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Article

Synthesis, Characterization, and Spectral Studies of 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol and its Metal Complex with Co(II), Ni(II), Cu(II), and Zn(II)

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ABSTRACT

Triazole-derived Schiff base ligand, 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol (EPMTH), and its metal complex with Co(II), Ni(II), Cu(II), and Zn(II) ion was synthesized in solid state. The prepared compounds were characterized by elemental analysis and spectral techniques such as Fourier-transform infrared spectroscopy and ^{1}H and ^{13}C NMR spectroscopy. The shift in the bands of infrared spectra of the complexes indicates that ligand is bidentate and donating from Nitrogen and Sulfur atom. All the prepared metal complexes have tetrahedral geometry.

Key words: Triazole, Schiff base ligand, Metal complex, Synthesis, Characterization.

1. INTRODUCTION

Schiff bases and their metal complexes have wide range of applications as catalyst, polymers, dyes, drugs, food packaging, and O_2 detectors [1-5]. Triazoles are important class of heterocyclic compounds as they have shown good pharmacological applications as antimicrobial, antiviral, anticonvulsant, antioxidant, anti-depressant, and anti-inflammatory compounds [6-8]. The bivalent, trivalent, and tetravalent metal complexes with unsymmetrical substituted triazole derived Schiff base ligand have been studied extensively [9]. Transition metal complexes containing Triazole based Schiff base ligand, 4-[(E)-benzylideneamino]-5-methyl-4H-1,2,4-triazole-3-thiol have been prepared, studied and they have antibacterial potency [10]. Schiff base ligand prepared from condensation of 4-amino-5-mercapto-3-methyl/ethyl-1,2,4-triazole with 2/3/4-nitrobenzaldehyde and its metal complex with Co(II) ion have shown good antimicrobial activity [11]. Co(II), Ni(II), and Cu(II) metal complexes of 1,2,4-triazole Schiff base have been synthesized and studied through IR, magnetic susceptibility, conductivity measurement, and atomic force microscopy widely due to their pharmacological importance [12]. In the present research work, we have synthesized 1,2,4-triazole based Schiff base by condensation of 4-amino-5-ethyl-1,2,4-triazole-3-thiol [13] with benzaldehyde. Co(II), Ni(II), Cu(II), and Zn(II) complexes have been prepared from this Schiff base ligand. All the compounds have been characterized by micro-analytical and spectral techniques.

2. MATERIALS AND METHODS

In the experiment AR/ACS grade, chemicals were used. The melting point was determined using classical Kjeldahl method. The elemental analysis data were obtained using CHNS Analyzer: ELEMENTAR Vario EL III. The Infrared spectrum was recorded in the range 4000 cm^{-1}–450 cm^{-1} by Agilent Cary 360 FTIR Spectrometer using KBr pellets. The ^{1}H and ^{13}C NMR spectrum was obtained in $CDCl_3$ solvent using 400 MHz FT NMR: Bruker Advance III. The conductivity measurement of was done using Systronic Digital Conductivity meter 304 in DMF solvent.

3. EXPERIMENTAL

3.1. Synthesis of Ligand, 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol (EPMTH)

0.2 moles of 4-amino-5-ethyl-4H-1,2,4-triazole-3-thiol and 0.2 moles of benzaldehyde were refluxed for 3 h in ethanolic medium containing few drops of acetic acid and cooled down. Cream colored crystals separated, filtered, washed with ethanol, and dried in dessicator. The compound was recrystallized by ethanol anhydrous. Color-White, Melting Point-170°C.

3.2. Synthesis of Co(II), Ni(II) and Zn(II) Complex

02 mmol of corresponding Metal (II) chloride was dissolved in methanol and it was added to 04 mmol of ligand dissolved in methanol. The solution obtained was refluxed for 0.5 h, cooled and 2 mL conc. ammonia was added. It was again refluxed for 10 min, metal complex precipitated, filtered, washed with methanol, and dried in dessicator.

