Synthesis, Characterization And Biological Studies Of Mn(II) Transition Metal Complex Derived From (*E*)-3-(1-(2-(Benzo*[D]*Thiazol-2yl)Hydrazono)Ethyl)-1-Ethyl-4-Hydroxyquinolin-2(*1H*)-One Hydrazone Schiff Base Ligand.

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Abstract:

Coordination compound of Mn(II) with newly synthesized Schiff base ligand (E)-3-(1-(2-(benzo[d]thiazol-2yl)hydrazono)ethyl)-1-ethyl-4-hydroxyquinolin-2(1H)-one. The obtained ligand and Mn(II) complex is characterized on the basis of elemental analysis, magnetic susceptibility, UV visible spectra, FTIR ,^{1}HNMR spectra, mass spectra, TG-DTA and X-ray powder diffraction. Form the analytical data the stoichiometry of metal complex has been found to be the 2:1 ligand to metal ratio. Therefore the complex may be formulated as $[Mn(L_2)]$*. All the analysis data shows that complex is monomeric hexa coordinated octahedral structure. The ligand and metal chealate have been screened for their antibacterial activity using the Agar cup method at fixed concentration of 1% Against microbial strains, Eschershia coli, Salmonalla typhi, Staphylococcus aureus, Bacillus substilis. The antibacterial activity of ligand and Mn(II) complex illustrates that the ligand and complex seems to be inert towards the E. coli , S. typhi the complex show higher activity than ligand against Staphylococcus aureus and Bacillus substill. Antifungal activity of ligand and complex were tested against in vitro against fungi that is Aspergillus niger, Penicilum chrysoganum, Fusarium moniliforme, Aspergillus flavus by poison plate method using potato dextrose agar medium at fixed (1%) concentration. Ligand does not show fungal activity but it Mn(II) complex show better activity. Which suggest that the incorporation of metal in the ligand results in increasing the antimicrobial activity. X-ray diffraction data suggests triclinic structure of Mn(II) complex.*

Keywords: *Schiff metal complex, antimicrobial activity, ^{1}HNMR spectra, TG-DTA, P-XRD.*

Introduction:

Transition metal complexes containing Schiff base hydrazone ligands have been specific interest for many years. Transition metal complexes of hydrazone compounds have been screened for their medicinal properties[1]. The metal complexes of Schiff base derived from heterocyclic compounds have been a center of attraction of many workers in recent years. But the chelating abilities of Schiff bases derived from nitrogen heterocycle is 2-quinolone. Quinolones are famous categories of compounds known by their intensive biological activity and their vital importance in medicines and pharmaceuticals this prompted us to carry out intensive research work on these classes of compounds[2-3].

In the present communication, we describe the synthesis and characterization of Mn(II) metal complex containing a tridentate (ONN) Schiff base ligand. In addition to physicochemical studies, the complex have been tested *in vitro* to assess their antibacterial activities against some common reference bacteria and fungi and results were compared with standard.

Experimental:

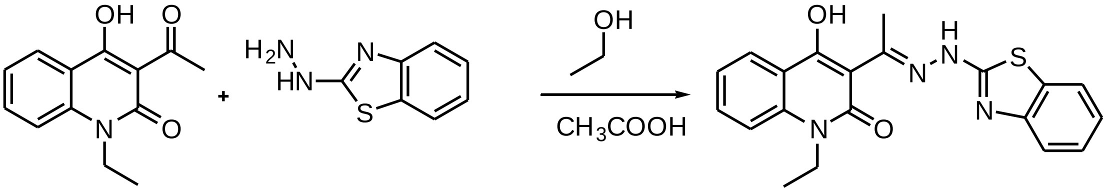
Material and methods :

All chemicals were of AR grade purchased from Sigma Aldrich and used for synthesis of ligand. AR grade metal acetate of Mn(II) from S. D. Fine chemicals are used for complex preparation. Spectral grade solvents were used for spectral measurements. The carbon, hydrogen, nitrogen contents were determined on Perkin Elmer(2400) CHNS analyzer. IR spectra were recorded on a FTIR Brucker spectrophotometer in 400-4000cm-^{1} range. The UV/ Vis spectra were recorded on Shimadzu UV 160 spectrophotometer for complex in DMSO. ^{1}HNMR spectra of ligand measured in DMSO using TMS as an internal standard. The LC- MS spectra was recorded on a Waters, Q-TOF Micromass (LC-MS). Magnetic moments was measured by Guoy's method and was corrected for diamagnetism of the components using Pascal's constants. Conductance was measured on Elico Cm-180 Conductometer using 10^{-3} M solution in DMSO. Powder XRD study was carried out with a Bruker AXS D8 Advance X-ray diffractometer.

