



IJRASET

International Journal For Research in
Applied Science and Engineering Technology



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 11 **Issue:** IX **Month of publication:** September 2023

DOI: <https://doi.org/10.22214/ijraset.2023.55892>

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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 possess 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, ¹H & ¹³C NMR spectroscopy. The IR spectra of the metal complex revealed that the ligand is bidentate and donates to the metal ion from the deprotonated thiol group (S⁻) and the 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 possess 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 groups have been studied as ligands 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)-benzylidene 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 has 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) complexes 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 4000-450 cm⁻¹ using KBr pellets. The ¹H & ¹³C NMR was taken in CDCl₃ 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 a water bath for 3 hrs with a few drops of acetic acid. Cream colored crystals separated on cooling, filtered, washed with cold ethanol and dried in a desiccator. It was recrystallized by hot ethanol.

White fibrous crystal; mp 170°C; ¹H NMR (400 MHz, CDCl₃) δ 1.35-1.37 (t, 3H, CH₃), 2.82-2.87 (q, 2H, CH₂), 5.27 (s, 1H, NH), 7.25-7.80 (m, 5H, arH), 10.34 (s, 1H, -HC=N-), 11.80 (s, 1H, SH); ¹³C NMR (100 MHz, CDCl₃) 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(H₂O)₂].2H₂O*

Methanolic solution of 0.3 mmol MnCl₂.4H₂O 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(H₂O)₂].2H₂O*

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(H₂O)Cl].2H₂O*

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.

