonding pattern of the ligands and the geometry of their manganese(II) complexes have been deduced on the basis of UV, IR, 1H NMR, 13C NMR spectral and X-ray diffraction studies.Some selected metal complexes and their parent ligands have been screened for their antifungal activities and the observed results have been explained.**

I. INTRODUCTION

This chapter incorporates the coordination behaviour and characterization of several azomethine ligands and their manganese(II) complexes. The ligands and their metal complexes were prepared by the conventional method as well as by microwave method1.Green synthesis under solvent free and less solvent conditions are attractive offering reduced pollution, low cost and offer high yields together with simplicity in processing and handling. The authenticity of the ligands and their complexes has been established by elemental analyses, melting point determinations, molecular weight determinations, and various spectroscopic techniques like, EPR, IR, 1H NMR, 13C NMR, UV-Visible and X-ray powder diffraction studies.

II. EXPERIMENTAL

The present research work incorporates the synthesis of a variety of fluoroimine complexes of manganese(II) by using different methods and apparatus, which have been discussed in this section. The details of these techniques are given in the following pages:

1. APPARATUS

The well cleaned apparatus was rinsed with rectified spirit and then dried at 110-120 ^{o}Cin an electric oven for few hours and cooled at the room temperature by keeping them in desiccators. **MATERIALS**

The starting materials of metals used for carrying out the reactions were hydrated chromium trichloride and vanadium oxytrichloride. All the chemicals and solvents used were dried and purified by the standerd methods.

(a) **Methanol** (B.D.H., B.P.: 65 ^{o}C) was refluxed over magnesium methoxide (prepared from magnesium ribbon and methanol in presence of iodine) and then distilled.

(b) **Dimethylformamide** (E. Merck, B.P.: 66 ^{o}C/35 mm) was distilled after storing it over anhydrous sodium carbonate and further redistilled under reduced pressure.

(c) ***n*-Hexane** (B.P.: 69 ^{o}C) was dried by refluxing over sodium wire.

(d) **Cyclohexane** (B.P.: 80 ^{o}C) was dried by refluxing over sodium wire

(e) **Ether** (B.P.: 34.6 ^{o}C) was kept over calcium chloride (anhydrous) for 3-4 days and then distilled. It was then refluxed and distilled over sodium wire.

(f) **Tetrahydrofuran** (SISCO, B.P.: 66.5 ^{o}C) was dried by distilling it over sodium wire and then tested it with benzophenone.

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(g) **Benzene** (B.D.H., B.P: 80 ^{o}C) was dried by storing and refluxing over sodium wire for 2-3 days, followed by azeotropic distillation with ethanol

(h) **Chloroform** (B.D.H., B.P.: 61.2 ^{o}C) was collected after storing it for two days over barium oxide.

III. ANALYTICAL METHODS

The analyses of synthesized azomethines and their metal complexes were performed by the following methods.

(i) Estimation of Carbon and Hydrogen

Carbon and hydrogen analyses of the complexes as well as the ligands were performed at the *Microanalytical Laboratory, Chandigarh*.

(ii) Estimation of Nitrogen [2]

Nitrogen was estimated by the Kjeldahl's method.

(iii) Estimation of Sulphur[3-4]

Sulphur was estimated as $BaSO_4$ by the Messenger's method.

(iv) Estimation of Chlorine[5]

Chloride was estimated volumetrically by Volhard's method.

(v) Estimation of Metals

Manganese Estimation [(6)]

The weighed amount of the compound was dissolved in methanol (10 mL) and diluted to 250 mL with distilled water. 25 mL of the manganese solution was pipetted out into a 250 mL conical flask and about 0.5g of hydroxyl ammonium chloride (to prevent oxidation) was added. It was then warmed and diluted upto 100 mL by the addition of distilled water and followed by mixing 3 mL of triethanolamine. The pH of the solution was adjusted upto 10 with the help of buffer solution. The resulting solution was titrated against standard 0.05 M EDTA solution using Eriochrome Black-T as an indicator. At the endpoint, the colour changed sharply from red to blue.

IV. INSTRUMENTAL METHODS

The instrumental methods adopted during these studies are as follows:

(i) Thin Layer Chromatography

To test the purity of the synthesized compounds, T.L.C. was employed on silica gel G using various solvents.

(ii) Molecular Weight Determinations[7-9]

The molecular weights were determined by the Rast Camphor method using resublimed camphor (M.P. 178^{o}C). The depression in freezing point from that of pure camphor was determined with sufficient accuracy and the molecular weight of the compound was calculated by using the formula:

$$M = \frac{K.w.1000}{T.W.}$$

Where,

M = Molecular weight of the compound
K = Molecular depression constant for camphor (39.7)
w = Weight of the compound taken
W= Weight of the camphor taken
T = Difference of the melting point temperatures of camphor and the mixture of camphor and the compound

(iii) Ultraviolet Spectra

Ultraviolet spectra were recorded on a Perkin-Elmer model spectrophotometer.

