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Synthesis, Characterization and Antifungal Activities of Some Mn(III) Mixed Ligand Complexes

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ABSTRACT

Mixed ligand complexes of Mn (III) with general chemical formula [$Mn(acac)_2XSH_2$] $X=NCS^-$, N_3^-, Cl^-, Br^- were synthesized in the presence of Acetyl acetone, Hydrochloric acid, Hydrobromic acid, Potassium thiocynate, Sodium azide and Hydrogen sulphide. The structures of synthesized complexes were determined by magnetic susceptibility, electrical conductivity and spectral (UV and IR) studies. The magnetic moment values of synthesized complexes indicate the presence of four unpaired electrons. The electronic conductivity data show the non-electrolytic in nature. Our results indicate the octahedral nature of Mn (III) complexes. The synthesized complexes were also screened for their antifungal activity against the fungal strains As per gillusflav us and Cladosporiumherbarium.

Keywords: *Mixed ligand complexes, Acetyl acetone, thiocyanato, azido, chloro, bromo and hydrogen sulphide.*

INTRODUCTION

For the last two decades, the synthesis of coordination compounds with the transition metal and their application have become an attractive field because of their peculiar properties such as catalysis, ion exchange, microelectronics, nonlinear optics, porous material etc.[1-7] The mixed ligand complexes of transition metals play important role in different fields like photochemistry, analytical chemistry and magneto-chemistry.[8] The coordination chemistry of manganese has been studied in bioinorganic chemistry as an interested field.[9] The magnetic properties and diverse catalytic activity of such compounds are now being explored for their biological importance.[10-12] Manganese (Mn) in its +3 oxidation state forms complexes with charged and neutral ligands.[13] The X-ray crystallographic data of tris (acetylacetonato)-manganese(III) has been given for the single crystal synthesized in our lab.[14] Manganese(III) octahedral complexes have been found susceptible to Jahn-Teller distortion. We further synthesized four novel mixed ligand Mn (III) complexes viz; [$Mn(acac)_2(NCS)SH_2$], [$Mn(acac)_2(N_3)SH_2$], [$Mn(acac)_2(Cl)SH_2$] and [$Mn(acac)_2(Br)SH_2$] and studied for their magnetic susceptibility, UV and antifungal properties against the fungal strains *A. flavus* and *C. herbarium.*

MATERIAL AND METHODS

C zapek agar medium, DMSO, Acetone, ethyl alcohol, streptomycin, sprit lamp, enoculating needle, cork borer, petridishes, antifungal drug Fluconazole as standard, fungal strains A. flavus and C. herbarium. Reagent and Chemicals: KMnO4 (pure), KSCN, HBr, HCl, acetyl acetone were purchased and H2S gas was prepared in our lab.

Physical Measurement

The electronic spectra were recorded at room temperature on a Hitachi (Japan) Model.U-2000 UV-Vis spectrophotometer in the 200-1100 nm range. IR spectra were recorded on a FTIR spectrophotometer (Varian 3100 FTIR) in the range 400-4000 cm- using KBr pellet. Magnetic susceptibility measurements were carried out at room temperature using EV7VSM (ADE-DMS USA) on AD MAGNETICS vibrating sample magnetometer software.

General Methods for Preparation of the Complexes

All the four Mn(III) complexes were synthesized using the same general method reported previously.[15]

Preparation of [Mn(acac)2(Cl)SH2]

The compound [Mn(acac)2Cl] (0.25g 0.80mmol) was dissolved in DMSO (20mL). To this solution H2S gas was passed for 2 min under nitrogen atmosphere. Yellow coloured precipitate was obtained that was filtered under vacuum and dried over P2O5. The colour of the complex changed from yellow to dark brown.

Yield: 0.08g, (29.6%)

Found for: C10H16ClO4SMn, C=37.5%, H=4.84, Cl=10.75%, O=20.0%, S=10.0%, Mn=17.51%

Calcd: C=37%, H=4.95%, Cl=11.0%, O= 19.83%, S=9.91%, Mn=17.03%.

Preparation of [Mn(acac)2(Br)SH2]

The compound [Mn(acac)2Br] (0.250g 0.75mmol) was dissolved in 20 ml of DMSO, and passed H2S gas followed by creating inert atmosphere by dinitrogen introducing through Pt needle. Yellow coloured precipitate was obtained that was filtered off and dried under vacuum over P2O5. The colour of the complex again changed from yellow to dark brown.