Synthesis of ligand:

3-Acetyl-1-ethyl-4-hydroxy-2(*1H*)-quinolone (10.85 gm 0.05 mol) was taken in clean and dry round bottomed flask and 50 mL ethanol was added in it. The solution was warmed. To this, 5-10 mL of glacial acetic acid was added as a catalyst and (8.26 gm, 0.05 mol) of 2-hydrazino benzothiazole was added in it. This reaction mixture was refluxed and stirred for 1/2 hr. on rotaheatingmantel. Yellow solid product formed was filtered off, washed with ethanol and dried in vacuum desiccators.

The product was recrystallized from DMF-ethanol mixture (yield 85%), m.p.-241°C.



Synthesis of metal complex :

To the hot solution of ligand in ethanol (0.02 mol in 25mL), hot ethanolic solution of metal salt (0.01 mol in 25 mL) was added drop wise. For the synthesis of Manganese complex, salt of Manganese acetate was used. To this reaction mixture, 10% ethanolic ammonia was added to adjust the pH of solution to 7.5 to 8.5. The reaction mixture stirred for 3-5 hours in warm condition on magnetic stirrer to get complex in solid form. The solid complex was filtered off, washed several times with ethanol and dried in vacuum over $CaCl_2$.

Results and discussion :

Complex was coloured solids, stable for air and heat. The complex was insoluble in water, ethanol, methanol, DCM but easily soluble in polar solvents DMF /DMSO.

The analytical data like color, melting point, % of elements, magnetic moments and conductance are presented in Table 1. The elemental analysis and ^{1}HNMR spectra of the complex show 1:2 (metal : ligand) stoichiometry for Mn(II) complex.

Molar conductance and Magnetic susceptibility measurements:

Molar conductance measurements was performed in DMSO (10^{-3}M) solutions at room temperature. The molar conductance data indicate that complex is non electrolytic in nature. Magnetic susceptibility of the powdered complex was carried out by using Guoy's balance method at room temperature with $Hg[Co(SCN)_4]$ as a calibrant.

The Mn(II) complex has a magnetic moment 5.29 BM indicating the presence of five unpaired electrons in agreement with high spin octahedral complex[4-5].

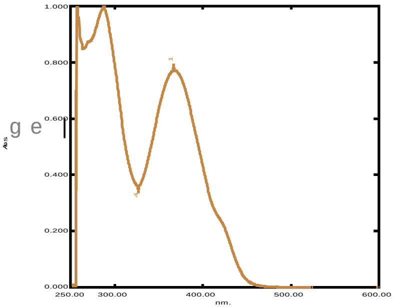
Table 1 : Physical, analytical data of ligand and its metal complex:

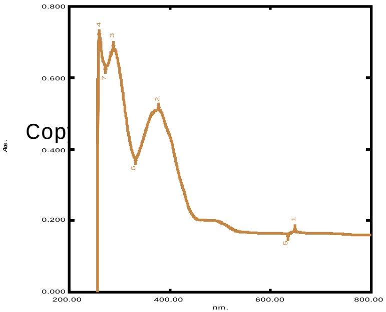
Compound	**Mol.formula**	**colour**	**M.P.° C**	**Mol..Wt.**	**C%**	**H%**	**N%**	**O%**	**S%**	**Metal %**	**$\mu_{(eff)}$ B.M.**	**Molar conductance Ohm^{-1} cm^2 mol^{-1}**
HL	$[C_{20}H_{18}N_4O_2S]$	Yellow	241	378	63.10 (63.48)	4.34 (4.79)	15.18 (14.80)	8.91 (8.46)	8.47 (8.47)			---
(MnL_2)	$[C_{40}H_{36}N_8O_4S_2Mn]$	Reddish brown	>300	811	56.89 (56.26)	3.46 (3.97)	14.32 (13.81)	7.91 (7.88)	8.12 (7.90)	6.23 (6.77)	**5.29**	**10.9**

Electronic absorption spectra:

The electronic absorption spectra of ligand and its Mn(II) complex was recorded in DMSO over the range 200-800 nm. The electronic spectrum of ligand exhibit two absorption transitions at 27248 cm^{-1} (367.5nm) and 30581 cm^{-1} (327nm) assigned to the n-π* and π-π* transitions of azomethine and 2-quinolone.