(iv) Infrared Spectra

IR spectra were recorded on a Perkin-Elmer model spectrophotometer, in the range 4000–200 cm^{-1} in KBr optics as well as in Nujol mulls.

(v) ^{1}H and ^{13}C NMR Spectra

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer in DMSO-d_6 using TMS as the internal standard.

(vi) EPR Spectra

ESR spectra of the complexes were monitored on Varian E- 4X band spectrometer at SAIF, IIT, Madras, Chennai.

(vii) Magnetic Measurements

Magnetic measurements were recorded at vibrating sample magnetometer Model 155 room temperature at SAIF, IIT, Madras, Chennai.

(viii) Molar Conductance Measurements

The molar Conductivity of the resulting compounds were determined on Century Digital Conductivity Meter Model CC 601 at room temperature. The solutions of the order of 10^{-3}M concentration were employed for the conductivity measurements.

(ix) X-Ray Powder Diffraction

X-Ray powder diffractograms of the compounds were obtained on a RIGAKU miniFlex automatic diffractogram using Cu (Kα) target with Mg filter. The wavelength used was 1.540 Å.

Preparation:

V. SYNTHETIC METHODS

Preparation of the Ligands

Preparation of hydrazinecarbothioamides: ($L^{1}H$,$L^{2}H$ and $L^{8}H$)

The hydrazinecarbothioamides of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl coumarinwere prepared by the condensation of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl

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coumarin with thiosemicarbazide in 1:1 molar ratio in the medium of ethanol. The contents were refluxed for about 4-5 hours in thermal method and about 5-6 minutes in microwave method. After refluxing, the contents were separated out as crystalline solids. These were dried and purified by recrystallisation from the same solvent. Analysis of the above ligands is as follows.

(a) [2-(2-fluorophenyl)methylene]hydrazinecarbothioamide (L^1H):($C_8H_8N_3SF$)Colour, White, M. P., 190°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
195.29 (197.22)	47.90 (48.71)	4.00 (4.08)	21.09 (21.30)	15.90 (16.25)	84	77	5-6	3-4

(b)[2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarbothioamide (L^2H): ($C_9H_{10}N_3SF$) Colour, White, M. P., 121°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
210.96 (211.25)	51.01 (51.16)	04.00 (04.77)	19.12 (19.89)	14.70 (15.17)	91	80	6-7	5

(c)[1-(2-oxo-2H-chrome-3yl-ethylidene)]-hydrazinecarboxamide (L^8H): ($C_{12}H_{11}N_3SO_2$) Colour, Brown, M. P., 212°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
260.56 (261.28)	54.93 (55.15)	04.01 (04.24)	15.90 (16.08)	11.90 (12.24)	92	81	6	4-5

***Preparation of hydrazinecarboxamides:* (L^3H,L^4H and L^7H)**

The hydrazinecarboxamides of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl coumarin were prepared by the condensation of o-fluorobenzaldehyde, o-fluoroacetophenone and 3-acetyl coumarin with semicarbazide hydrochloride (in presence of sodium acetate) in 1:1 molar ratio using ethanol as a solvent. The contents were refluxed for about 3-5 hours in thermal method and about 5-7 minutes in microwave method. After refluxing, the contents were separated out as crystalline solids. These were dried and purified by recrystallisation by the same solvent. Analyses of the above ligands are as follows:

(a)[2-(2-fluorophenyl)methylene]hydrazinecarboxamide(L^3H): ($C_8H_8N_3OF$) Colour, Off white, M. P., 218°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
180.70 (181.16)	52.11 (53.03)	03.98 (04.45)	22.29 (23.19)	-	87	76	5	4-5

[2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarboxamide (L^4H) ($C_9H_{10}N_3OF$) Colour, White, M. P., 195°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
194.13 (195.19)	52.68 (53.37)	05.00 (05.16)	22.74 (23.15)	-	91	87	5	4

(c)[1-(2-oxo-2H-chrome-3yl-ethylidene)]-hydrazinecarbothioamide (L^7H): ($C_{12}H_{11}N_3O_3$) Colour, Light brown, M. P., 234°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
243.45 (245.22)	57.01 (58.77)	04.40 (04.51)	17.00 (17.13)	-	88	76	5-6	5