Yield: 0.10g, (37%)

Found for: C10H16BrO4SMn

C=33.5%, H=4.34%, Br=22.05%, O= 17.55%, S=8.9%, Mn=14.9%

Calcd: C=32.78%, H=4.37%, Br=21.82%, O= 17.48%, S=8.74%, Mn=15.0%.

Preparation of [Mn (acac)2(NCS)SH2]

The compound [Mn(acac)2NCS] (0.250g 0.80mmol) was dissolved in 20 ml of DMSO, and passed H2S gas, dinitrogen injected through Pt needle for about 2 minutes, Yellow coloured precipitate was obtained that was filtered off and dried under vacuum over P2O5. This complex also changed from yellow to dark brown in colour.

Yield: 0.09g, (33.33%)

Found for: C11H16BrNO4SMn

C=39.05%, H=4.74%, N=4.15%, O= 18.8%, S=18.40%, Mn=16.01%

Calcd: C=38.24%, H=4.63%, N=4.05%, O= 18.54%, S=18.54%, Mn=15.9%.

Preparation of [Mn(acac)2(N3)SH2]

The compound [Mn (acac)2N3] (0.250g 0.84mmol) was dissolved in 20 ml of DMSO, H2S was passed in similar way to produce yellow coloured precipitate that was also changed into dark brown colour.

Yield: 0.10g, (37.40%)

Found for: C10H16BrN3O4SMn

C=36.05%, H=4.74%, N=5.04%, O= 18.80%, S=9.49%, Mn =16.71%

Calcd: C=38.24%, H=4.63%, N=4.05%, O= 18.54%, S=18.54%, Mn=15.9%.

RESULTS AND DISCUSSION

Conductivity Measurement

The measurement for electrical conductivity of the synthesized complexes has been done in DMSO (1x10-3 m) solution. The molar conductance values were found to be in the range from 0.27 to 0.81Ω-1cm2mol-1 which indicates that the complexes are non-electrolytic in nature. [16]

The physical properties and analytical data of these complexes are tabulated in Table 1

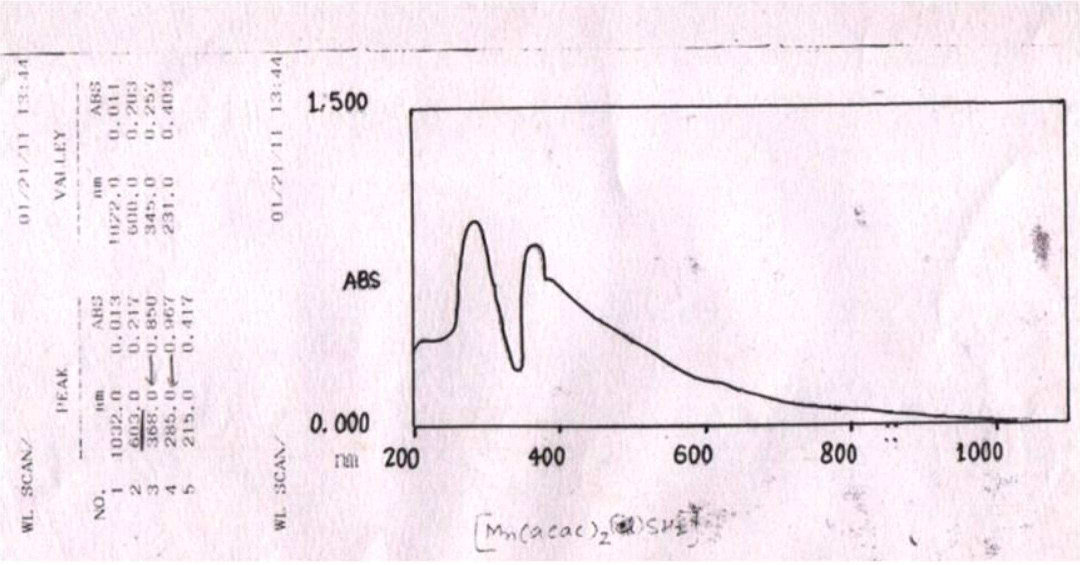
Table1. *Physical properties and analytical data of the Mn(III) mixed ligand complexes*