3.3. Synthesis of Cu(II) Complex

02 mmol of $CuSO_4.5H_2O$ was dissolved in aqueous methanol and added to methanolic solution of 04 mmol of ligand. The solution was refluxed for 15 min. The green colored metal complex precipitated, filtered, washed with methanol, and dried in dessicator.

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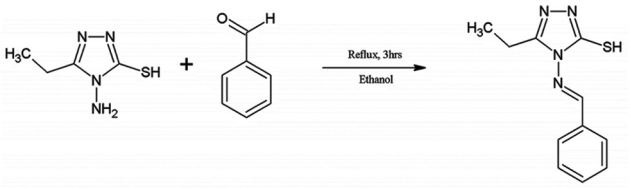
4. RESULTS AND DISCUSSION

4.1. Chemistry

The synthesized ligand EPMTH and its metal complexes with Co(II), Ni(II), Cu(II), and Zn(II) were stable in air and non-hygroscopic in nature. The conductivity data indicates that Cu(II) complex is 1:1 electrolyte whereas rest of the metal complexes are non-electrolytes in DMF [14]. The elemental analysis data are in good agreement with calculated values. The physicochemical properties and elemental analysis data are provided in Table 1.

4.2. NMR Spectra

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 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, ar H), 10.34 (s, 1H, -HC=N-), 11.80 (s, 1H, SH).



Scheme 1: Synthesis of Ligand, 5-ethyl-4-[(E)-(phenylmethylidene) amino]-4H-1,2,4-triazole-3-thiol (EPMTH).

^{13}C NMR (100MHz, CDCl3) δ (ppm): 10.4 (CH_3); 18.9 (CH_2); 128.7, 128.9, 132.4, 132.6 (Aromatic C-C ring); 153.8 (Azomethine C); 161.2,161.9 (Triazole ring C) [15] [Figures 1 and 2].

4.3. Infrared Spectra

The EPMTH and its metal complexes have been characterized with the help of Infrared spectra. The IR frequency of the ligand EPMTH and its metal complexes are provided in Table 2. The formation of EPMTH have been strongly supported by –HC=N- (azomethine) stretching at 1583.03 cm^{-1} [16]. In all the complexes, –HC=N- stretching is shifting toward lower frequency indicating donation to metal from azomethine N-atom [10]. The S-H stretch which is present in ligand at 2763.18 cm^{-1} as weak band is completely absent in all the metal complexes revealing that the donation from deprotonated thiol S [17]. Lattice water is present in all the metal complexes which are figured out by bulgy region around 3400 cm^{-1} which corresponds to O-H symmetric and anti-symmetric stretch and H-O-H bending bands have also been observed around 1610–1640 cm^{-1} in metal complexes [18]. However, no coordinated water peaks have been observed. In Cu(II) complex, a very sharp peak at 1067.78 cm^{-1} is observed which corresponds to SO_4^{2-} ion [19]. Furthermore, the frequency of C-S stretch in Cu(II) complex is higher than ligand indicating coordination from thioketone S-atom. The IR studies clearly indicate that ligand (EPMTH) is bidentate and donating from azomethine N-atom and thiol S-atom in Co(II), Ni(II), and Zn(II) complex and in case of Cu(II) complex binding is taking from azomethine N-atom and thioketonic

Table 1: Physicochemical and elemental analysis data.

Composition	Color	Melting Point (°C)	Found (Calculated) %					Conductivity ($Scm^{-2}mol^{-1}$)
			C	H	N	S	Metal	
EPMTH	White	170	56.85 (56.87)	04.05 (05.21)	24.80 (24.12)	13.90 (13.80)	-	-
Co $(EPMT)_2.3H_2O$	Bluish	110 d	45.87 (45.91)	04.98 (04.90)	19.44 (19.47)	11.08 (11.14)	10.29 (10.24)	38
Ni $(EPMT)_2.3H_2O$	Green	135 d	45.91 (45.93)	04.94 (04.91)	19.52 (19.48)	11.18 (11.14)	10.43 (10.20)	35
Cu $(EPMTH)_2.SO4._2H_2O$	Green	150 d	40.00 (40.02)	04.35 (04.27)	16.85 (16.97)	14.60 (14.57)	09.70 (09.62)	79
Zn $(EPTM)_2.H_2O$	White	207 d	48.35 (48.40)	04.35 (04.27)	16.85 (16.97)	14.60 (14.57)	09.70 (09.62)	42