***Preparation of isonicotinoyl hydrazones:* (L^5H-L^6H)**

The Isonicotinoyl hydrazones of o-fluorobenzaldehyde and o-fluoroacetophenone were synthesized by the condensation reaction of isonicotinic acid hydrazide with o-fluorobenzaldehyde and o-fluoroacetophenone in 1:1 molar ratio, respectively, in the medium of ethanol. After refluxing the contents by using both the techniques (thermal as well as microwave),the contents were separated out as crystalline solids. These were dried and purified by recrystallisation, from the same solvent.Analyses of the above ligands are as follows:

(a) [2-(2-fluorophenyl)methylene]isonicotinoyl hydrazone(L^5H):($C_{13}H_{10}N_3OF$) Colour, Whitish cream, M. P., 181°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
242.48 (243.23)	59.54 (60.21)	03.12 (03.88)	15.88 (16.20)	-	87	75	5	5

(b) [2-{1-(2-fluorophenyl)ethyledene}]isonicotinoyl hydrazone (L^6H): ($C_{14}H_{12}N_3OF$) Colour, Cream, M. P., 187°C

Mol. Wt.	Found (Calc.) %				Yield (%)		Time	
Found (Calc)	C	H	N	S	MW	T	MW (Minutes)	T (H)
271.96 (273.31)	59.36 (61.51)	04.04 (04.41)	13.91 (15.37)	-	85	72	5-6	4

***Structure of Schiff Base ligands:* (L^1H– L^8H)**

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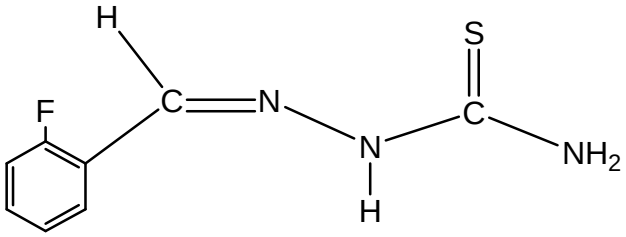
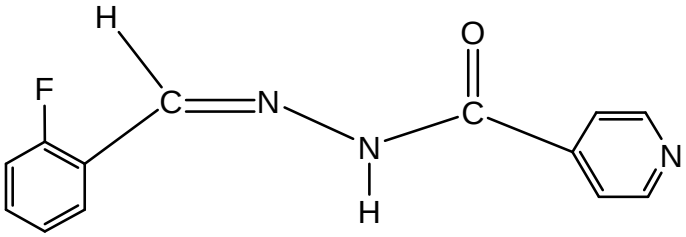


[2-(2-fluorophenyl)methylene]hydrazinecarbothioamide
(L^1H)



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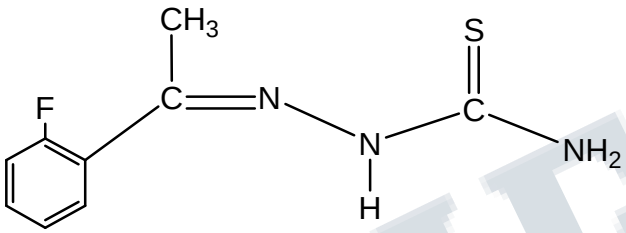
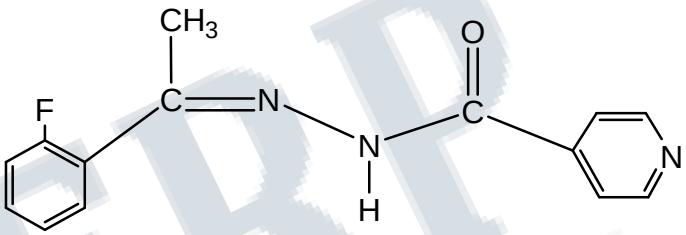
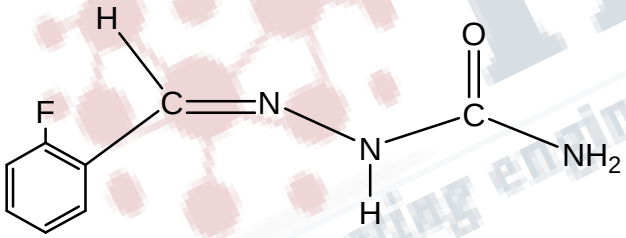


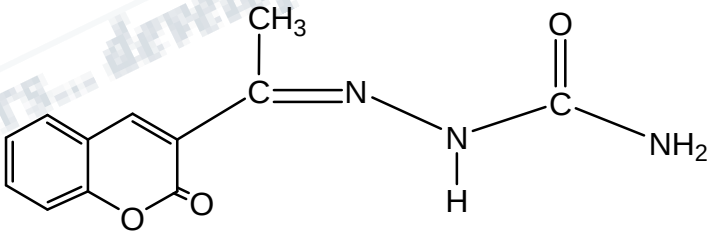
[2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarbothioamide
(L^2H)