The electronic absorption spectra of Mn(II) complex was showed three bands at 25000 cm^{-1} (400nm), 26490 cm^{-1} (377nm) and 30165 cm^{-1} (331.5nm) assignable to $^6A_{1g}\rightarrow{}^4T_{2g}$(G), $^6A_{1g}\rightarrow{}^4E_{1g}$ or $^6A_{1g}\rightarrow{}^4T_{1g}$ (G) and to charge transfer band respectively. Electronic spectra of Fe(III) complex show transitions at **25316 cm^{-1} (395nm) due to $^6A_{1g}\rightarrow{}^4T_{2g}$ and** charge transfer band at **34542 cm^{-1} (289nm) [6-7].**

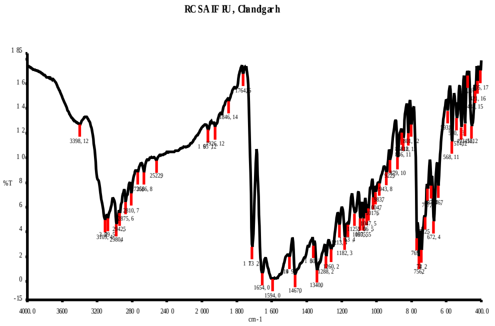


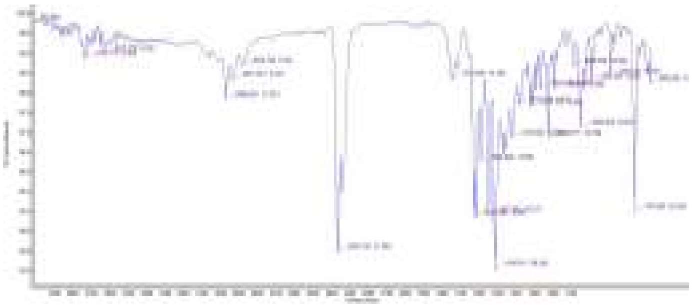


UV Spectra of ligand **UV Spectra of Mn(II) complex**

FTIR spectra:

The FTIR spectrum of Mn(II) metal complex was compared with that of free ligand in order to investigate the mode of chelation of metal ion with ligand. In FTIR spectrum of free ligand, some characteristic bands at 3398, 3109, 1654, 1594, 1556, 742 cm^{-1} assigned to enolic -OH, NH, C=O(quinolone), >C=N(azomethine), >C=N (ring), **N-H out of plane** stretching respectively. In Mn(II) complex the ligand behaves as a ONN tridentate via the >C=O (quinolone), >C=N (azomethine) and >C=N (in benzothiazole ring) groups. This fact is supported by the following evidences. In complex there is presence of a band in the region 3400 cm^{-1} due to OH indicating 4-hydroxy group of quinolone does not take part in coordination. The IR stretching frequency of >C=O(quinolone) in the complex observed at the region 1620 $cm^{-1.}$ This Shift to lower frequency of carbonyl group of quinolone by 34 cm^{-1}. The shift of azomethine >C=N group to lower frequency region by 10 cm^{-1} with respect to free ligand. indicates that the nitrogen of the azomethine group coordinate to the metal ion. The >C=N(benzothiazole ring) groups shift to lower frequency range by 10 cm^{-1} which indicates that they form coordinate bond with metal atom[6,7]. The IR stretching frequency of >C=O(quinolone), >C=N(azomethine), >C=N (benzothiazole ring) groups shift to lower frequency range which indicates that they form coordinate bond with metal atom[8].