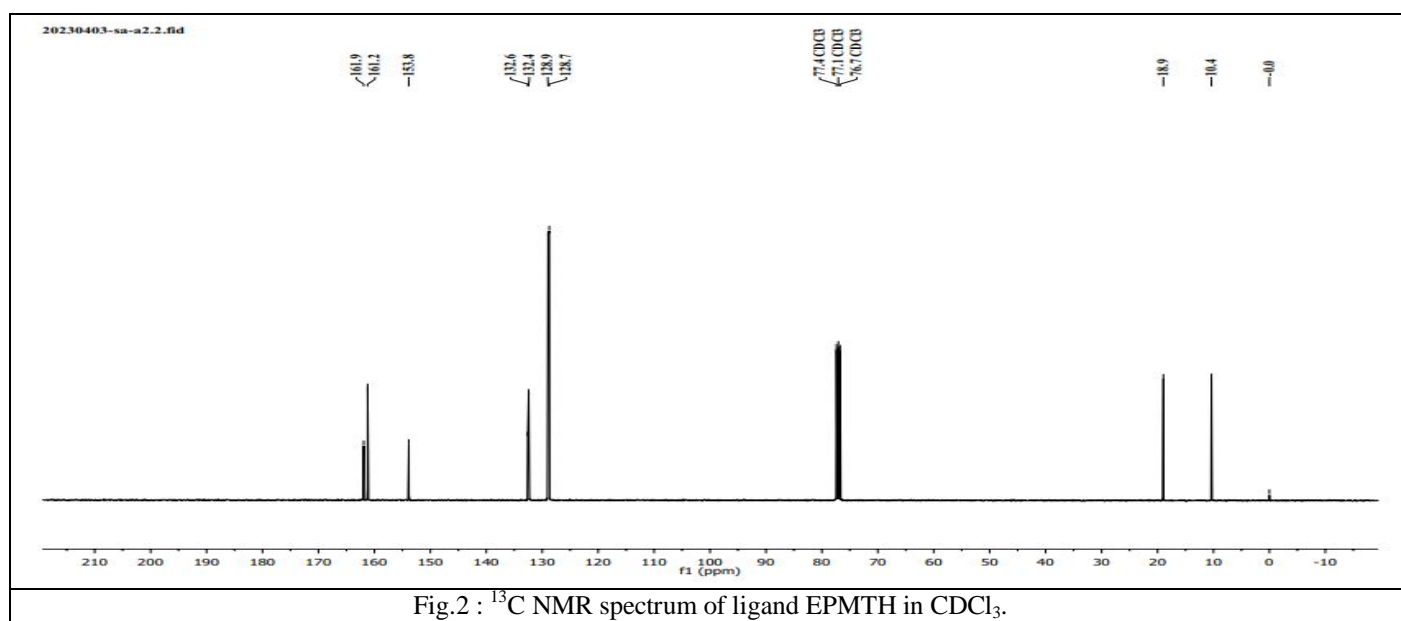
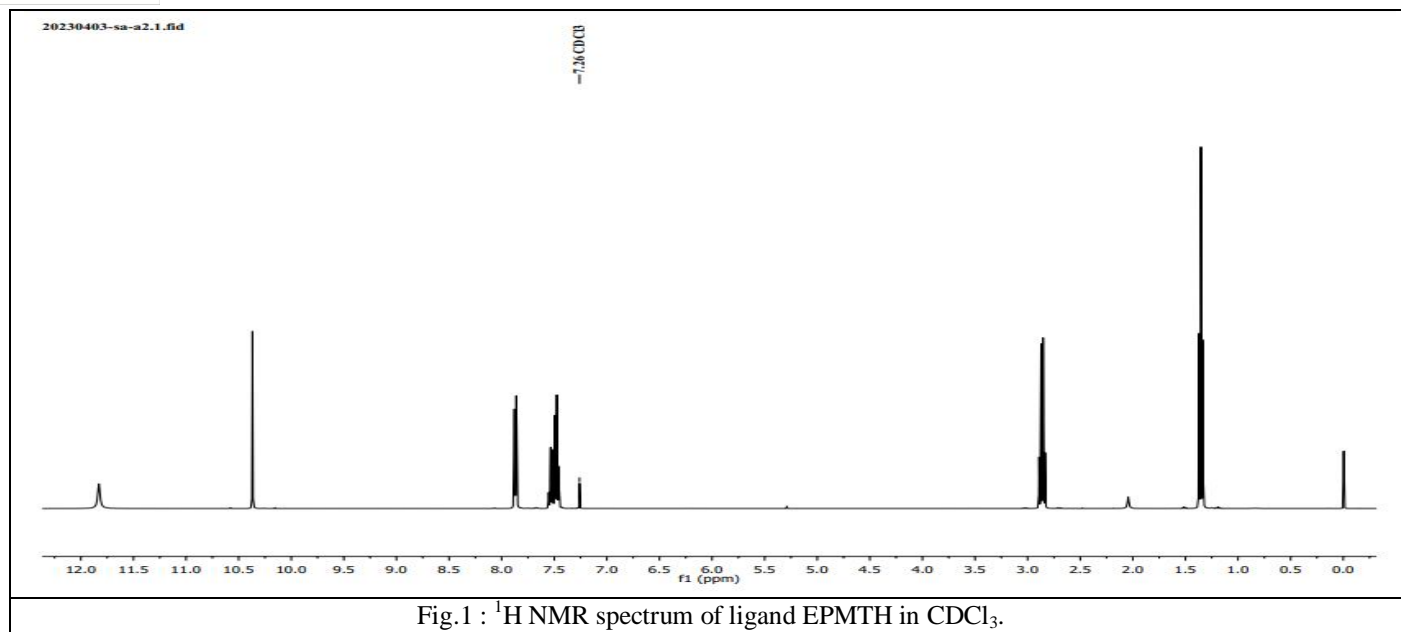
| COMPOUNDS/ SOLVENTS | WATER | METHANOL | DMF | DMSO |
|---------------------|-------|----------|-----|------|
| Ligand | NS | S | S | S |
| Mn(II) complex | NS | PS | S | S |
| Fe(II) complex | NS | PS | S | S |
| Fe(III) complex | NS | PS | PS | S |

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.

| 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 ₂ O) ₂].2H ₂ O | 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 ₂ O) ₂].2H ₂ O | 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 ₂ O)Cl].2H ₂ O | 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 & ¹³C NMR spectral analysis. ¹H and ¹³C NMR spectra of ligand are provided in Fig.1 and Fig.2.



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) | | | | | | |
|-----------------|--------------------------------|---------|---------|---------|---------|-----------------------------------|--------|
| | vH ₂ O/O-H | vC-H | vS-H | δH-O-H | v-HC=N- | δCH ₃ &CH ₂ | vC-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 EPMTM was confirmed by FT-IR in which a peak at 1583.03 cm^{-1} was observed which corresponds to azomethine ($-\text{HC}=\text{N}-$) 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 $3500\text{--}3400\text{ cm}^{-1}$ [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.