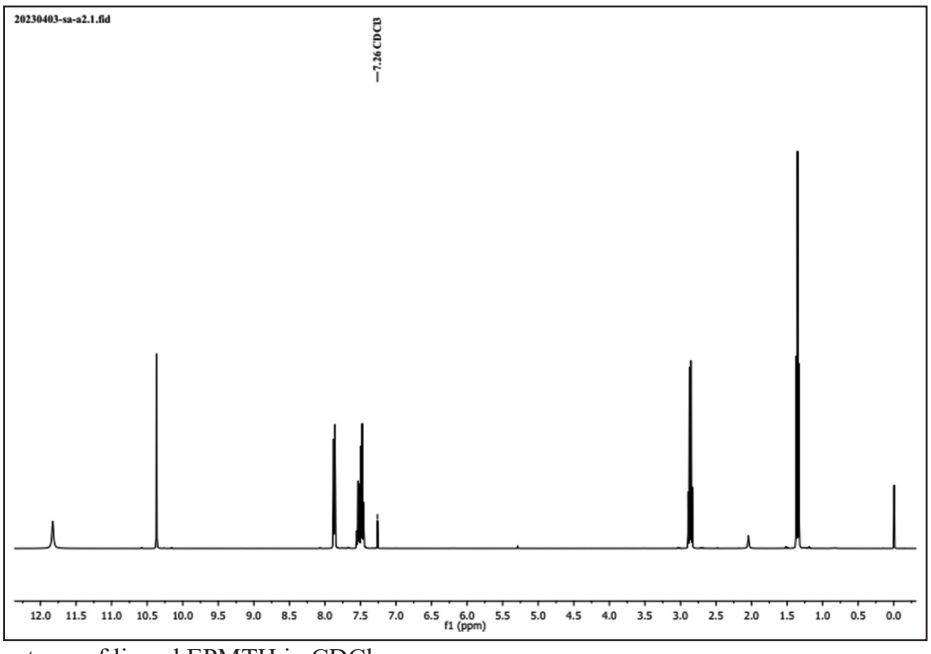


Figure 1: ^{1}H NMR spectrum of ligand EPMTH in $CDCl_3$.

Table 2: IR frequency and band assignments.

Band assignments	Infrared spectral frequencies (cm^{-1})				
	EPMTH	Co (II) complex	Ni (II) complex	Cu (II) complex	Zn (II) complex
H_2O/O-H stretch	-	3399.89	3398.31	3401.49	3402.05
C-H stretch	3062.14, 2938.30	2977.70, 2935.63	2976.86, 2934.18	2920.69	2978.41, 2935.94
S-H stretch	2763.18	-	-	-	-
H-O-H bending	-	1610.58	1610.63	1630.77	1642.46
-HC=N- stretch	1583.03	1552.28	1572.43	1560	1552.49
CH_3, CH_2 bending	1492.36, 1384.22	1450.87, 1382.35	1450.91, 1382.80	1384.53	1436.19, 1385.24
C-S stretch	757.19	757.17	757.14	768.14	757.87
H_2O wagging	-	605.68	605.66	616.87	601.48
Triazole ring deformation	575.72, 511.68	560.40, 512.28	564.15	-	514.54