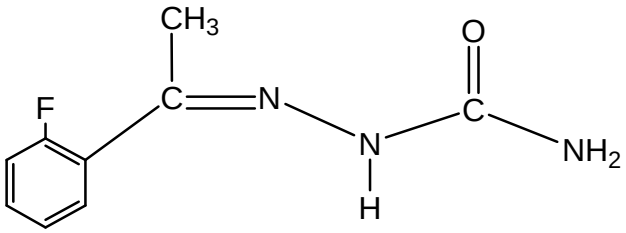
[2-{1-(2-fluorophenyl)ethyledene}]isonicotinoyl hydrazone(L^6H)



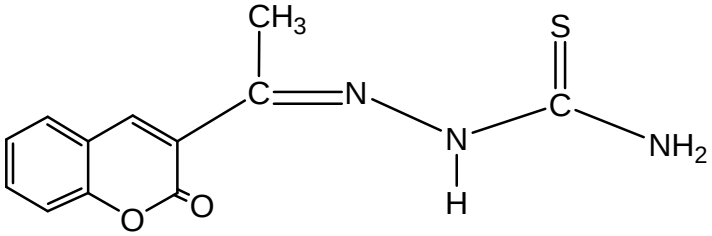
[2-(2-fluorophenyl)methylene]hydrazinecarboxamide
(L^3H)



[1-(2-oxo-2H-chrome-3yl-ethylidene)]-hydrazinecarbothioamide(L^7H)



[2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarboxamide
(L^4H)



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[1-(2-oxo-2H-chrome-3yl-ethylidene)]-hydrazinecarboxamide(L^8H)

VI. SYNTHESIS OF MANGANESE(II) COMPLEXES

Preparation of the manganese(II) complexes of isonicotinoyl hydrazones:(L^5H-L^6H)

The calculated amount of hydrated manganese dichloride ($MnCl_2.4H_2O$) was reacted with a methanolic solution of the ligands (L^5H and L^6H)in unimolar and bimolar ratios. The reaction was carriedout by two defferent methods, thermal as well as microwave. In thermal method the reaction mixture was refluxed for 14-15 hours and for ~10 minutes in microwave method. The thermal method required a large amount of solvent but the microwave method required only few mL of solvent as reaction media. After the complete the reaction, the excess of the solvent was removed and the complexes were dried for 1-2 hours *in vacuo*. Finally the product was purified by repeated washing with methanol and n-hexane. They were further subjected to check their purity by TLC using silica gel G. The physical properties and analytical data of these complexes were reported as follows:

Manganese(II) complex with L^5H (monofunctional bidentate N^O)	
(1:1) $[MnCl(L^5)(H_2O)]$ Dark yellow	Mol. Wt., 347.81 (350.62), C, 42.52 (44.52), H, 03.05 (03.12), N, 10.10 (11.90), Cl, 09.98 (10.12), Mn, 14.84 (15.66), $\mu_{eff.}$ (B.M.), 5.76, M.P., 229°C(d),
(1:2) $[Mn(L^5)_2]$ Light yellow	Mol. Wt., 536.64 (539.39), C, 55.67 (57.89), H, 03.13 (03.30), N, 14.77 (15.52), Mn, 09.39 (10.18), $\mu_{eff.}$ (B.M.), 5.91, M.P., 222°C(d)

Manganese(II) complex with L^6H (monofunctional bidentate N^O)	
(1:1) $[MnCl(L^6)(H_2O)]$ Yellow	Mol. Wt., 362.27 (364.65), C, 44.51 (46.12), H, 03.48 (03.59), N, 10.54 (11.52), Cl, 09.24 (09.72), Mn, 14.24 (15.06), $\mu_{eff.}$ (B.M.), 5.82, M.P., 232°C(d),
(1:2) $[Mn(L^6)_2]$ Pale yellow	Mol. Wt., 563.51(567.43), C, 59.00 (59.23), H, 03.73 (03.91), N, 13.07 (14.81), Mn, 08.27 (09.62), $\mu_{eff.}$ (B.M.), 5.79, M.P., 237°C(d)

➢ ***Preparation of the manganese(II)* heterochelates derived from specific aldimine with different aldimine/ketimines**

