Advancements in Coordination Chemistry: A Comprehensive Review on the Synthesis and Characterization of Transition Metal Complexes with 4-Amino-5-pyridyl-4H-1, 2, 4-triazole-3 thiol Ligands

Harshadkumar P. Patel[1], Himani M. Raval[2]

Lecturer, Swami Sachchidanand Polytechnic College, Sankalchand Patel University, Visnagar, India.[1]
Assistant Professor, Urban Bank Science College, Mehsana, India.[2]

hppatel.sspc@spu.ac.in[1], himani.raval3244@gmail.com[2]

Abstract: This review paper offers an in-depth analysis of recent advancements in coordination chemistry, specifically focusing on the production and portrayal of transition metal complexes that incorporate5-pyridyl 4-Amino-3-thiol -4H-1,2,4-triazole ligands. The study explores the various methods used to synthesize these complexes, covering a range of transition metals and diverse reaction conditions. It provides a thorough examination of the structural attributes, spectroscopic characteristics, and potential applications of the resulting complexes. The objective of the paper is to present valuable insights into the design, synthesis, and properties of these transition metal complexes, highlighting their importance in coordination chemistry and their promising applications in fields such as catalysis, medicine, and materials science.

Keywords: Spectral Analysis, Metal Complexes, PMR, Magnetic properties, Synthesis.

I. INTRODUCTION

Heterocyclic chemistry, a specialized field with a long-standing history, plays an essential role in modern society and presents significant potential for future advancements. Nitrogen, oxygen, and sulphur are identified as pivotal hetero atoms in these compounds. Among the various heterocyclic compounds, triazoles, particularly 1, 2, 3-triazoles and 1,2,4-triazoles, are of particular interest due to their importance in pharmaceuticals and industrial research. These five- membered rings, with the molecular formula C2H3N3, have been thoroughly explored for their wide range of applications.

In particular, triazoles substituted with amine or thione groups exhibit notable anti-inflammatory and antimicrobial activities. As ligands, triazoles are highly valued for their ability to coordinate, as they contain both hard nitrogen and soft sulphur atoms. The coordination sites within the triazole structure include the sulphur from thiol groups, nitrogen from primary amino groups, and two nitrogen atoms within the triazole ring. This polydentate nature enables the formation of stable chelate complexes through bidentate coordination to metal ions, resulting in five-membered rings with enhanced stability.

The review further discusses the synthesis and portrayal of copper (ii), nickel (ii), zinc (ii), cadmium (ii), and tin (ii) complexes, utilizing5-pyridyl 4-Amino-3-thiol, 4-H-1, 2, and 4-triazoleby way of ligand.

II. RESOURCES AND PROCEDURES

Entire chemicals, components, and solvents used in this study were obtained from commercial sources and employed without further purification. Melting points were measured using a co slab melting point device. Fundamental analysis for carbon, hydrogen, nitrogen, and sulphur was performed using a Faison E.A.Analyser. Infrared spectrum was documented on a Shimadzu spectrophotometer, in the 4000–200 cm^{-1}. UV–Visible spectra (UV–VIS) were acquired with a Shimadzu spectrophotometer, covering the wavelength 250–1500 nm.

Magnetic susceptibility was determined at the room temperature with a Magnetic Vulnerability Balance from Jonson mathey. Conductivity was measured using a WTW conductivity meter, and atomic absorption spectroscopy was carried out with a Simatzu

https://doi.org/10.63766/spujstmr.24.000001

685 blaze instrument. Proton and carbon PMR spectrum was documented on Brukar spectrometer, with deuterated DMSO as the solvent and tetra amethylsilane (TMS) as the interior reference.

A. Production of5-pyridyl -4-Amino -3-thiol -4H-1,2,4-triazole(Ligand):

Solution was prepared by dissolving 1 gram of iso nicotinic acid (0.0072 mol) and 0.44 grams of potassium hydroxide (0.008 mol) in 10 ml of ethanol. Once the solid was fully dissolved, 2.0 ml (0.015mol) of carbon disulphide was gradually additional to the mix. The reaction stirred for 12 hours. Following this, 12 ml of dry ether got introduced, leading to formation of the yellow ppts, which were subsequently filtered and washed with ether and dried. Obtained K salts were nearly quantitatively recovered and used in the following step. This yellow ppts (K salts) was then treated with extra hydrazine hydrate (25 ml), refluxed having continuous stirring till hydrogen sulphide gas evolution stopped, as established with Pb- Acetate rag. Later chilling, mix got filtered, hydrochloric acid were added to acidify the solution, resulting in the formation of a white precipitate. The overall yield was 62%, and the product had a melting point between 210–212 °C.