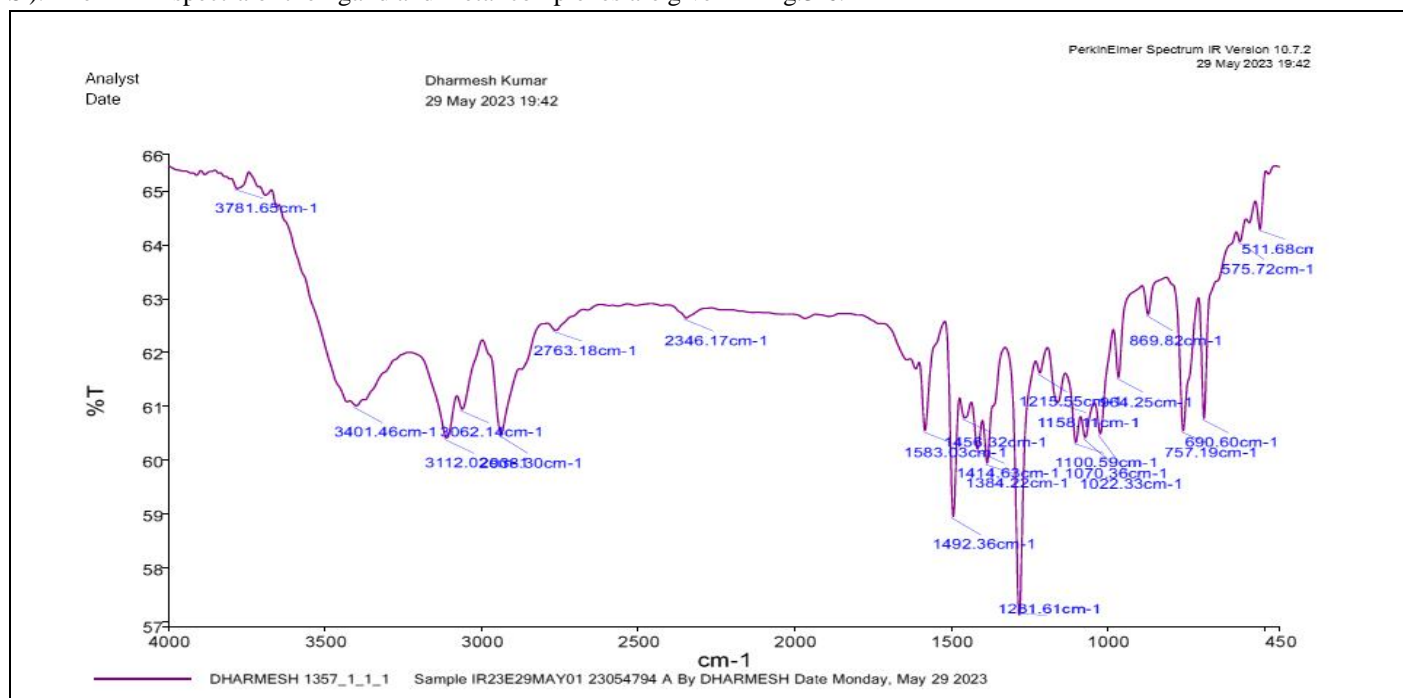


Fig.3 : FT-IR spectra of ligand EPMTM.