S.No	Complex	Mol.wt	% Yield	Colour	Melting Point (°C)	Molar Conductance ($ohm^1 cm^2 mol^{-1}$)	μ_{eff}(BM)
1	$[Mn(acac)_2(Cl)SH_2]$	322	29.60	Dark brown	>300	0.27	4.87
2	$[Mn(acac)_2(Br)SH_2]$	367	37.00	Dark brown	>300	0.81	4.92
3	$[Mn(acac)_2(NCS)SH_2]$	345	33.33	Dark brown	>300	0.73	4.89
4	$[Mn(acac)_2(N_3)SH_2]$	329	37.40	Dark brown	>300	0.54	4.95

Magnetic Susceptibility and Electronic Spectra

Magnetic Susceptibility data of the Mn(III) complexes have been taken at room temperature are given in table 1. The Mn(III) complexes have µeff values in the range of 4.87 to 4.95 BM showing the presence of four unpaired electrons confirming high spin d4 system.[17-28]

The electronic spectra of all complexes were recorded in 1x10-3m DMSO at 30°C. The electronic spectra of Mn(III) complexes show band (I-V) which lie in the range of 603-605nm, 356-448nm, 285-359nm, 215-285nm and 215 nm respectively (Figure 1a-1d). The absorption bands at 605nm and 448 nm may be assigned to charge transfer transitions. These charge transfer bands are due to the spin allowed d-d transition that are expected to show up in this region by the Mn(III) complex. [29]



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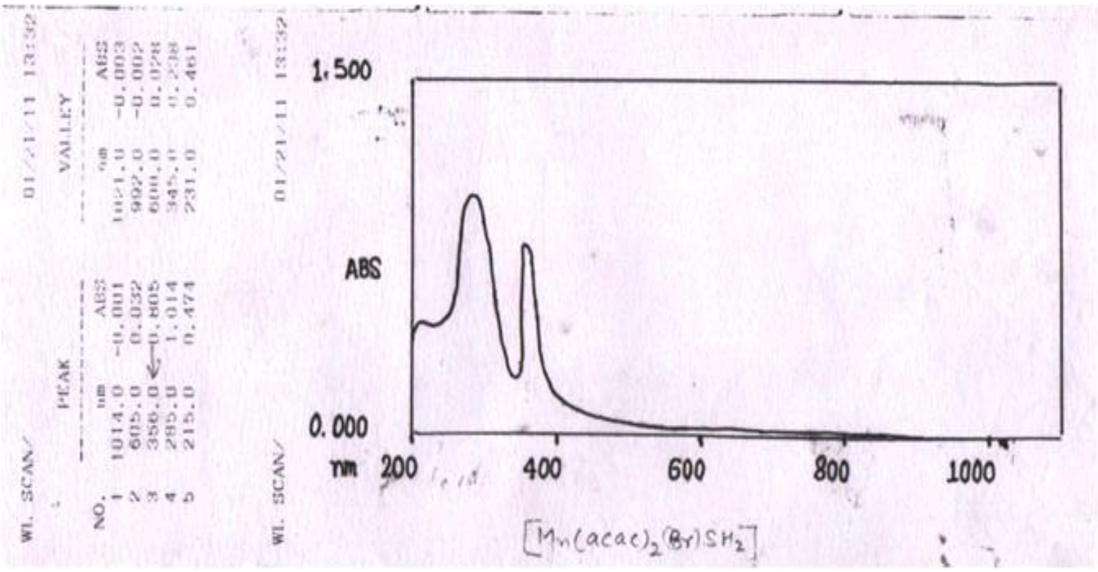
NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	1032.0	0.013	1022.0	0.011
2	603.0	0.217	600.0	0.203
3	368.0	0.850	345.0	0.257
4	285.0	0.967	231.0	0.403
5	215.0	0.417		

