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Synthesis and Characterization of Novel Mn(II), Fe(II) and Fe(III) complex of 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol

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Abstract: ***The synthesis and characterization of metal complexes with Triazole Schiff Base ligand is of great utility as these compounds possesses a wide variety of biological and medicinal properties. 1,2,4-triazole Schiff base ligand, 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol and its metal complexes with Mn(II), Fe(II) and Fe(III) were prepared. The ligand was characterized by micro analytical technique and FT-IR, ^{1}H & ^{13}C NMR spectroscopy. The IR spectra of the metal complex revealed that ligand is bidentate and donating to metal ion from deprotonated thiol group (S^{-}) and azomethine N-atom. On the basis of elemental analysis data, octahedral geometry was proposed for the prepared metal complexes. Lattice water is also associated with all the prepared metal complexes.***

Keywords: 1,2,4-Triazole Schiff Base, Metal Complex, Synthesis, Characterization, Ligand.

I. INTRODUCTION

1,2,4-triazole based Schiff base and their metal complexes are pharmaceutically important compounds as they possesses a wide array of biological activity such as antibacterial, antifungal, antihelmintic, antiproliferative, antioxidant etc [1], [2], [3]. The derivatives of 1,2,4-triazole containing thiol and amino group have been studied as ligand to prepare Ni(II), Co(II), Cu(II), Zn(II), Pd(II), Cd(II) and Pb(II) complexes [4]. Some of the metal complexes of 1,2,4-triazole Schiff base, 4-[(E)-benzylidine amino]-5-methyl-4H-1,2,4-triazole-3-thiol have been prepared, characterized by spectral techniques and molecular docking studies revealed that they are potentially anti-bacterial [5]. Pb(II) complex of 1,2,4-triazole derivative have been studied by IR, NMR and elemental analysis [6]. In this paper, we are reporting the synthesis and characterization of three novel Mn(II), Fe(II) and Fe(III) complex with 1,2,4-triazole based Schiff base ligand which was prepared by condensation of 4-amino-5-ethyl-1,2,4-triazole-3-thiol and benzaldehyde.

II. MATERIALS AND METHODS

All the chemicals procured were AR/ACS grade. The melting point was determined by open capillary method. The elemental analysis data was obtained by CHNS analyzer : ELEMENTAR Vario ELIII. The FT-IR spectra were recorded by Agilent Cary 360 FTIR Spectrometer in the range 4000-450cm^{-1} using KBr pellets. The ^{1}H & ^{13}C NMR was taken in $CDCl_3$ solvent using 400 MHz FT NMR : Bruker Advance III. The percentage of metal and chloride was estimated by standard procedure [7].

A. Experimental

1) Synthesis of Ligand (EPMTH):

Ligand was prepared by reported method [8]. Equimolar quantity of 4-amino-5-ethyl-4H-1,2,4-triazole-3-thiol and benzaldehyde was taken in RB flask and dissolved in ethanol. It was refluxed on water bath for 3hrs with few drops of acetic acid. Cream coloured crystals separated on cooling, filtered, washed with cold ethanol and dried in dessicator. It was recrystallized by hot ethanol.

White fibrous crystal; mp 170°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35-1.37 (t,3H,CH_3), 2.82-2.87 (q,2H,CH_2), 5.27 (s,1H,NH), 7.25-7.80 (m,5H,arH), 10.34 (s,1H,-HC=N-), 11.80 (s,1H,SH); ^{13}C NMR (100MHz, $CDCl_3$) δ 10.4, 18.9, 128.7, 128.9, 132.4, 132.6, 153.8, 161.2, 161.9.

2) Synthesis of [$Mn(EPMT)_2(H_2O)_2$].$2H_2O$

Methanolic solution of 0.3 mmol $MnCl_2.4H_2O$ was drop wise added to hot methanolic solution of 06 mmol ligand. Mn(II) complex separated on adjusting the pH to 7.5-8.0, filtered, washed with methanol and dried in dessicator.

3) Synthesis of [$Fe(EPMT)_2(H_2O)_2$].$2H_2O$

Aqueous solution of 03 mmol Mohr's salt was prepared and diluted with methanol. It was drop wise added to hot methanolic solution of 06 mmol ligand. Fe(II) complex precipitated on increasing the pH, filtered, washed with methanol and dried in dessicator.