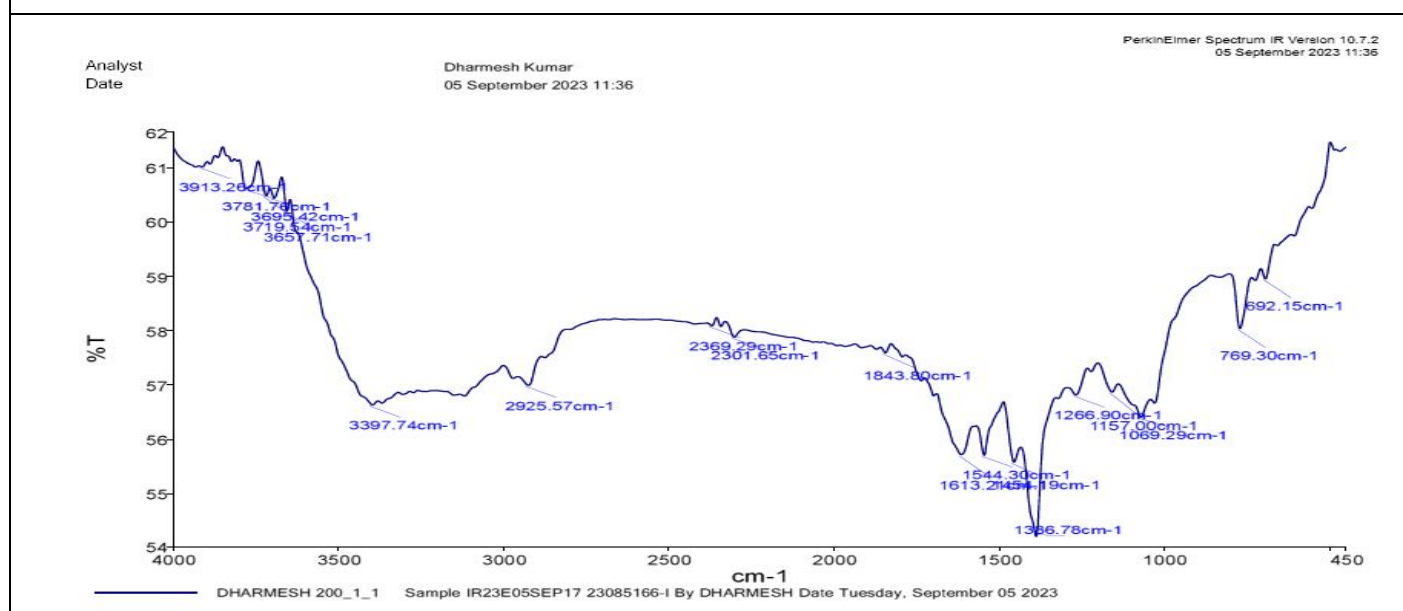


Fig.4 : FT-IR spectra of $[\text{Mn}(\text{EPMT})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