IR Spectra of ligand

IR Spectra of Mn(II) complex

Table 2 : Salient features of IR spectral data of ligand and Mn(II) metal complex.

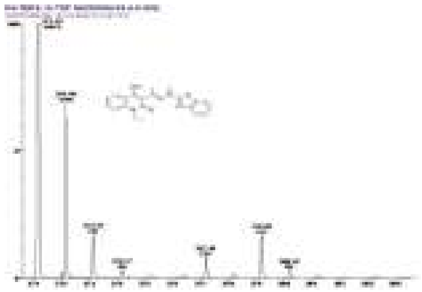
(Assignment of band frequencies to bond vibration modes)

Ligands	ν(OH) Enolic	ν (NH) Hydrazone	ν (C=O) Quinolone	ν (C=N) Azomethine	ν (C=N) Ring nitrogen	ν (C=C)	ν (-NH) out of plane
L	3398	3109	1654	1594	1556	1467	742

	(m)	(m)	(s)	(b)		(s)	(s)
MnL_2	3400 (m)	3323 (s)	1620 (s)	1584 (s)	1542 (s)	1416 (s)	747 (s)

Mass spectra of ligand:

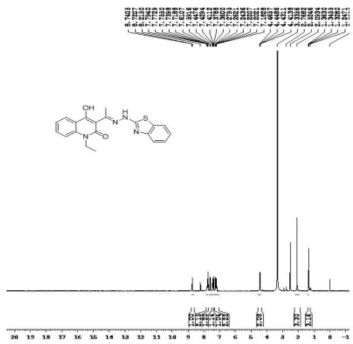
Mass spectrum of the ligand supports its proposed formulation. It reveals the molecular ion peak m/z at 378.1 a.m.u., consistent with the molecular weight of the ligand. Also there is presence of [M+2], [M+1], at m/z 380.19, 379.20.



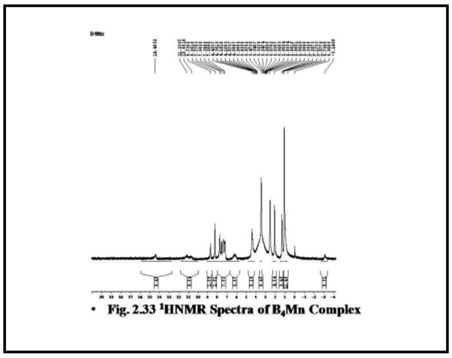
Mass spectra of ligand

^{1}**HNMR spectra of ligand and Mn(II) metal complex :**

^{1}HNMR Spectra of ligand was recorded in DMSO. It shows signals at 1.34 δ ppm. (t,3H,N-CH_2-CH_3*), 2.76 ppm. (s,3H, N=C-CH_3), 4.44 ppm. (s,2H,N-CH_2), 7.18-8.21 δ ppm. (m, 8H, H_{arom}), 11.98 δ ppm. (s,1H, N-H), 16.81 δ ppm. (s,1H,OH_{enolic}).



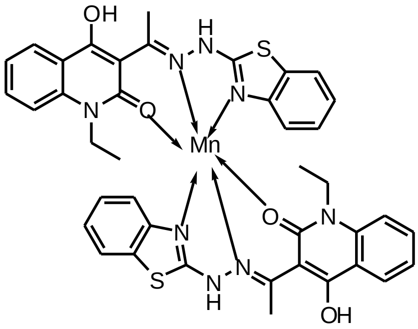
^{1}**HNMR Spectra of Ligand**



^{1}**HNMR Spectra of Mn(II) complex**

The formation of metal complex is confirmed by ^{1}H NMR spectral study of Mn(II) complex. The ^{1}HNMR spectra of ligand show chemical shift at 16.80 δ ppm assigned to enolic proton of 4-hydroxy-quinolone. The appearance of this chemical shift in the complex at 14.46 δ ppm. that indicate non coordination of enolic -OH. The upfield shift in the δ chemical shift of -OH may be due to the change in environment of enolic -OH group. The value of -NH proton in the ligand appear at 11.98 δ ppm. but in complex the δ chemical shift for -NH proton appears at 11.23 δ ppm in the upfield region evidence for the coordination of adjacent C=N of hydrazone to metal ion. The azomethine -CH_3 proton having δ chemical shift at 2.75 δ ppm in the ligand appear in at 3.03 δ ppm. in the complex. This downfield shift indicates coordination of azomethine nitrogen to the metal ion[9].