4) Synthesis of [$Fe(EPMT)_2(H_2O)Cl$].$2H_2O$

Methanolic solution of 03 mmol FeCl3 was drop wise added to hot methanolic solution of 06 mmol ligand. Fe(III) complex separated on increasing the pH, filtered, washed with methanol and dried in dessicator.

III. RESULTS AND DISCUSSION

All the prepared compounds were in solid state at room temperature. They were stable in air and non-hygroscopic. Ligand was soluble in almost all the common organic solvents but metal complexes were soluble in DMF and DMSO. Solubility chart of the compounds is provided in Table-I.

Table-I : SOLUBILITY CHART

COMPOUNDS/ SOLVENTS	WATER	METHANOL	DMF	DMSO
Ligand	NS	S	S	S
Mn(II) complex	NS	PS	S	S
Fe(II) complex	NS	PS	S	S
Fe(III) complex	NS	PS	PS	S

NS = Not Soluble, PS = Partially Soluble, S = Soluble.

The elemental analysis data of all the compounds are quite consistent with the proposed structure of the ligand and metal complexes. The elemental data is provided in Table-II.

Table-II : Elemental Analysis Data

COMPOSITION	COLOUR	MELTING POINT (°C)	FOUND (CALCULATED) %					
			C	H	N	S	Cl	M
EPMTH	White	170	56.85 (56.87)	4.05 (5.21)	24.80 (24.12)	13.90 (13.80)	-	-
[$Mn(EPMT)_2(H_2O)_2$].$2H_2O$	Cream	>240	44.98 (44.82)	5.29 (5.13)	19.06 (19.01)	10.75 (10.88)	-	9.50 (9.32)
[$Fe(EPMT)_2(H_2O)_2$].$2H_2O$	Chocolate Brown	160 d	44.98 (44.75)	5.30 (5.12)	18.80 (18.98)	10.60 (10.86)	-	9.72 (9.46)
[$Fe(EPMT)_2(H_2O)Cl$].$2H_2O$	Dark Brown	220 d	44.02 (43.47)	4.85 (4.64)	18.52 (18.43)	10.91 (10.55)	6.01 (5.83)	9.85 (9.19)

The ligand was fully characterized by FT-IR, ^1H & ^{13}C NMR spectral analysis. ^1H and ^{13}C NMR spectra of ligand are provided in Fig.1 and Fig.2.