Figure1a. *UV Spectrum of [Mn(acac)2(Cl)SH2]*



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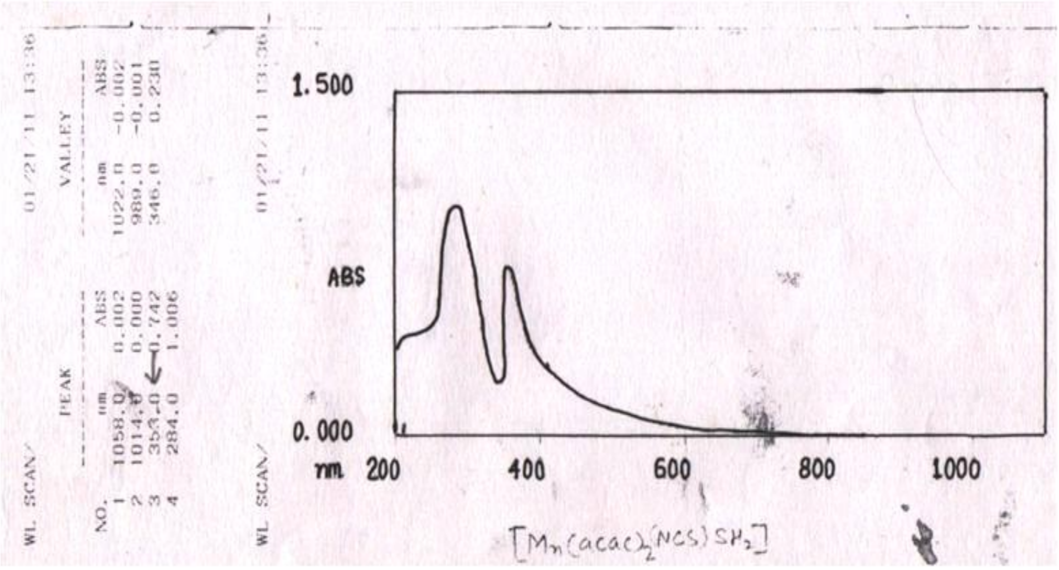
NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	1014.0	-0.001	1021.0	-0.003
2	605.0	0.032	902.0	-0.002
3	356.0	0.805	600.0	0.028
4	285.0	1.014	345.0	0.238
5	215.0	0.474	231.0	0.461

Figure1b. *UV Spectrum of [Mn(acac)2(Br)SH2]*



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NO.	PEAK nm	PEAK ABS	VALLEY nm	VALLEY ABS
1	1058.0	0.002	1022.0	-0.002
2	1014.0	0.000	989.0	-0.001
3	353.0	0.742	346.0	0.230
4	284.0	1.006		

Figure1c. *UV Spectrum of [Mn(acac)2(NCS)SH2]*

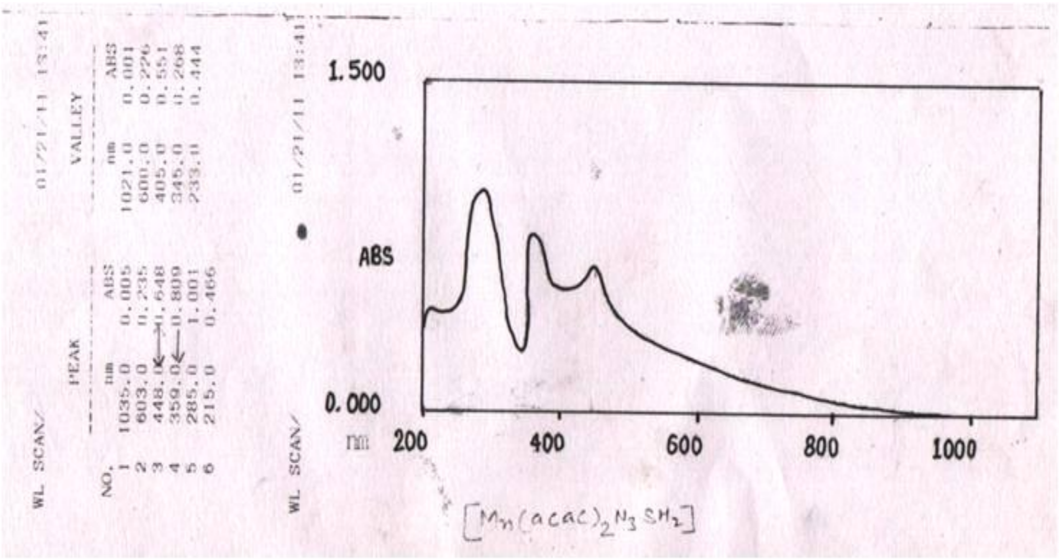

Figure1d. *UV Spectrum of [$Mn(acac)_2(N_3)SH_2$]*

In the case of an octahedral Mn(III) complex only such transition in the form of an intense band is expected near 448nm corresponding to 5T2g_ 5Eg transition.[30] The ligand field parameters such as 10 Dq, B and β have been calculated for all these Mn (III) complexes. The Value of Racah inter electronic repulsion parameter (B) are found to below the free ion value for Mn(III) on (1140cm-1).[31] It suggests the covalent nature of metal-ligand bonding in all the four complexes. The covalency factor β is varying in the range of (0.88-0.92). The electronic spectral data of Mn (III) complexes has been shown in Table 2 and Table 3