Proposed structure of Mn(II) complex :



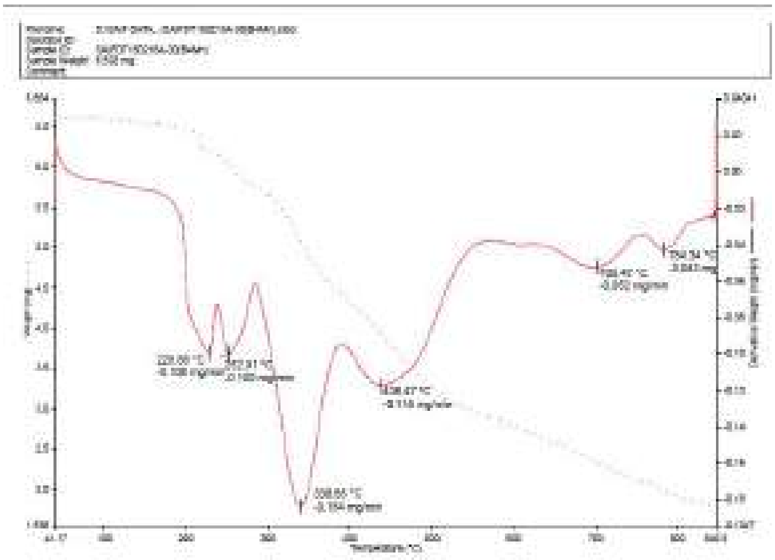
Thermo gravimetric studies:

The simultaneous TG/DTA analysis of a Mn(II) complex was studied.

The first step shows decomposition within temperature range 220-500˚C with 57% (calc. wt. loss 56%). This may be due to oxidative decomposition of non coordinated part of ligand. Which is authenticated by broad endothermic peak in DTA at 338.85˚C. The second step of decomposition with weight loss 39% within temperature range 550 to 800˚C, which is supported by broad endothermic peak in DTA curve 700.47˚C, corresponds to the decomposition of coordinated part of the complex. Above 800˚C, TG curve attain a constant level corresponding to Mn(II) oxide.

The thermal kinetic parameters ΔS, Ea and Z for non- isothermal decomposition of complexes have been calculated by Coats-Redfern method from TG-DTA curves and are presented in Table 3.

Generally, with decreasing value of ΔE, the value of Z increases, and higher value of activation energy suggest higher stability (10). In the present complexes, the value of E_a decrease with the increasing value of (Z) i.e. frequency factor indicating that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and that the reactions are slower than normal.



TG/DTA of Mn(II) complex

Table 3

Thermodynamic and kinetic parameters

Metal complex	Method	Step	Decomp. Temp.	Order of Reaction	Ea(KJ mol^{-1})	ΔS(KJ mol^{-1})	ΔG(KJ mol^{-1})	Z (S^{-1})	Correlation Coefficient (r)
MnL$_2$	H-M C-R	I	500	0.55	104.05 71.27	-142.13 -144.01	114.69 82.06	490227.9481 390904.17	0.9999 0.9999
	H-M C-R	II	840	0.55	32.26 13.89	-160.10 -140.71	57.25 54.22	117718.1 1211966	0.998 0.9957

X-ray diffraction study:

The X-ray diffractogram, of Mn(II) metal complex was scanned in the range 0-60˚ at wavelength 1.54 A˚ The X-ray diffraction pattern of the complex with respect to major peaks having relative intensity greater than 10% have been indexed by using computer program. The above indexing program gives hkl planes, unit cell parameters and volume of the unit cell. The diffractogram and associated data gives 2θ values for each peak , relative intensity and inter planer spacing (d-values). On the basis of X-ray diffraction analysis Mn(II) complex crystallize in triclinic system with space group P2/m [11]. having unit cell volume 1599.16 A$^{˚3}$. The observed density and calculated density is 0.8575 gcm^{-3}, 0.8421 gcm^{-3} respectively. The lattice parameters were a=21.34 A˚, b=9.97˚, c= 8.75 A˚, α= 70.125˚, β= 107.5˚, γ = 81˚ and the crystal contains one atom per unit cell which satisfies the condition a≠b≠c, α≠β≠γ=90˚.