$MnCl_2.4H_2O$ was dissolved in methanol and to this, methanolic solutions of both the ligands i.e. aldimine and aldimine/ketimine in 1:1:1 molar ratio were added and heated under reflux for 5-6 hrs. The solvent was removed and the products so obtained were washed with n-hexane and dried in vacuo. The aldehydic ligand which is common in all the reactions is L^3H and different aldimine and ketimine used are L^1H, L^2H, L^4H, L^7H and L^8H. The physical properties and analytical data of these complexes were reported as follows:

Manganese(II) heterochelates complex derived from specific aldimine L^3H with L^1H and L^4H	
$[Mn(L^3)(L^1)]$ Dark yellow	Mol. Wt., 429.81 (431.32), C, 43.52 (44.52), H, 03.03 (03.27), N, 18.10 (19.48), Mn, 11.84 (12.73),S 06.96 (07.43), $\mu_{eff.}$ (B.M.), 5.91, M.P., 226°C(d),
$[Mn(L^3)(L^4)]$ Light yellow	Mol. Wt., 428.64 (429.27), C, 45.67 (47.52), H, 03.13 (03.75), N, 18.77 (19.57), Mn, 11.39 (12.79), $\mu_{eff.}$ (B.M.), 5.76, M.P., 223°C(d)
Manganese(II) heterochelates complex derived from specific aldimine L^3H with L^2H, L^7H and L^8H	
$[Mn(L^3)(L^2)]$ Yellow	Mol. Wt., 443.27 (445.34), C, 43.51 (45.80), H, 03.48 (03.62), N, 17.54 (18.87), S, 06.78 (07.19), Mn, 11.24 (12.33), $\mu_{eff.}$ (B.M.), 5.79, M.P., 222°C(d),
$[Mn(L^3)(L^7)]$	Mol. Wt., 478.51(479.31), C,

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Brown	49.00 (50.11), H, 03.43 (03.57), N, 16.07 (17.52), Mn, 11.27 (11.46), $\mu_{eff.}$ (B.M.), 5.82, M.P., 239°C(d)
[Mn(L^3)(L^8)] Brown	Mol. Wt., 588.51(591.45), C, 55.00 (56.82), H, 02.73 (02.81), N, 13.07 (14.20), S, 04.78 (05.41), Mn, 08.27 (09.20), $\mu_{eff.}$ (B.M.), 5.78, M.P., 230°C(d)

VII. RESULT AND DISCUSSION:

(1) MANGANESE

(2) FLUOROIMINE COMPLEXES

Isonicotinoyl hydrazone complexes:-

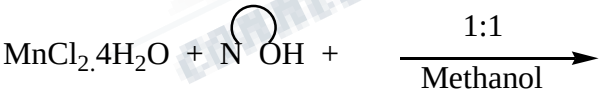
(i) [MnCl(L^5)(H_2O)] and [Mn(L^5)$_2$]

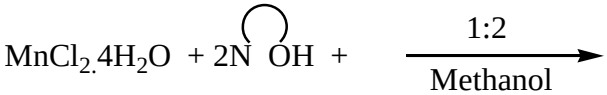
Where, L^5H: [2-(2-fluorophenyl)methylene]isonicotinoyl hydrazone

(ii) [MnCl(L^6)(H_2O)] and [Mn(L^6)$_2$]

Where, L^6H: [2-{1-(2-fluorophenyl)ethyledene}]isonicotinoyl hydrazone

The manganese(II) complexes of two monofunctional bidentate isonicotinoylhydrazones(L^5H and L^6H) were prepared by dissolving a calculated amount of metal chloride ($MnCl_2.4H_2O$) in methanol and then adding a methanolic solution of the ligands to this solution. The reactions were carried out in 1:1 and 1:2 molar ratios. Overall reaction of 1:1 and 1:2 manganese(II) complexes with isonicotinoylhydrazonesare as follows:





(Where,  is the donor system of the isonicotinoylhydrazones (L^5H+L^6H))

The resulting manganese(II) complexes have been obtained as coloured solids and are insoluble in most of the common organic solvents but their solubility is appreciable in methanol, ethanol, dimethylformamide and dimethylsulfoxide. The monomeric nature of these products has been confirmed by the molecular weight determinations. The low value of molar conductivity (8.75-13.00 ohm^{-1} cm^2 mol^{-1}) of $1X10^{-3}$ M solutions of metal complexes adequately supports the non-electrolytic nature of the metal complexes. The bonding pattern and the geometry of these complexes have been deduced on the basis of IR and UV-Vis spectral studies.