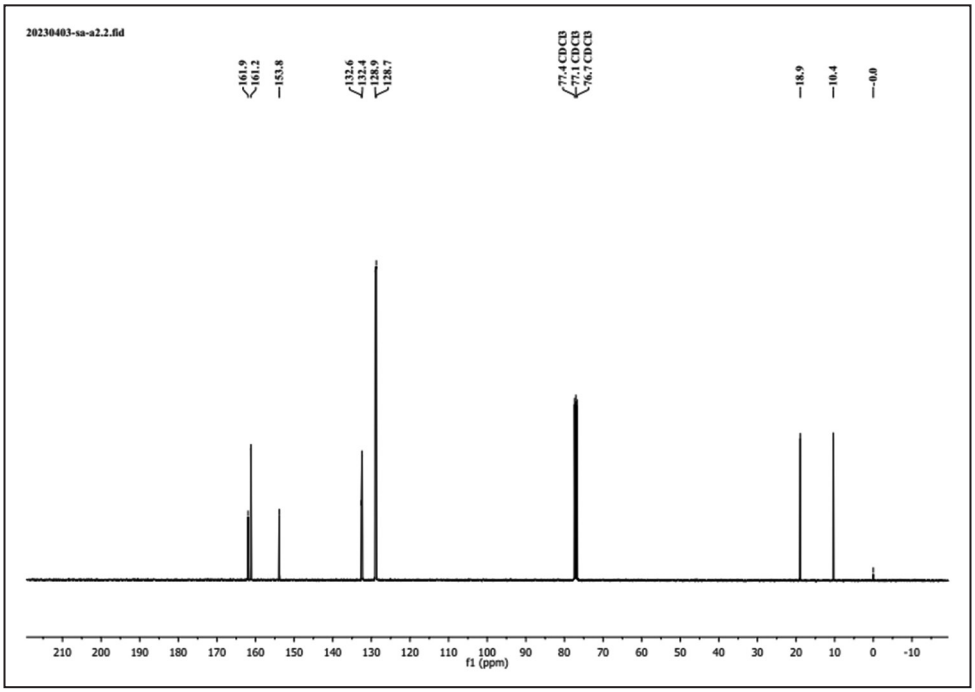


Figure 2: ^{13}C NMR spectrum of ligand EPMTH in $CDCl_3$.

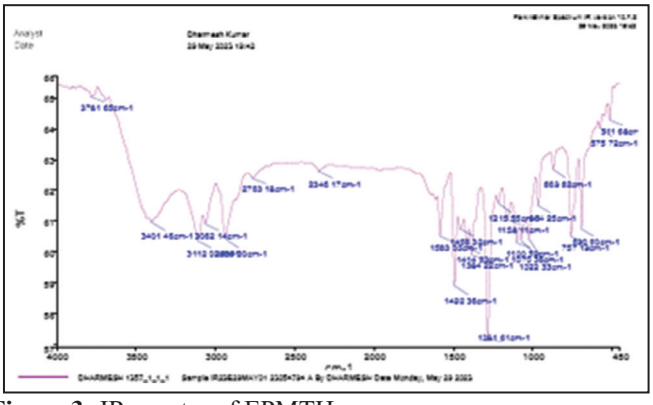


Figure 3: IR spectra of EPMTH.

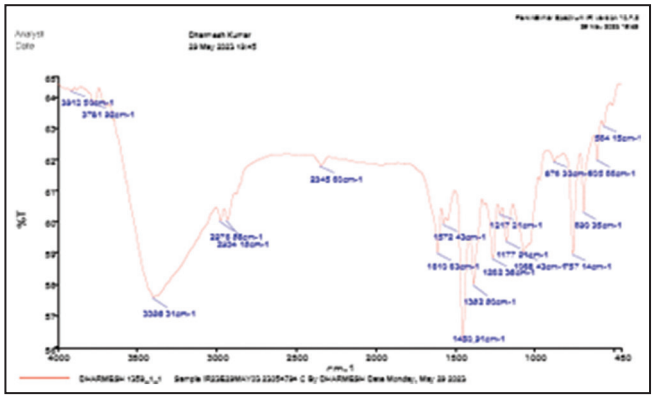


Figure 4: IR spectra of Ni(II) complex.