X-ray diffraction data are presented in Table 4.

Table -4: Indexed X -ray diffraction data of Mn(II) complex of ligand

Peak No.	2θ (observed)	2θ (calculated)	d (observed)	d (calculated)	Miller indices of Planes			Relative intensities (%)
					h	K	l	
1	10.624	10.743	8.32067	8.22840	-1	0	1	100
2	12.024	12.009	7.35465	7.36358	-1	1	1	26
3	13.028	13.159	6.78992	6.72264	1	1	1	12
4	14.015	14.004	6.31405	6.31875	1	0	1	11
5	15.212	15.212	5.81987	5.81958	-2	1	0	9.82
6	15.833	15.807	5.59294	5.60201	2	1	1	29.5
7	17.468	17.462	5.07294	5.07446	-4	0	1	8.92
8	18.703	18.602	4.74046	4.76614	1	2	1	5
9	19.626	19.762	4.51960	4.48888	0	-2	0	8.9
10	20.751	20.627	4.27710	4.30261	-2	1	2	4.58
11	21.895	21.788	4.05611	4.07579	-3	1	2	10.87
12	22.639	22.712	3.92442	3.91207	-5	-1	1	11.67
13	23.600	23.623	3.76677	3.76326	0	2	2	5.8
14	24.166	24.153	3.67983	3.68479	-2	2	2	14.3
15	24.710	24.672	3.60008	3.60545	1	2	2	20.87
16	25.582	25.560	3.47923	3.48226	-5	-2	0	10.2
17	28.451	28.495	3.13466	3.12991	3	1	2	5.37