The electronic spectra of the isonicotinoylhydrazones (L^5H and L^6H) and their manganese(II) complexes have been recorded in methanol. The electronic spectra of the ligands show a broad band at 26490- 27295 cm^{-1} which can be assigned to the n-π* transitions of the azomethine (>C=N) group and undergo a blue shift on complexation, indicating the coordination through azomethine group of the ligand to the metal ion. The electronic spectra of metal complexes in the visible region were studied to determine the possible spatial arrangements of donor atoms around the metal ion. Some weak spin forbidden d-d transitions were observed in the region16418-16921 and 20029-23854 cm^{-1} assignable to $^6A_1 \rightarrow {}^4T_2$ and $^6A_1 \rightarrow {}^4$Etransitions. These transitions are typical of tetrahedral environment around the manganese(II) metal atom (Table1).

Table 1: Electronic spectral data of manganese(II) complexes

Compound	Transitions	Spectral bands cm^{-1}	μ_{eff} (BM)
[MnCl(L^5)(H_2O)]	$^6A_1 \rightarrow {}^4T_2$ $^6A_1 \rightarrow {}^4E$	16509 20029	5.69
[Mn(L^5)$_2$]	$^6A_1 \rightarrow {}^4T_2$ $^6A_1 \rightarrow {}^4E$	16451 23325	5.71
[MnCl(L^6)(H_2O)]	$^6A_1 \rightarrow {}^4T_2$ $^6A_1 \rightarrow {}^4E$	16921 23854	5.82
[Mn(L^6)$_2$]	$^6A_1 \rightarrow {}^4T_2$ $^6A_1 \rightarrow {}^4E$	16418 22931	5.99

In IR spectra a medium intensity band appears in the regions 3160-3189 cm^{-1} [ν(NH) mode in the ligands, which disappeared in the spectra of the metal complexes,which indicates the expected deprotonation of functional group on complexationan. A absorption band due to the azomethine (>C=N) group was observed in the spectra of the free

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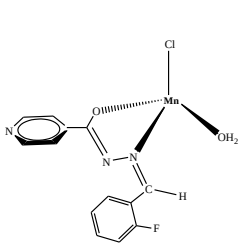
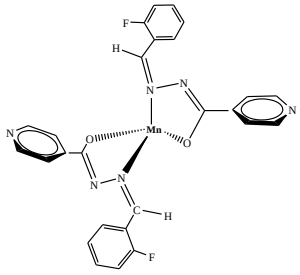
ligands which is shifted to a lower frequency in the spectra of the corresponding metal complexes, probably due to the coordination of the azomethine nitrogen to the metal atom. The bands due to symmetric and asymmetric vibrations of (NH_2) group in the ligands remain unchanged in the spectra of complexes, indicating non-involvement of the this group in coordination.. The bands at 1690-1710 cm^{-1} due to ν(C=O) vibrations, in the spectra of free ligands, are shifted towards lower frequency in the spectra of metal complexes, indicating complexation takes place through the enolic oxygen atom to the central metal ion. Non ligandbands occurring at 548−586 cm^{-1} and 451−472 cm^{-1}have been assigned to ν(Mn–O) and ν(Mn←N), respectively. In the spectra of (1:1) manganese(II) complexes a band observed at 842-860 cm^{-1}, due to the rocking mode of vibrations of the coordinated water molecule and the bands due to the ν(Mn−Cl) appears in the region 320–333 cm^{-1}, which remains absent in the spectra of (1:2) manganese(II) complexes (Table 2).The overall infrared spectral evidences suggest monobasic bidentate nature of the ligands and the coordination of the ligands through oxygen and nitrogen donor atoms forming a five-membered chelate ring.

Table 2: IR (cm^{-1}) Spectral data of the ligands and their manganese(II) complexes

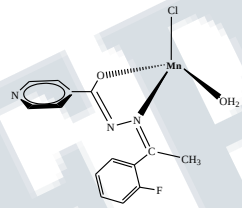
Compound	IR Spectral data (cm^{-1})					
	ν(C=N)	ν(NH)	ν(OH) (water molecule)	ν(Mn←N)	ν(Mn-O)	ν(Mn-Cl)
L^5H	1610	3189		-	-	
L^6H	1602	3160		-		
$[MnCl(L^5)(H_2O)]$	1571	-	849	459	586	333
$[Mn(L^5)_2]$	1579	-		469	574	-
$[MnCl(L^6)(H_2O)]$	1591	-	858	451	561	321
$[Mn(L^6)_2]$	1599	-		472	548	-

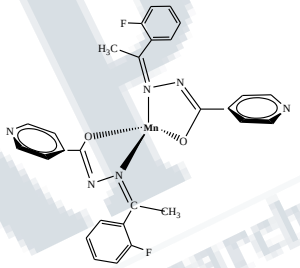
On the basis of the electronic and IR spectral studies the expected bonding mode of the ligands towards the metal atom and the tetra-coordinated geometries have been established for the 1:1 and 1:2 manganese(II) complexes.