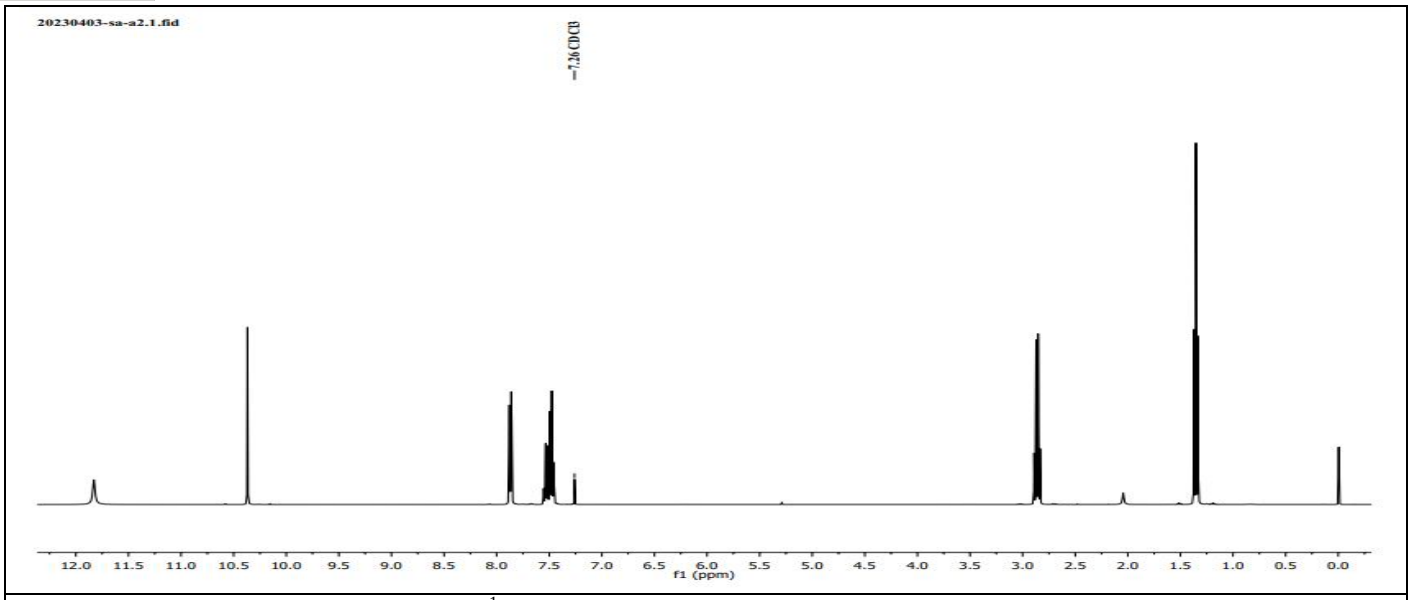

Fig.1 : ^{1}H NMR spectrum of ligand EPMTH in $CDCl_3$.

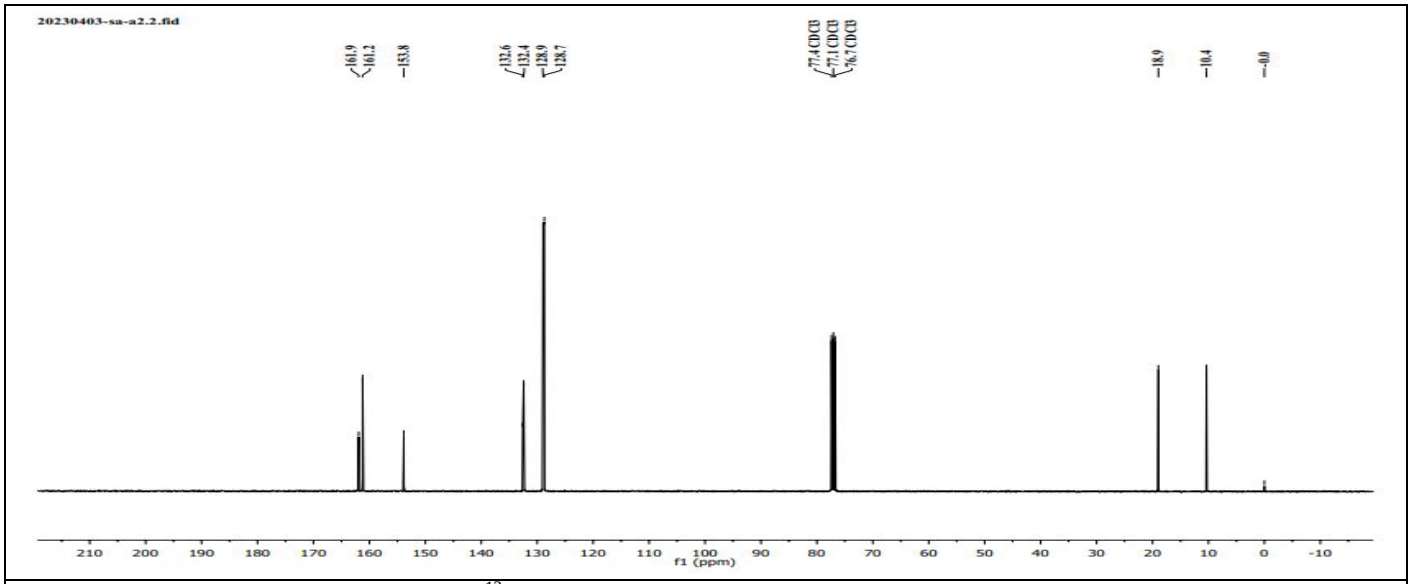

Fig.2 : ^{13}C NMR spectrum of ligand EPMTH in $CDCl_3$.

The important FT-IR frequencies and their band assignments have been provided in Table-III.

Table-III : FT-IR frequencies of prepared compounds and their band assignments.