Table2. *Absorption maxima, λ_{max}(nm) for Mn(III) mixed ligand complexes*

S. No	Complex	λmax (nm)				
		I	II	III	IV	V
1	[$Mn(acac)_2(Cl)SH_2$]	603	368	285	215	-
2	[$Mn(acac)_2(Br)SH_2$]	605	365	285	215	-
3	[$Mn(acac)_2(NCS)SH_2$]	603	448	353	284	-
4	[$Mn(acac)_2(N_3)SH_2$]	603	448	359	285	215

Table3. *Ligand field parameter Calculated for Mn (III) complexes*

No	Complex	10Dq(cm^{-1})	B	β
1	[Mn(acac)2(Cl)SH2]	27170	1006	0.88
2	[Mn(acac)2(Br)SH2]	28090	1040	0.91
3	[Mn(acac)2(NCS)SH2]	28330	1049	0.92
4	[Mn(acac)2(N3)SH2]	27860	1031	0.90

FTIR Studies

FTIR spectral data of the Mn (III) complexes have been shown in table 4 and figure 2a-2d. The characteristic infrared spectra of starting complexes [Mn(acac)2NCS], [Mn(acac)2N3], [Mn(acac)2Cl] and [Mn(acac)2 Br] have already been reported in literature.[32-34]

The IR spectra of synthesized Mn (III) complexes display band in the regions 1627-1655 cm-1 and 1535–1567cm-1 due to ν(C=O) and ν(C=C) respectively. Moreover the spectra of these complexes exhibit weak bands between 616-667 cm-1 that correspond to the ν(Mn-O).

The band in the range of 974-1080 cm-1 suggests that the Mn (III) is coordinated with two acetylacetona to ligands.[35] A broad band appearing in the range of 2907-2997cm-1 can be assigned for ν(C-H). The significant band in the range of 870-900 cm-1 represents ν(S-H) stretching vibration. These bands are diagnostic for deciding the mode of sulfur attachment to the metal ion. A weak band in the range of 460-466 cm-1 for all these four complexes is tentatively assigned as the ν(Mn-S).

The spectrum of the complex [Mn (acac)2(NCS)SH2]shows two bands at 2077 cm-1 and 787 cm-1, characteristic band for the coordinated NCS- group corresponding to ν(C-N) and ν(C-S) respectively. The role of ν(C-S) is more significant in deciding whether N or S is coordinated with metal ion, the observed 787cm-1 for this complex falls in the region expected for an N bonded NCS- group. [36] The spectrum of the complex [Mn(acac)2(N3)SH2] shows two bands for coordinated azido group. A strong absorption band at 1107cm-1 for ν(N-N) and another peak at 2050cm-1 indicate the coordination of N3 group with the metal ion.[37] Therefore the spectrum of this complex shows a weak band due to ν(Mn-N) at 525cm-1. [38]

Table4. *FTIR spectral data (cm^{-1})*

S. No.	Complex	ν(C-H)	ν(N-N)	ν(C=O)	ν(C=C)	ν(C-N)	ν(S-H)	ν(Mn-O)	ν(Mn-N)	ν(Mn-S)
1	[Mn(acac)$_2$(Cl)SH$_2$]	2907	-	1651	1558	-	898	617	-	462
2	[Mn(acac)$_2$(Br)SH$_2$]	2997	-	1655	1540	-	870	667	-	462
3	[Mn(acac)$_2$(NCS)SH$_2$]	2950	-	1650	1567	2077	885	617	553	460
4	[Mn(acac)$_2$(N$_3$)SH$_2$]	2907	2020	1627	1535	-	900	616	525	466