$[MnCl(L^5)(H_2O)]$ Complex
$[Mn(L^5)_2]$Complex
(1:1) **(1:2)**





$[MnCl(L^6)(H_2O)]$ Complex
$[Mn(L^6)_2]$Complex
(1:1) **(1:2)**

(3.2)Manganese(II) heterochelates derived from specific aldimine and different aldimine/ketimines:-

(i) *$[Mn(L^3)(L^1)]$ and $[Mn(L^3)(L^4)]$*

Where,

L^1H: [2-(2-fluorophenyl)methylene]hydrazinecarbothioamide

L^3H: [2-(2-fluorophenyl)methylene]hydrazinecarboxamide

L^4H: [2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarboxamide

(ii) *$[Mn(L^3)(L^2)]$, $[Mn(L^3)(L^7)]$ and $[Mn(L^3)(L^8)]$*

Where,

L^2H: [2-{1-(2-fluorophenyl)ethyledene}]hydrazinecarbothioamide

L^7H: [1-(2-oxo-2H-chrome-3yl-ethylidene)]-hydrazinecarboxamide

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L^8H: *[1-(2-oxo-2H-chrome-3yl-ethylidene)]hydrazinecarbothioamide*

[*2-(2-fluorophenyl)methylene]hydrazinecarboxamide*

along with one of the another ligand (hydrazinecarboxamide or hydrazinecarbothioamide) reacts with manganese dichloride in 1:1:1 molar ratio to form products of the type $[Mn(N\overset{\frown}{O})(N\overset{\frown}{X})]$. The reactions were carried out in refluxing methanol and could be completed in 9-10 hours of refluxing.

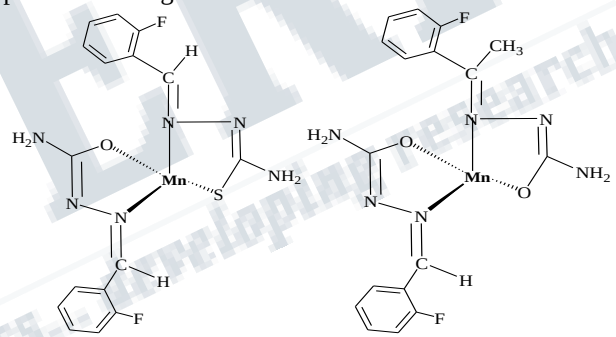
$$MnCl_2.4H_2O + N\overset{\frown}{O}H + N\overset{\frown}{X}H \xrightarrow[\text{Methanol}]{1:1:1} [Mn(N\overset{\frown}{O})(N\overset{\frown}{X})] + 2HCl + 4H_2O$$

(Where, X = S/O)

The heterochelates so formed are bright coloured solids with sharp melting points, soluble in methanol, DMF and DMSO. These are monomers and non electrolytes. The products have been washed repeatedly with cyclohexane and ether so as to isolate them in a pure form. Their purity was further checked by TLC using anhydrous chloroform as the solvent.

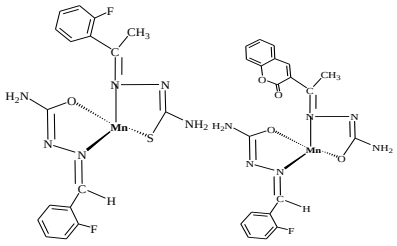
The electronic spectra of the complexes in the visible region show weak absorptions at ca. 21898 cm^{-1} and ca. 23800 cm^{-1} which may be assigned to $^6A_1 \rightarrow {}^4E(G)$ and $^6A\text{-}{}^4A_1(G)$ transitions respectively , suggesting a possible tetrahedral environment around the metal ion. Strong absorptions around 37695-37354 cm^{-1} and 34234-32246cm^{-1}, arise due to π -π^* electronic transitions of the ligands.