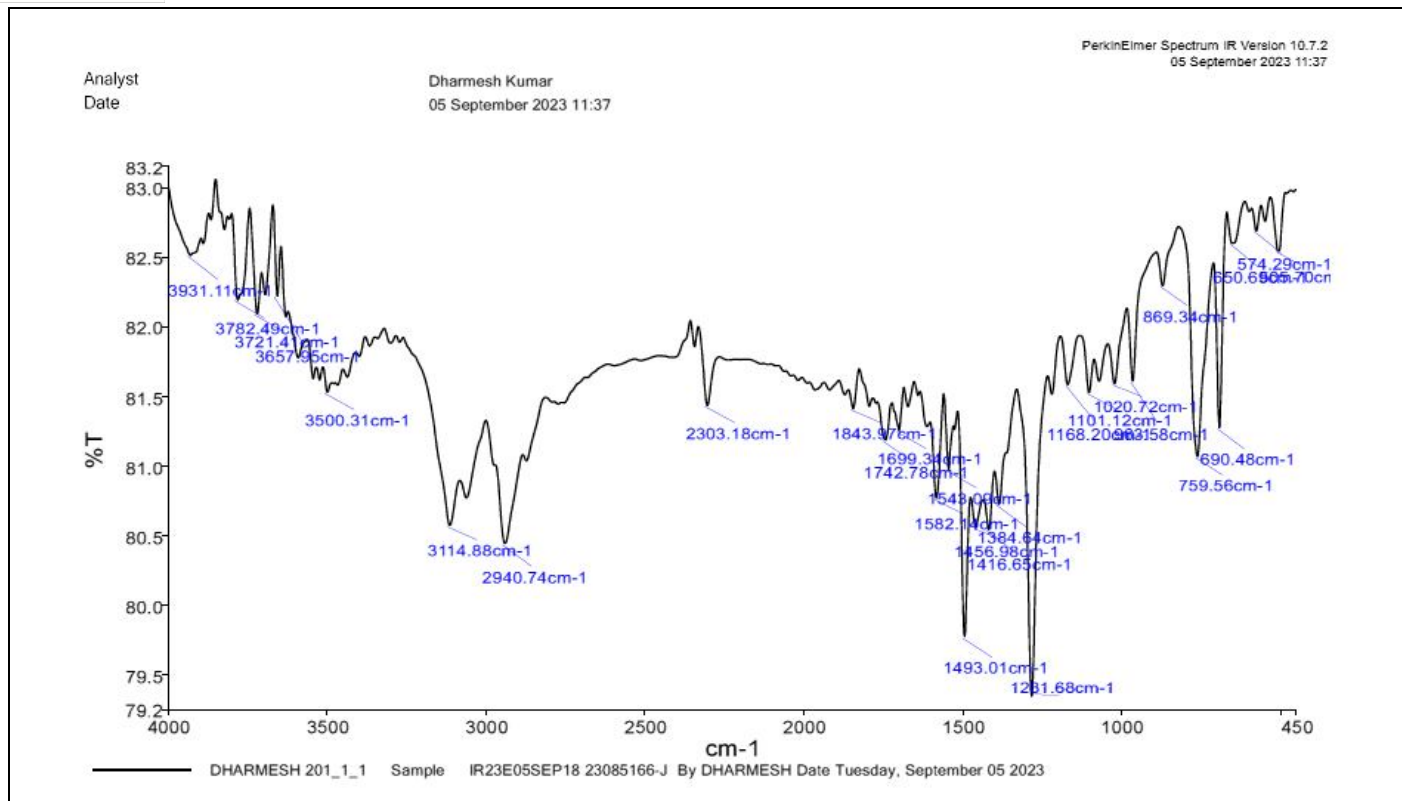


Fig.5 : FT-IR spectra of [Fe(EPMT)₂(H₂O)₂].2H₂O

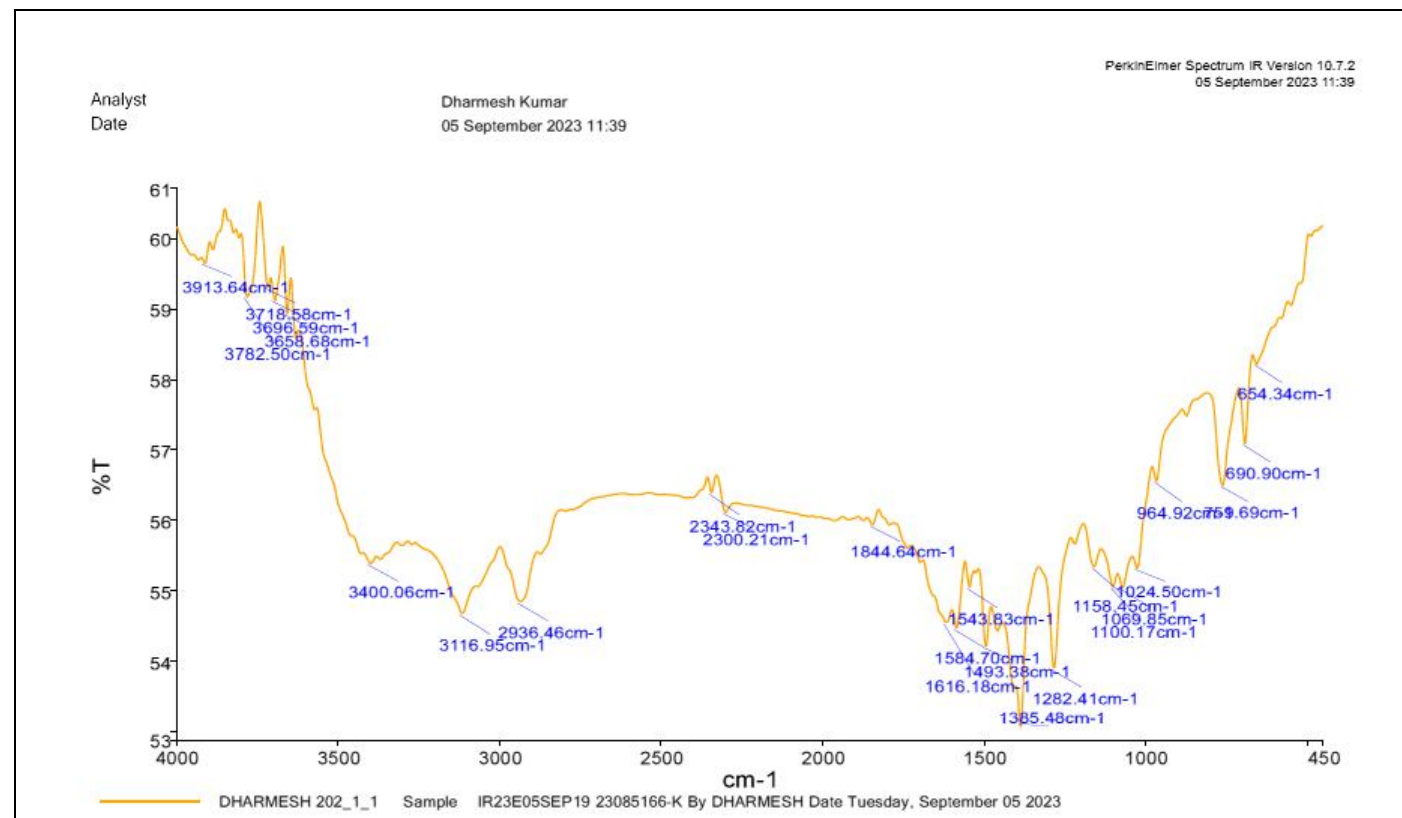


Fig.6 : FT-IR spectra of [Fe(EPMT)₂(H₂O)Cl].2H₂O

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

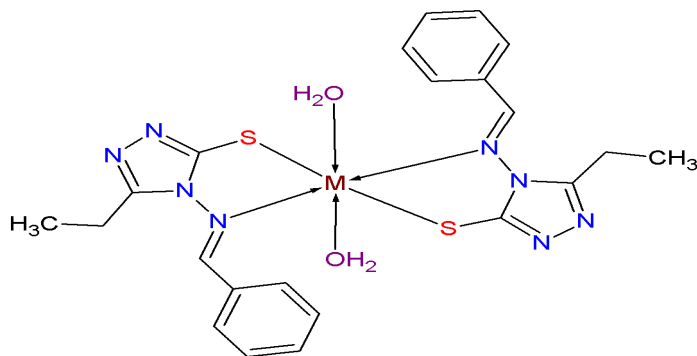


Fig.7 : Expected structure of Metal Complex where M= Mn(II) and Fe(II).

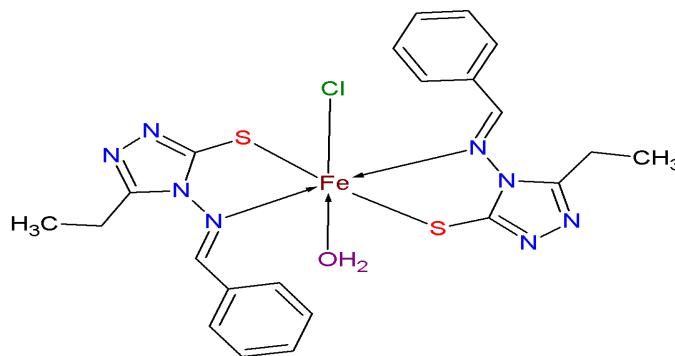


Fig.8 : Expected structure of Fe(III) complex.

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, ^1H & ^{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 possess medicinal properties.

V. ACKNOWLEDGEMENT

We are thankful to DST-SAIF Cochin and SAIF-CDRI Lucknow for providing elemental analysis and spectral data. One of the author (Vivek Kumar), CSIR-SRF wants to acknowledge CSIR-HRDG, New Delhi for providing financial help in research work under CSIR-NET-JRF/SRF scheme, File No.- 09/138(0078)/2019-EMR-I.