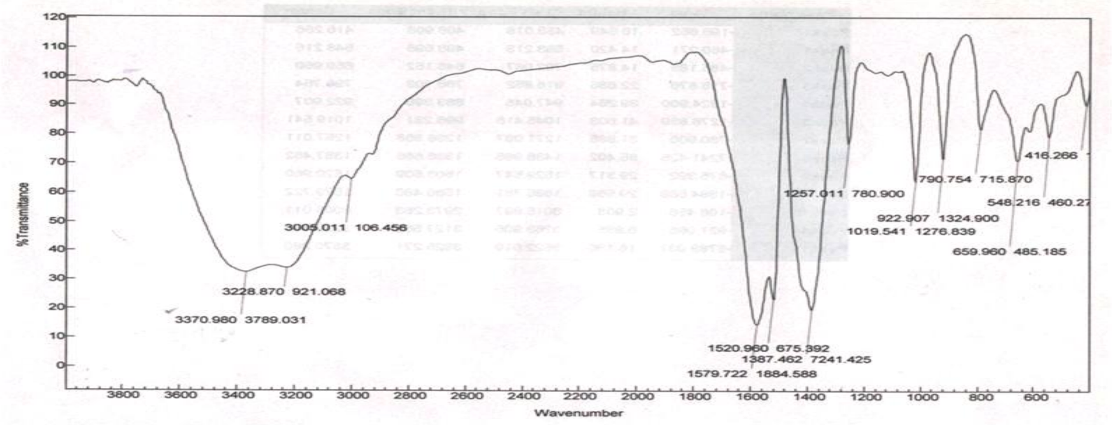

Figure2a. *FTIR Spectrum of [Mn(acac)2(Cl)SH2]*

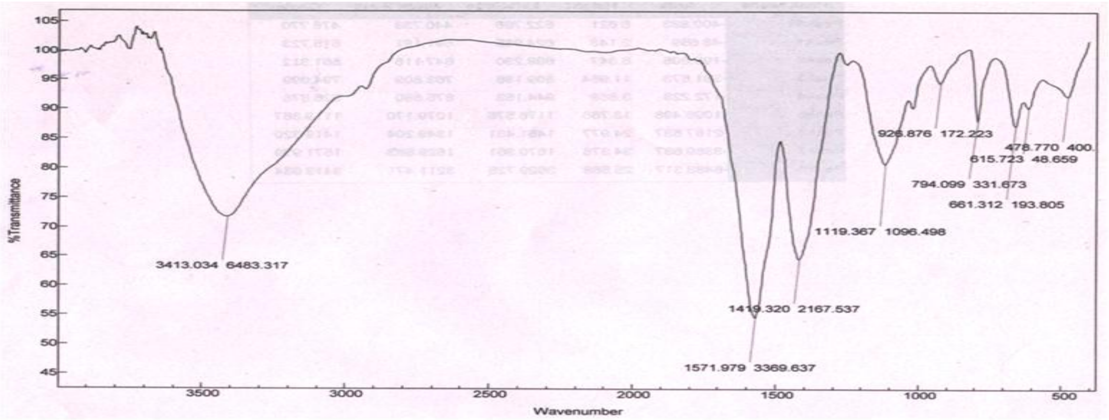

Figure2b. *FTIR Spectrum of [Mn(acac)2(Br)SH2]*

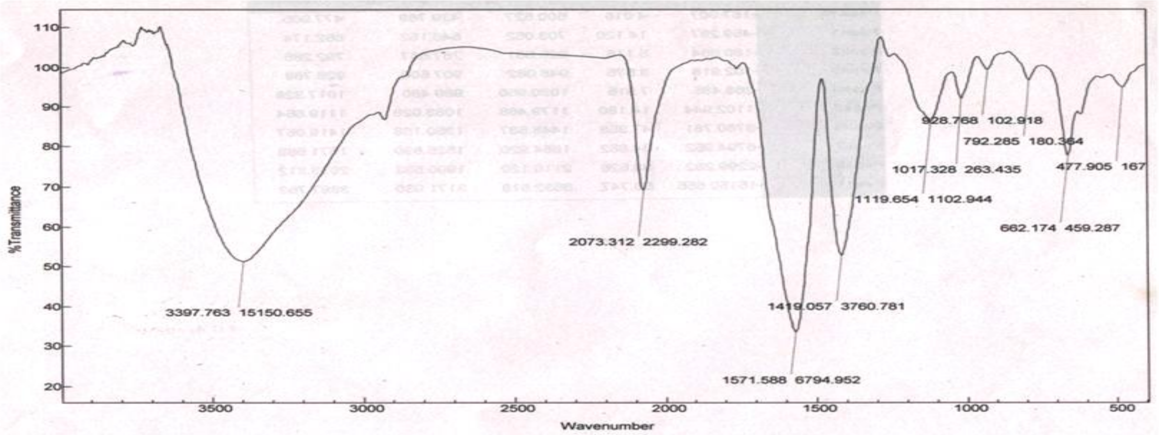

Figure2c. *FTIR Spectrum of [Mn(acac)2(NCS)SH2]*

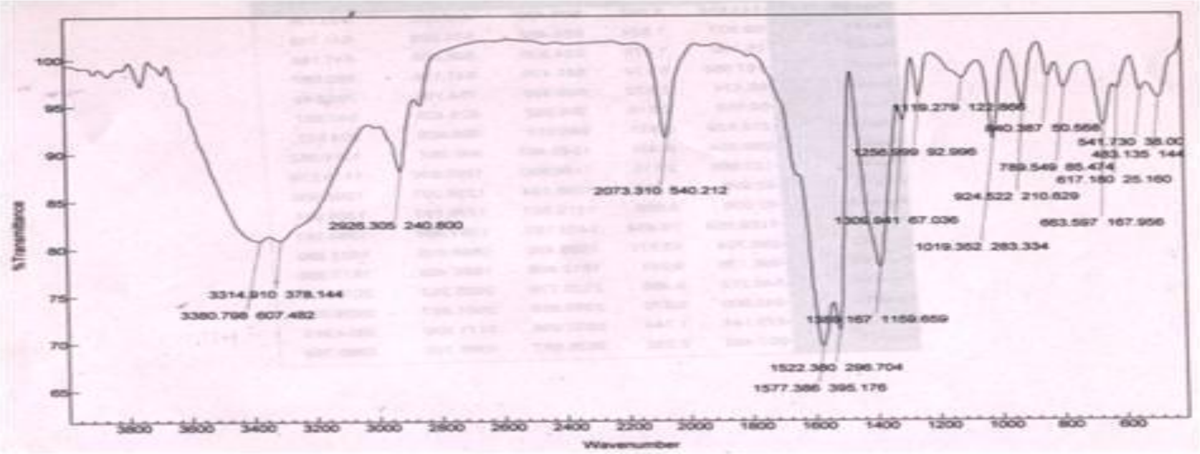

Figure2d. *FTIR Spectrum of [Mn(acac)2(N3)SH2]*

Antifungal Activity

The antifungal activities of the Mn (III) complexes were investigated against the two fungal strains, namely A. flavus and C. herbarium. It is also compared with the antifungal activity of the standard drug fluconazole. The antifungal activity (% inhibition) of these complexes, along with fluconazole, has been given in Table 5. Out of the four complexes, [Mn(acac)2(NCS)SH2] shows the highest percentage inhibition against both the fungal strains, this high antifungal activity is explained on the basis of the presence of thiocynato group.[39] However the complexes [Mn(acac)2(Cl)SH2], [Mn(acac) 2(Br) SH2] and [Mn(acac)2(N3)SH2] showed 49%, 50% and 50% inhibition of mycelial growth against C. Herbarium respectively.