B. Formation of Complexes:

To prepare the metal complexes with this ligand, an ethanoic soln. of appropriate metal salts [Copper acetate, Tin chloride, Zincacetatdehydrate, Cadmium acetat, and Nickelacetat] was mixed with ethanoic soln. of5-pyridyl 4-amino-3-thiol, 4-H-1,2,4-triazolein 1 is to 2 molar ratio of Metal to Ligand. The resulting mixture was refluxed for 2 hours, during which crystal-like, colour ed ppts formed upon cooling at the room temperature. The obtained solids was filtered and eroded with warm methanol, allowed to dry, then re crystallized using ethanol.

III. OUTCOMES AND CONVERSATION

The malting points besides corporeal characteristics as the all compounds studied are provided in Table: 1. C-H-N-S analysis was performed by means of the atomic flame absorption method, with experimental values closely matching the calculated ones. A summary of corporeal and analytical information, including malting points, elemental composition, for the ligand and its corresponding complexes, is presented in Table-1.

TABLE- 1
CORPOREALINFORMATION OF SYNTHESIZED COMPLEXES

Compounds	Colour	Melt. Pnt.	Fundamental examination theoretical and Investigational				
			% of Carbon	% of Hyd	% of Nitrgn	% of Sulphur	% of Metal
Ligand	Snowy	210–215	55.94(56.25)	4.33(4.65)	23.42(23.62)	12.31(12.56)	--
Ni(Ligand)2	Lime	242–245	30.05(39.27)	4.26(5.51)	39.18(40.11)	12.25(14.54)	11.20(11.48)
Cu(Ligand)2	Dusky green	223–226	49.69(42.21)	4.14(4.85)	38.82(39.62)	13.53(14.87)	12.07(14.13)
Zn(Ligand)2	Off silvery	175–182	36.43(39.09)	4.57(5.18)	38.70(23.70)	15.05(14.34)	12.47(13.17)
Cd(Ligand)2	Snowy	256–258	43.89(39.27)	5.76(4.49)	39.28(48.78)	11.02(13.38)	22.15(22.57)
Sn(Ligand)2	Creamy	232–234	43.55(34.19)	5.47(4.65)	35.91(35.47)	22.90(22.70)	22.64(21.04)

A. Infrared spectrography:

The FTIR spectra of the ligand exhibited distinct widening groups at 3352 and 3225 cm^{-1} (NH_2), 2736 cm^{-1} (S-H), 1645 cm^{-1} (C=N in the triazole ring), and 673 cm^{-1} (C-S bond stretch). Similar bands were observed in complexes 1–5, consistent with findings from various studies. The triazole ring may exist in different tautomeric forms (see Figure 1). The complete absence of the (S-H) band in the spectrum of complexes suggests de protonation prior to complex formation. Following de protonation, ligand can coordinate to metal ion via either nitrogen or sulphur atoms of the thiamine group, with sulphur coordination being preferred, foremost to the development of a stable 5-membered chelate.

An exception is noted in the C=N stretching bands of complexes 1–5, which shift to lower wavelengths compared to the free ligand (L), indicating coordination through the nitrogen atom. Additionally, the NH_2 stretching bands also shift upon complextion. The disappearance of the S-H band and the shifts in the C-S and C=N bands suggest changes in bond orders and indicate coordination through sulphur. New bands corresponding to M-S and M-N bonds appear, further confirming the coordination. The significant IR bands and their likely assignments were summarized in Table: 2.

TABLE: 2
IR INFORMATION OF LIGAND AND COMPOUNDS

Centres	-NH2	-S–H bond	C = N bond	C–S bond	M–N bond	M–S bond
Ligand	3255, 3215	2632	1646	675	-	-
$Ni(L)_2$	3285, 3220	-	1642	696	532	455
$Cu(L)_2$	3318, 3282	-	1626	693	531	423
$Zn(L)_2$	3323, 3285	-	1642	692	527	436
$Cd(L)_2$	3435, 3389	-	1633	697	523	453
$Sn(L)_2$	3250, 3155	-	1647	691	525	452

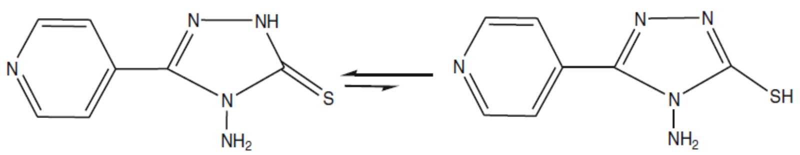

Fig. 1. Tautomeric form in triazole.