SAMPLE	Frequency (cm^{-1})						
	$\nu H_2O/O-H$	$\nu C-H$	$\nu S-H$	$\delta H-O-H$	ν-HC=N-	$\delta CH_3 \& CH_2$	$\nu C-S$
Ligand	-	2938.30	2763.18	-	1583.03	1492.36 1384.22	757.19
Mn(II) complex	3397.74	2925.57	-	1613.21	1544.30	1454.19 1386.78	769.30
Fe(II) complex	3500.31	2940.74	-	1699.34	1543.09	1493.01 1384.64	759.56
Fe(III) complex	3400.06	2936.46	-	1616.18	1543.83	1493.38 1385.48	759.69

The formation of Schiff base ligand EPMTH was confirmed by FT-IR in which a peak at 1583.03 cm^{-1} was observed which corresponds to azomethine (–HC=N–) stretching [9]. All the prepared metal complexes were characterized with the help of IR spectra. In comparison to ligand spectra azomethine stretching band in the metal complexes is shifting towards the lower frequency which is strongly suggesting donation from azomethine N-atom to metal ion [10], [11]. The S–H stretching band which is present in ligand IR at 2763.18 cm^{-1} is missing in all the three metal complexes indicating that ligand is coordinating from deprotonated thiol group [12]. Lattice water is identified by bulgy peaks around 3500-3400 cm^{-1} [13]. H–O–H bending vibration is observed in metal complexes indicating water inside coordination sphere [14]. IR spectral studies strongly supported the formation of metal complex. It also revealed that ligand is bidentate in nature and donating to metal ion from azomethine N-atom and deprotonated thiol group(S^-). The FT-IR spectra of the ligand and metal complexes are given in Fig.3-6.

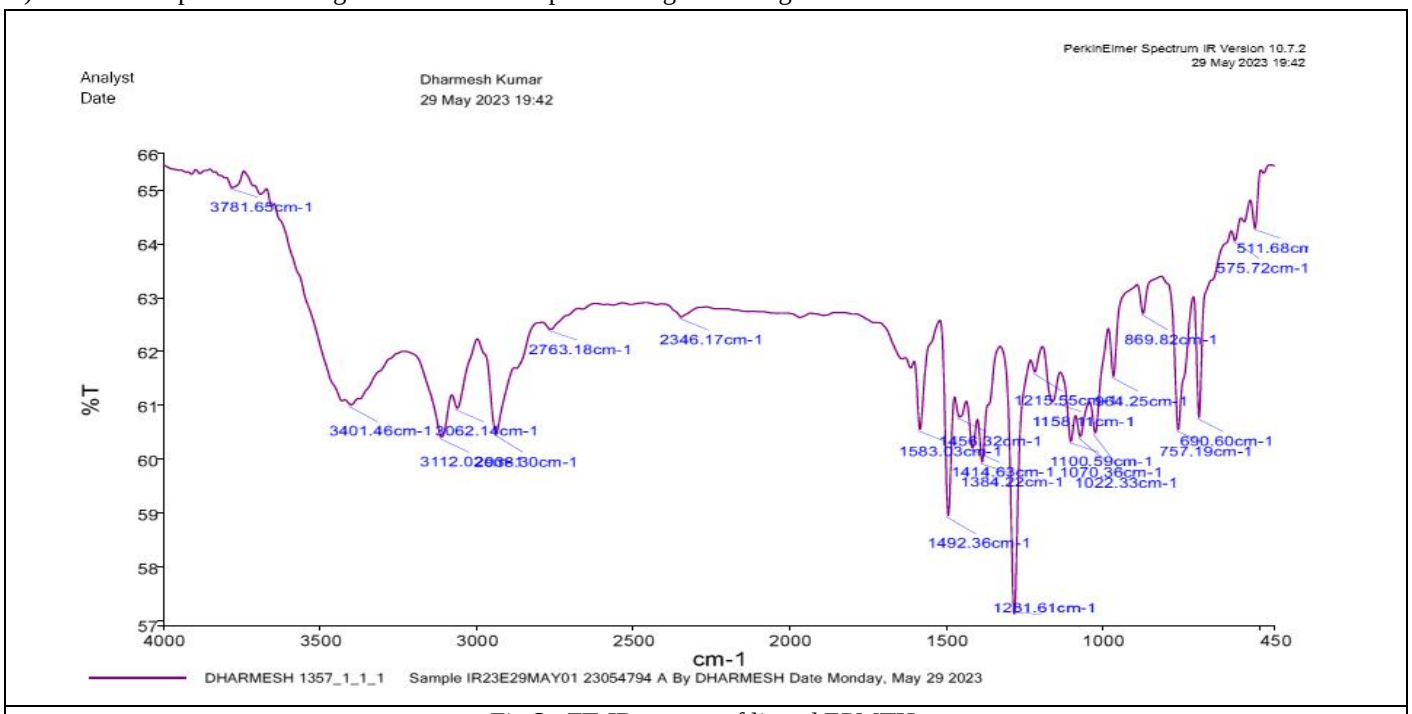

Fig.3 : FT-IR spectra of ligand EPMTH.