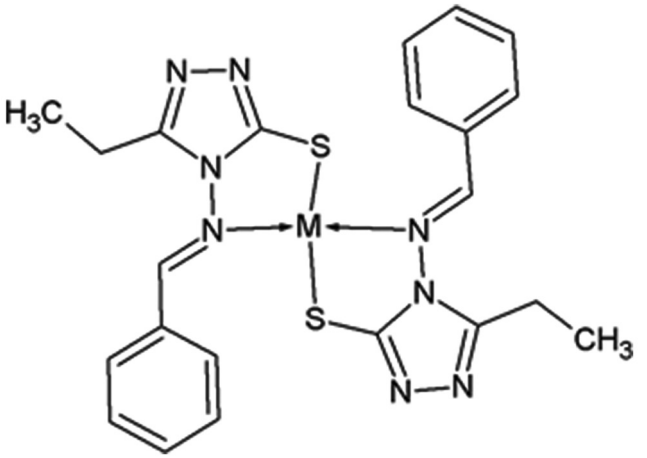


Figure 5: Expected structure of Metal (II) complex where M= Co(II), Ni(II), and Zn(II).

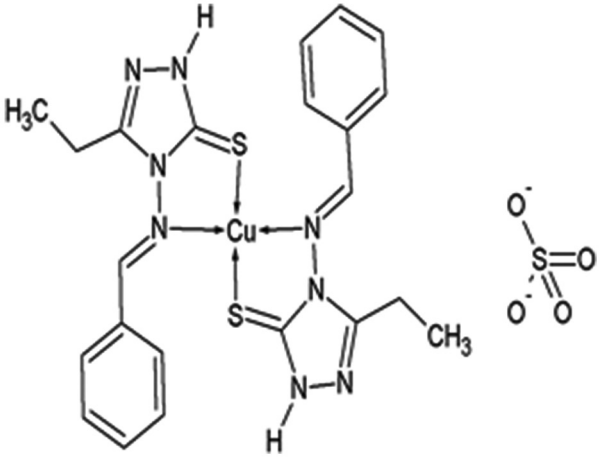


Figure 6: Expected structure of Cu(II) complex.

S-atom [Figures 3-6].

5. CONCLUSION

Triazole-based Schiff base ligand EPMTH and its 1:2 metal complexes with Co(II), Ni(II), Cu(II), and Zn(II) have been prepared. The prepared compounds were characterized by elemental analysis, ^{1}H and ^{13}C NMR, and IR spectroscopy. Infrared spectra revealed that the ligand is bidentate in nature and coordinates to metal from azomethine-N and Thiol-S. The conductivity measurements supported that Co(II), Ni(II), and Zn(II) complexes are non-electrolytes while Cu(II) complex is 1:1 electrolyte in DMF. The complex is expected to attain tetrahedral geometry. The ligand and the metal complexes could possess biological activity as they contain triazole moiety. Future studies on these compounds in biological domain can prove to be great for welfare of society.

6. ACKNOWLEDGMENT

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***Bibliographical Sketch**

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Mr. Piyush Kumar is research scholar at Department of Chemistry, Patna University, Patna, Bihar, India under the supervision of Dr. Abhay Kumar. He has joined PhD program in 2020 and working on metal complexes of Triazole and Tetrazole derivatives. He has presented his work in various national and international conferences. He has achieved two publications also.

Mr. Vivek Kumar is CSIR-SRF pursuing PhD program at Department of Chemistry, Patna University, Patna, Bihar, India under the supervision of Dr. Abhay Kumar. He specializes in Inorganic chemistry and joined PhD program in 2019. He is working on studies of metal complexes of Triazoles, Thiadiazoles, and Benzimidazoles derivatives. Coordination chemistry and Green chemistry are core area of his research interest. He has published four research papers in various reputed journals and presented his research work at various national and international conferences. He has also received various awards in academic field. He qualified the CSIR-NET-JRF Examination in 2017 and was awarded JRF.