B. Nuclear Magnetic Resonance:

The [1]H PMR and [13]C PMR spectra of Ligand and its metal compounds demonstrated outstanding solubility in the DMSO. The proton PMR spectra provided further evidence supporting the formation of the complexes. Shifts in the chemical positions of the peaks observed in the spectra suggest that complexation has taken place, as the electronic environment of the compound significantly affects its chemical shift.

i. 5-pyridyl -4-Amino -3-thiol -4H-1,2,4-triazole:

The [1]H PMR spectra of the ligand in DMSO at 300 MHz displays signs at 6.101 (2H, NH_2), 7.014, 7.025-8.744, and 8.755 (4-H d,d and aromatic C-H), 11.210 (1-H). The Carbon PMR spectrum demonstrations Chemical shifts on 112.435 (C- a), 153.097 (C- b), 153.792(C- c), 145.308 (C- d), and 148.429 (C- e) (Figure: 2).

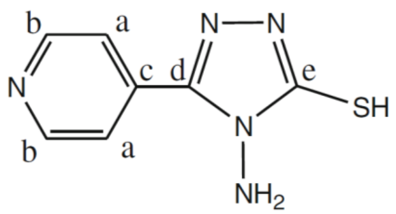

Fig.2. Construction of the ligand

ii. Compound-1:

The ^1H PMR spectrum for Complex 1 in DMSO-d6 at 300 MHz displays signs at 2.214 (2H, NH_2), which is moved downfield owed to coordination with zinc ion, as well as at 7.945, 8.014-8.739, and 8.678 (4H, d, d, aromatic CH), and 12.093 (1H, NH). The ^{13}C PMR spectrum displays chemical shifts at 123.004 (C- a), 134.584 (C - b), 142.993 (C- c), 146.685 (C- d), and 178.543 (C- e) (Figure: 3).

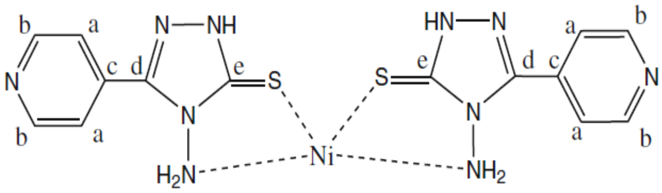

Fig.3. The configuration of compound-1 with Ni(Ligand)

TABLE: 3
PROTON PMR FIGURES OF LIGAND AND METAL COMPOUNDS OF 1, 3,4IN DMSOCENTRES

Compounds	C–H sigma bond Aromatic	-NH2	S-H sigma bond	N-H sigma bond
Ligand	(7.021,7.029-7.748,7.752)d,d	(4.303)s	(09.183)s	-
Ni(Ligand)2	(7.938,8.012-8.733,8.676)d,d	(2.315)s	-	(13.092)s
Zn(Ligand)2	(8.022-8.707)m	(2.352)s	-	(12.010)s
Cd(Ligand)2	(7.912,7.953-8,627,8.693)d,d	(2.272)s	-	(11.105)s

iii. Complex-2:

The ^1H NMR spectrum (ppm) for Complex 3 in Dimethyl sulfoxide-d6 at 300 MHz shows signs at 2.254 (2H, NH_2), which is downfield move do wing to coordination with the metal ion, 7.025-7.750 (4H, aromatic C-H), and 12.040 (1H, N-H). The ^{13}C PMR spectrum reveals organic shifts at 133.703 (C- a), 139.422 (C- b), 124.025 (C- c), 142.293 (C- d), and 169.149 (C- e) (Figure:4).

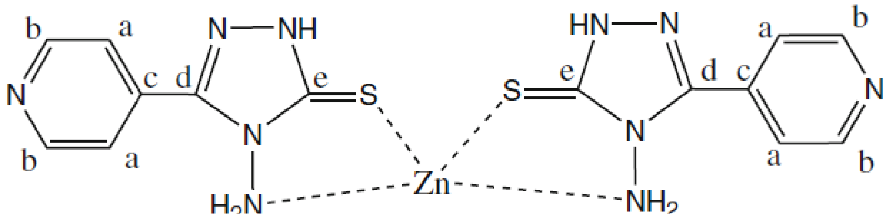

Fig. 4. Arrangement of compound: 3 with Zn (Ligand)

iv. Compound-3:

The ^1H PMR spectrum (ppm) for Complex 4 in Dimethyl sulfoxide-d6 at 300 MHz displays signs at 4.270 (2-H, NH_2), which is moved as a result of coordination with the metal ion, along with peaks at 7.901, 7.952-8.625, and 8.690 (4H, d, d, aromatic CH), and 12.205 (1-H,cNH). The ^{13}C PMR spectra demonstrations chemical changes at 132.943 (C- a), 135.625 (C- b), 152.016 (C- c), 145.293 (C- d), and 178.322 (C- e) (Figure:5).

Table: 3, 4 present the Proton and Carbon PMR information for the ligand plus Metal compounds: 1, 4, and 3 with Dimethyl sulfoxide, including their Chemical changes, δ .