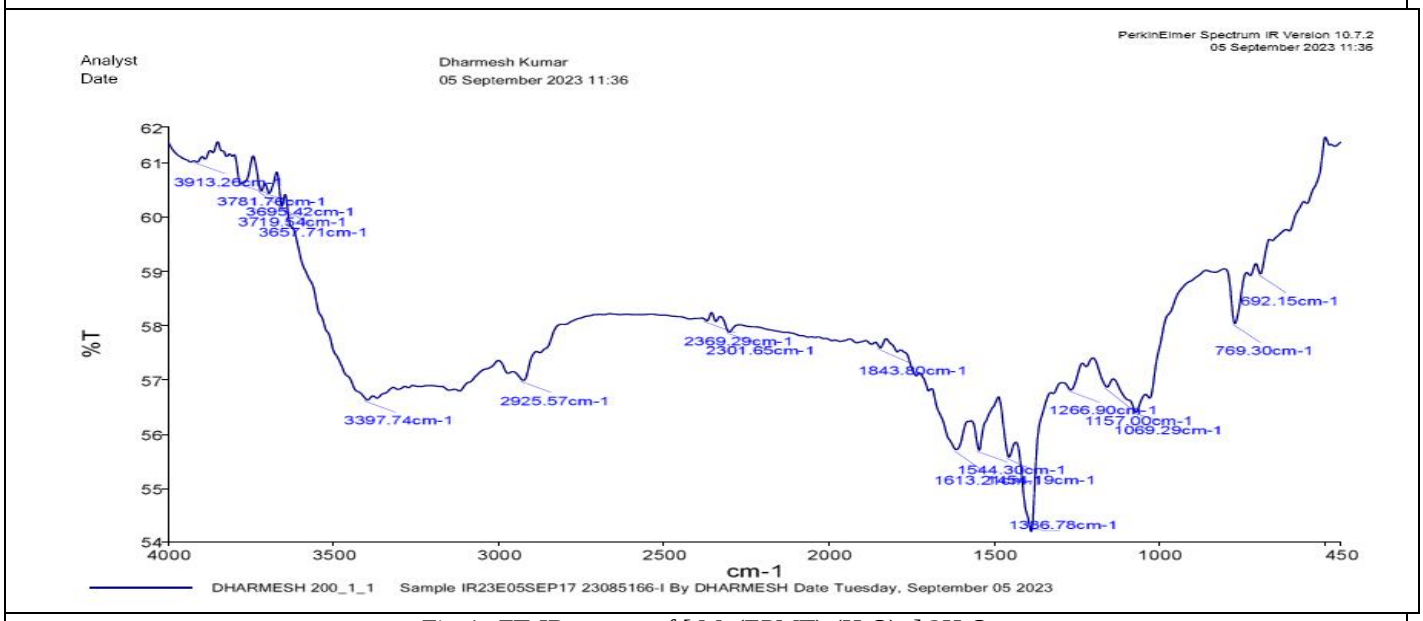

Fig.4 : FT-IR spectra of [$Mn(EPMT)_2(H_2O)_2$].$2H_2O$