Table5. *Antifungal activities of the Mn (III) mixed ligand complexes (zone of inhibition at 10000ppm (%))*

S.No.	Complex	*A. flavus*	*C.herbarium*
1	$[Mn(acac)_2(Cl)SH_2]$	(-)[a]	49
2	$[Mn(acac)_2(Br)SH_2]$	(-)[a]	50
3	$[Mn(acac)_2(NCS)SH_2]$	60	62
4	$[Mn(acac)_2(Br)SH_2]$	51	50
5	Fluconazole[b]	75	80

[a] =No activity; [b]= standard antifungal drug

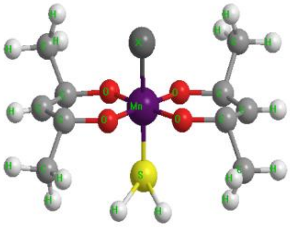

Figure3. *Proposed structure of [Mn(acac)2(X)SH2] complexes; X= Cl- , Br-, NCS-, N3-*

CONCLUSION

On the basis of the above analysis we have proposed octahedral structure for synthesized Mn (III) mixed ligand complexes wherein the Manganese is present in +3 oxidation state. The coordination number of the central Mn (III) is six, satisfied by two bidentate ligands and two mono dentate ligands. One of the axial positions is occupied by any one of negative ligands viz. Cl- , Br-, NCS-, N3- while the other axial position with the neutral ligand SH2. The proposed general octahedral structure of [Mn(acac)2(X)SH2] complexes has been shown in Figure 3 where X= Cl- , Br-, NCS-, N3-

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