Unit cell data and crystal lattice parameters

a (Å) = 21.345

b (Å) = 9.97

Volume (V) = 1599.16 Å^3

Density (obs.) = 0.8575 gcm^{-3}

c (A□) = 8.75

□ = 70.125□

□ = 107.5□

□= 81□

Density (cal.) = 0.8421 gcm^{-3}

Z = 1

Crystal system= Triclinic

Space group = P2/m

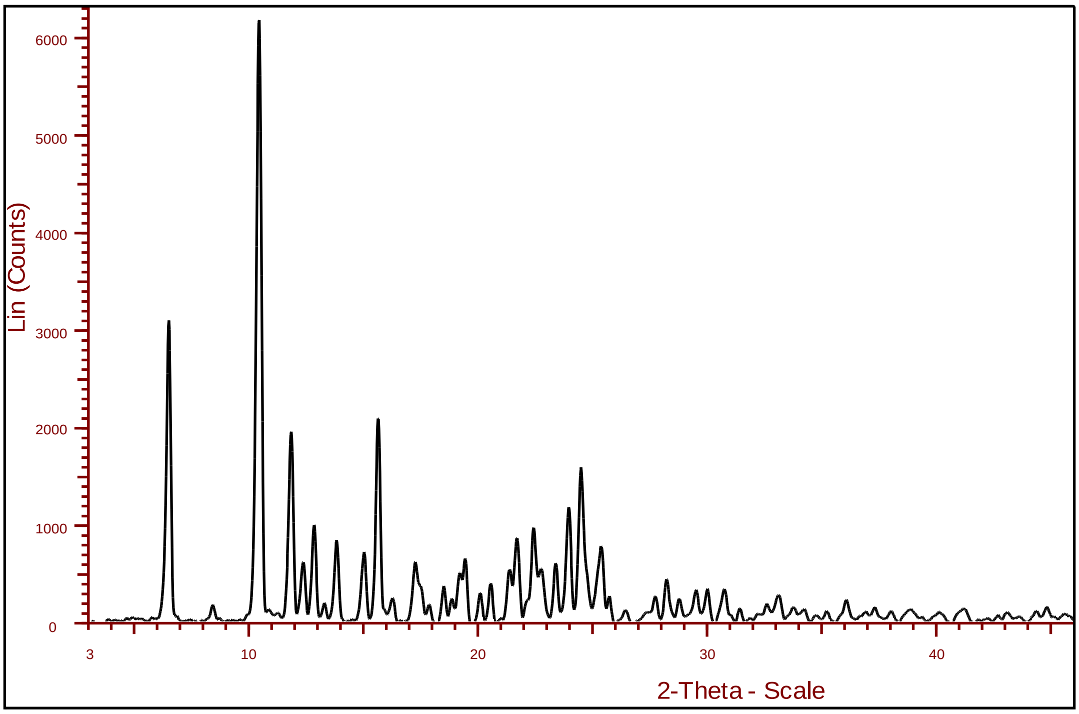


Fig X-ray diffractogram of Mn(II) complex of ligand

Biological activity of the compound:

In vitro antibacterial activity of the compounds:

The antimicrobial activity of the ligand and the complex was tested against the standard microbial strains, *Escherishia coli*, *Salmonella typhi*, *staphylococcus aurus*, *Bacillus substilis* by agar cup method at fixed concentration of 1% in DMSO. The test was performed on nutrient agar Cup of 10 mm diameter was borered in the agar plate with sterile cork borer. All solutions were prepared in DMSO(1%) was add on cup, One cup for DMSO as blank and other for standard reference penicillium was also placed on the seeded nutrient agar.

Then the plates were shifted to incubator at 37˚c and incubated for 24 hours. Activity measured in diameter (mm). The results obtained are presented in (Table 5)

Inspection of the data revealed that complex and ligand lack the activity towards the Gram-negative bacteria *E. coli* and *S. typhi*. On the other hand, ligand and complex shows activity against Gram-positive bacteria *S. aureus* and *B. substilius*. Activity of Mn(II) complex show highest antibacterial activity.

Table 5: Report for antibacterial testing.

Medium - Nutrient Agar

Method- Agar cup method

Dose of compound - 1%

cup size - 10 mm

compound	***Escherishia coli***	***Salmonella typhi***	***Stapylococcus aureus***	***Bacillus subtilis***
Ligand(L)	--	--	**13**	**-ve**
(MnL_2)	--	--	**24**	**12**
-ve control (DMSO)	--	--	**--**	**--**
Penicillin	28	36	**14**	**20**

Legends : -ve = No Antibacterial Activity

Zone of inhibition = --- mm

In vitro antifungal activity of the compounds

Compounds were screened in vitro against *Aspergillus niger, Penicilium chrysogenum*, *fusarium moneliforme* , *Aspergillus flavus*, by poison plate method with potato dextrose agar media. the compound were tested at the 1% concentration in DMSO and compared with control.

Gresiofulvin was prepared as standard reference plate. The fungal suspension was spot inoculated on the plates prepared using compound with nicrome wire loop. The plates were incubated at room temperature for 48 hours. The result obtained are presented in Table 6. The ligand does not show antifungal activity but Mn(II) complex show appreciable activity. Antifungal activity of complex increased several times on being coordinated with metal ions.

Table 6: Report for antifungal testing.

Ligand	**Antifungal growth**			
	Aspergillus niger	***Aspergillus flavus***	***Fusarium moniliforme***	***Penicillium chrysogenum***
	1%	**1%**	**1%**	**1%**
L	**+ve**	**+ve**	**+ve**	**+ve**
(MnL_2)	**-ve**	**-ve**	**-ve**	**-ve**
+ve control (DMSO)	**+ve**	**+ve**	**+ve**	**+ve**
-ve control (Griseofulvin)	**-ve**	**-ve**	**-ve**	**-ve**

Legends- + ve Growth -(Antifungal Activity absent)

-ve - No growth (More than 90 % reduction in growth Antifungal activity present)

Conclusion:

In the light of above discussion we have proposed octahedral geometry for Mn(II) complex. On the basis of physicochemical and spectral data discussed above, one can assume that the ligand behaves as, ONN tridentate, coordinating via quinolone carbonyl, azomethine nitrogen and nitrogen of benzothiazole ring in complex. The mass spectra of ligand is in great accordance with calculated and observed value . Thermogravimeric studies revealed that complex is rigid and stable. The XRD study suggests triclinic lattice type for Mn(II) complex. The Mn(II) complex was biologically active having greater activity compared to free ligand.

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