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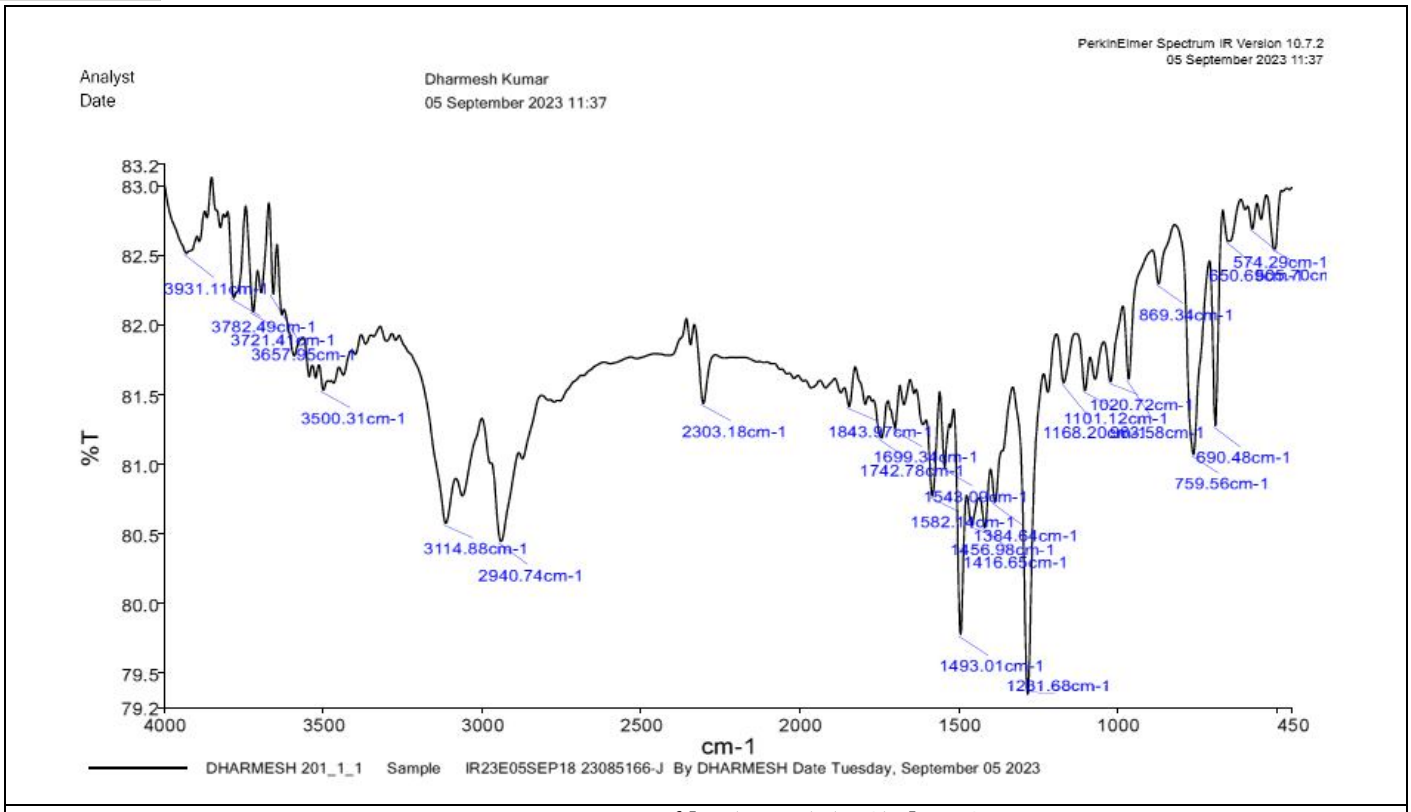