The strong bands at ca 3265-3275 cm^{-1} in the I.R. spectra of the free ligands, assigned to the (NH), are absent in the metal heterochelates indicating its deprotonation. Two sharp bands due to ν_{as} and ν_s of NH_2 in the region 3400-3300 cm^{-1}[1(10-13)] remain unchanged in the corresponding metal complexes and this shows the non- participation of this group in chelation. All the ligands show a strong band at 1610-1595 cm^{-1} due to (>C=N) group. The lowering of this frequency by ca.15- 20 cm^{-1} on complexation indicates that the unsaturated nitrogen of the azomethine is coordinated to the metal atom. Further a medium intensity band at ca. 1050±10 cm^{-1} due to νN-N in the ligands is shifted to higher frequency in the spectra of the complexes. The ν(C=S) and ν(C=O) bands appearing in the ligands at their respective positions are absent in the spectra of the metal complexes. As sulphur or oxygen atoms of the ligands coordinate with the central metal atom. Further, some new bands observed in the region 495-280 cm^{-1}[1(14-16)] are due to νM-O,νM-N and νM-S. The above discussion clearly affirms that the ligands behave as a monobasic bidentate chelating agents coordinating through azomethine nitrogen and sulphur or oxygen atoms. The e.s.r. spectra of *[$Mn(L^3)(L^4)$]* at room temperature showed only one isotropic signal centred at g=2.016. The spectrum of the complex is expected of high spin s=5/2 species, and is similar to electronic spin resonance spectra of closely related manganese(II) complexes reported earlier and assigned a tetracoordinated state to the central manganese atom . The magnetic moment values of manganese(II) complexes lie in the range 5.9+0.1 B.M. and which suggests a high spin state for these complexes. Since high-spin manganese(II) complexes have an orbitally non-degenerate ^6S ground term, a spin only magnetic moment of 5.92 B.M. is expected which will be independent of the temperature and the stereochemistry. The following structure can be proposed on the basic of above mentioned spectral and magnetic evidence.



$[Mn(L^3)(L^1)]$ Complex

$[Mn(L^3)(L^4)]$ Complex



$[Mn(L^3)(L^2)]$ Complex

$[Mn(L^3)(L^7)]$ Complex

ISSN (Online) 2456 -1304

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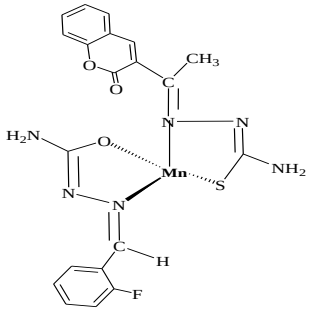


[Mn(L^3)(L^8)] Complex

Biological Activity:

The use of coordination compounds as biological probes represent one of the most successful application of bioinorganic chemistry. The chemistry of manganese complexes has attracted particular interest for their biological, medicinal, synthetic, and catalytic activities. Manganese compounds are potential oral drugs for diabetic patients and numerous investigations are carried out in this regard. Another reason for the study of vanadium containing complexes is their ability to catalyze important reactions. Schiff-base complexes of manganese(II) are among the most widely employed catalysts for aerobic and non-aerobic alkene epoxidation.This biological and catalytic relevance of manganese has promoted the synthesis of model manganese compounds containing O, N donor ligands.

Encouraged by the above findings and our interest in the biological and chemical properties of such compounds, we envisioned to design and synthesize some bioactive schiff bases and their manganese(II) complexes.

ANTIFUNGAL ACTIVITY

Fungi used:

i) *Macrophomina phaseolina*
ii) *S. rolfsi*
iii) *Alternaria alternata*

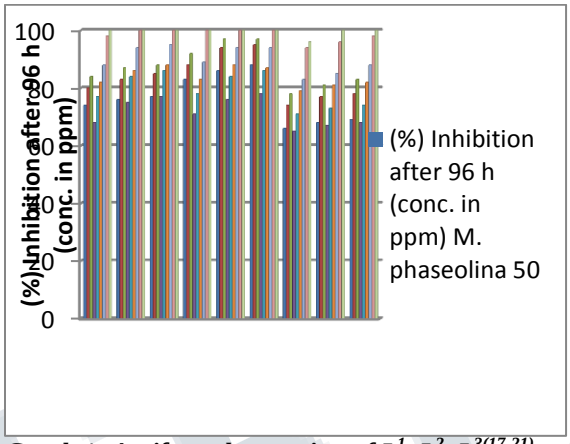
The antifungal activity of the synthesized compounds was evaluated by the "Agar Plate Technique."

Agar Plate Technique

Potato dextrose agar medium was prepared in the flask and then sterilized. The principle involved in this method is to "poison" the nutrient medium with a fungitoxicant (compound) and then allowing a test fungus to grow on such medium.

Results

The results of antifungal activities of the parent ligands and their manganese(II) complexes against various pathogenic fungi have been shown in Graph 1. The inferences drawn from these Graphs clearly indicate that sulphur containing ligands, are more active against various pathogenic fungi than oxygen containing ligands. The increased activity of these ligands may be explained on the basis that sulphur (as donor atom) containing compounds are more toxic than the oxygen containing compounds.



Graph 1: Antifungal screening of L^1, L^2, $L^{3(17-21)}$ and their Mn(II) complexes.

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