REFERENCES

- Zafar, W., Sumrra, S. H., & Chohan, Z. H. (2021). A review: Pharmacological aspects of metal based 1, 2, 4-triazole derived Schiff bases. *European journal of medicinal chemistry*, 222, 113602.
- Zafar, W., Ashfaq, M., & Sumrra, S. H. (2023). A Review on the Antimicrobial Assessment of Triazole-Azomethine Functionalized Frameworks Incorporating Transition Metals. *Journal of Molecular Structure*, 135744.
- Kumar, V., Kumar, A., & Kumar, R. (2022). Lemon Juice Catalysed Green Synthesis of Triazole Based Schiff Base, Its Physico-Chemical & Spectral Characterisation and Determination of its Binding Stoichiometry with Cu^{2+} ion. *International Journal for Research in Applied Science & Engineering Technology*, 10(2), 758-762. <https://doi.org/10.22214/ijraset.2022.40379>.
- Sinha, B. K., Singh, R., Srivastava, J. P., & Mishra, L. K. (1977). Substituted 1, 2, 4-triazoles as complexing ligands—I Ni (II), Co (II), Cu (II), Zn (II), Pd (II), Cd (II) and Pb (II) complexes with 4-amino-3, 5-dimercapto-1, 2, 4-triazole. *Journal of Inorganic and Nuclear Chemistry*, 39(10), 1797-1801.
- Kumar, A., Kumar, V., & Kumar, P. (2023). Synthesis, Physico-chemical, Spectral And Molecular Docking studies of 4-[(E)-benzylideneamino]-5-methyl-4H-1,2,4-triazole-3-thiol and Its Metal Complexes with Cu(II), Ni(II), Co(II) and Zn(II). *International Journal of Chemical and Environmental Sciences*, 4(3), 07-18. <https://doi.org/10.15864/ijcaes.4301>.
- Kumar, A., Kumar, V., Kumar, P., & Kumar, R. (2023). Synthesis, Characterization and Molecular Docking studies of 4-amino Triazole derivative ligand and its Pb (II) complex. *International Journal of Pharmaceutical Research and Applications*, 8(2), 1933-1937. DOI: 10.35629/7781-080219331937.
- Vogel, A. I. (1989). *Quantitative chemical analysis*. Addison-Wesley, Longman Inc.
- Dilmaghani, K. A. In Vitro Evaluation of Antibacterial and Antifungal Properties of Some New synthesized 1, 2, 4-triazole thioglycosides.
- Singh, K., Turk, P., & Dhanda, A. (2021). Synthesis, spectral characterization, and antimicrobial evaluation of new imine derived from 3-methylthiophene-2-carboxaldehyde and its Co (II), Ni (II), Cu (II), and Zn (II) metal complexes. *Applied Organometallic Chemistry*, 35(4), e6088.
- Andiappan, K., Sanmugam, A., Deivanayagam, E., Karuppasamy, K., Kim, H. S., & Vikraman, D. (2018). In vitro cytotoxicity activity of novel Schiff base ligand-lanthanide complexes. *Scientific reports*, 8(1), 3054.
- Deodware, S. A., Barache, U. B., Chanshetti, U. B., Sathe, D. J., Ashok, U. P., Gaikwad, S. H., & Kollur, S. P. (2021). Newly synthesized triazole-based Schiff base ligands and their Co (II) complexes as antimicrobial and anticancer agents: Chemical synthesis, structure and biological investigations. *Results in Chemistry*, 3, 100162.
- Devi, P., Singh, K., & Kubavat, B. (2023). Synthesis, spectroscopic, quantum, thermal and kinetics, antibacterial and antifungal studies: Novel Schiff base 5-methyl-3-((5-bromosalicylidene) amino)-pyrazole and its transition metal complexes. *Results in Chemistry*, 5, 100813.
- Milligan, D. E., & Jacox, M. E. (1965). Matrix-Isolation Infrared Spectrum of the Free Radical NH_2 . *The Journal of Chemical Physics*, 43(12), 4487-4493.
- Nakamoto, K., Fujita, J., Tanaka, S., & Kobayashi, M. (1957). Infrared spectra of metallic complexes. IV. Comparison of the infrared spectra of unidentate and bidentate metallic complexes. *Journal of the American Chemical Society*, 79(18), 4904-4908.



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