Fig.5 : FT-IR spectra of [$Fe(EPMT)_2(H_2O)_2$].$2H_2O$

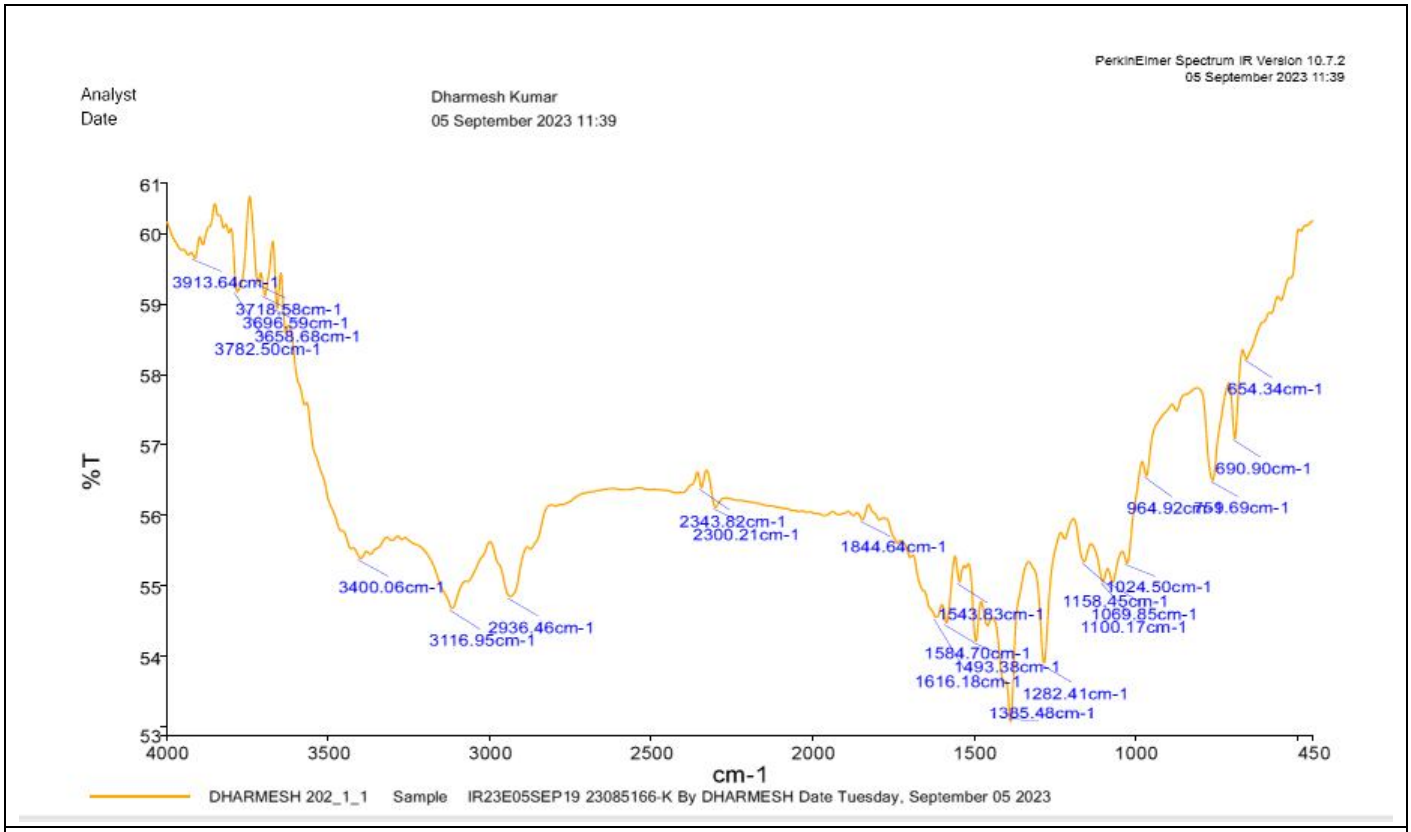

Fig.6 : FT-IR spectra of [$Fe(EPMT)_2(H_2O)Cl$].$2H_2O$

The proposed structures of the metal complexes are provided in Fig.7-8.

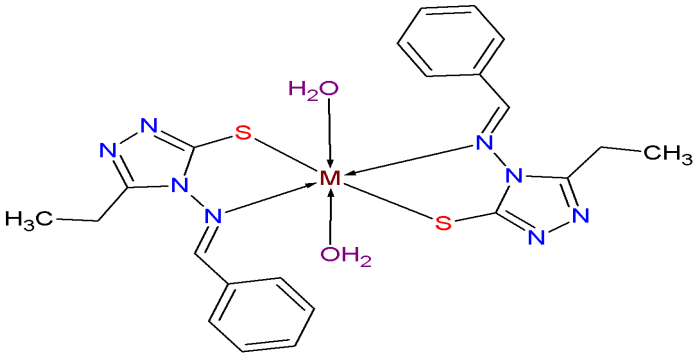

Fig.7 : Expected structure of Metal Complex where M= Mn(II) and Fe(II).

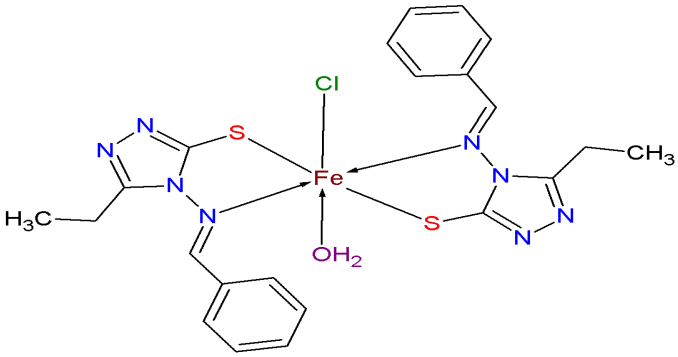

Fig.8 : Expected structure of Fe(III) complex.

IV. CONCLUSION

Novel Mn(II), Fe(II) and Fe(III) metal complexes with bidentate 1,2,4-triazole containing Schiff base ligand were prepared. All the compounds were characterized by elemental analysis and spectral techniques such as FT-IR, ^{1}H &^{13}C NMR. Geometry of the metal complexes was proposed to be octahedral. The ligand is found to be bidentate and binding to metal via azomethine N-atom and deprotonated thiol S^{-}. The synthesized compounds could be potentially biologically active and might posses medicinal properties.

V. ACKNOWLEDGEMENT

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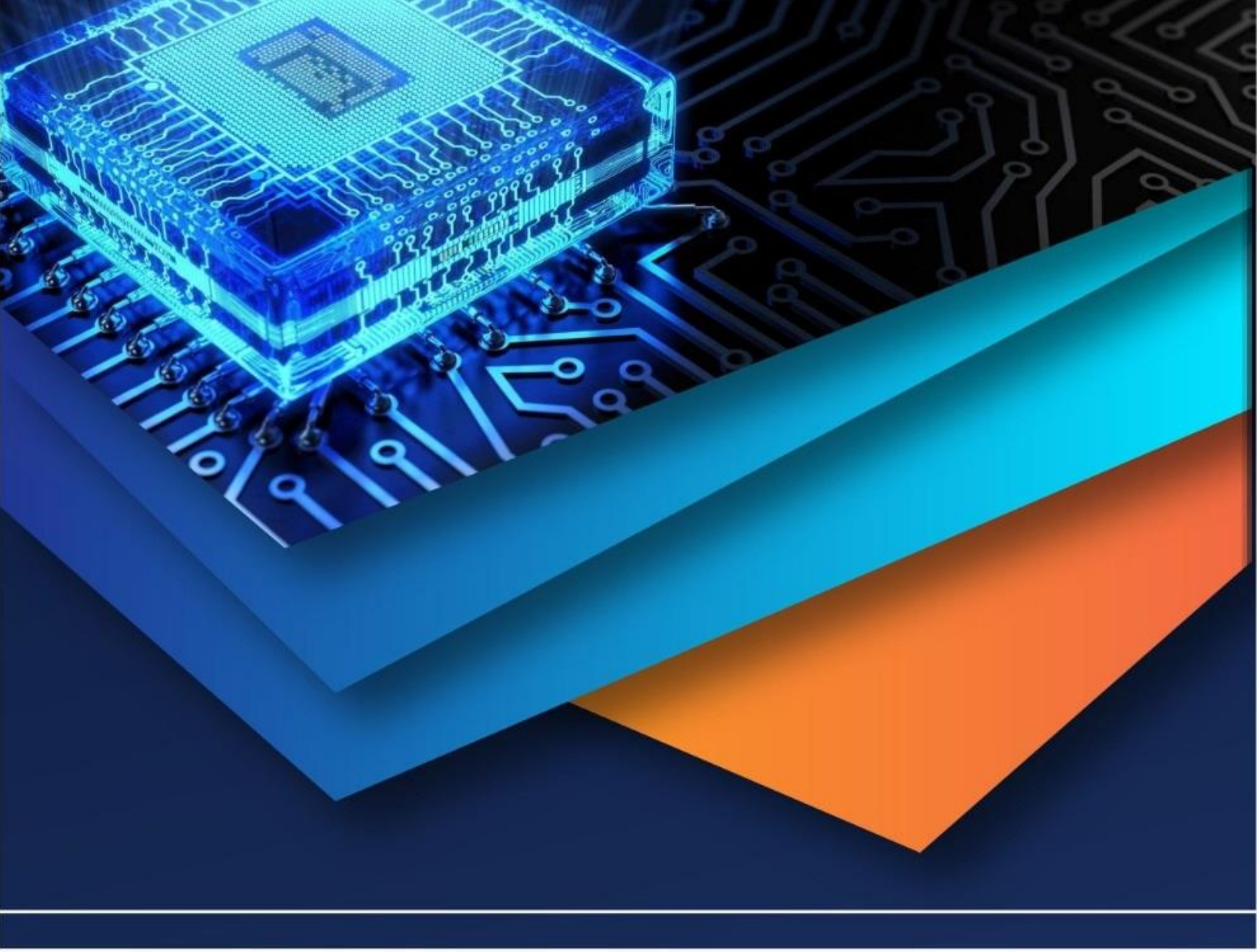

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