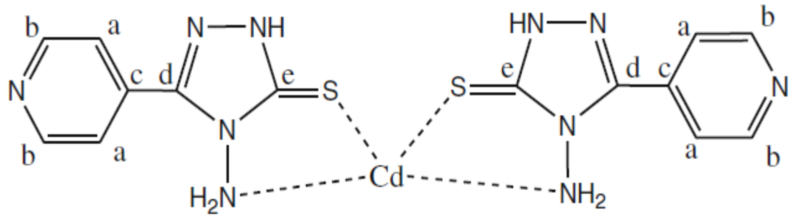

Fig. 5 Arrangement of complex: 4 withCd(Ligand)

TABLE: 4
13C PMR STATISTICS OF LIGAND BESIDES METAL COMPOUNDS 1, 4, 3 IN DMSO SOLVENT

Compounds	C- a	C- b	C- c	C- d	C- e
Ligand	123.563	152.132	131.892	144.306	163.552
Ni(L)2	122.005	144.586	133.994	153.684	182.544
Zn(L)2	124.707	146.324	132.033	154.295	185.113
Cd(L)2	122.987	147.607	135.032	152.293	183.326

C. UV–Visible Spectrography:

The captivation spectrum of the ligand and its metal complexes were measured in DMSO solvent within the wavelength series of 260–950 nm. A summary of the electric spectrum for (Ligand) and its compounds is presented in the Table-5. The ligand shows three distinct absorption bands at 263, 302, and 309 nm, corresponding to intra ligand transitions:(n - π*) and (π- π*), respectively. The electronic spectra of complexes 1–5 exhibit similar transitions, though with slight shifts when compared to the free ligand.

For compounds- 1, 2, additional changes associated with metallic d orbitals (d-d evolutions) were detected in the visible region, specifically for Ni and Cu. Now Ni, the d-d orbital evolution seemed on 590nenometers, attributed to the T:1 → T:1 and T:1 → 3A2 transitions. In Cu(ii), absorption groups at 310, 280, 349, and 415 nm were assigned to the (n-π*) nad (π-π*), charge transfer, and T2→ E2 transitions, correspondingly. However, complexes-4, 5, and 6 were found to be Dia-Magnetic, by way of probable for d-10 metal ion, showing not at all d-d orbital transitions in the visible section.

TABLE-5
ELECTRIC SPECTRUM OF SYNTHESIZED COMPOUNDS

Compounds	Preoccupation	Transition
Ligand	262, 304, 302	(n-π*) (π-π*)
Ni(Ligand)2	261, 613	T1(F) → T1(P)(π-π*),
Cu(Ligand)2	283, 301, 314, 452	L→Cu, (n-π*), T2→E2, (π-π*)
Zn(Ligand)2	265, 303, 312	(n-π*) (π-π*)
Cd(Ligand)2	265, 313	(n-π*) (π-π*)
Sn(Ligand)2	266, 312	(n-π*) (π-π*)

D. Magnetic Liability and Conductivity Dimensions:

Magnetic capacities are frequently castoff to investigate transition metal compounds, as unpaired electrons in the partially filled d-orbitals influence their magnetic behaviour. Complex 1 displayed a magnetic moment of 1.13B. M., indicating it is para magnetic. Complex-2, with a magnetic second of 0.8 B.M., is thought to have a copper (ii) centre in a biased square planar geometry. In contrast, complexes-3 to 5 were found to be diamagnetic, with no observable magnetic moment in this reading.

Conductivity tests were performed on the complexes in ethanol to assess their electrolyte properties. Molar conductivity values for compounds-1 to 5 are shown in Table-6, indicating that all the complexes are non-electrolytes.

From the spectrum data, it is suggested that complexes 1–5 adopt biased tetrahedral geometries, with the exception of complex 2, which is believed to have a biased square planar structure. The projected structures for compounds 1–5 are depicted in Figure: 6.

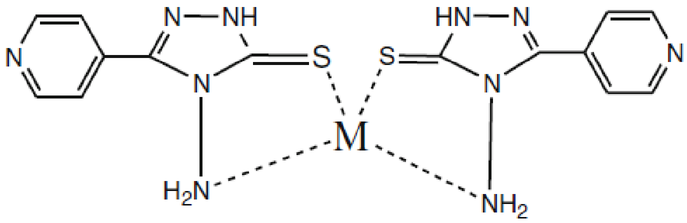

Fig.6.Theprojected structures of compounds 1–5 {M= Ni, Cu, Zn, Cd and Sn}.

TABLE: 6
CUNDUCTIVITY DIMENSION AND MAGNETIC MOMNTS. FOR LIGAND AND ITS COMPOUNDS

Compounds	Conductivity (μS/cm)	Magnetic moment (B.M.)
Ligand	--	--
Ni(Ligand)2	2	1.02
Cu(Ligand)2	1.5	0.4
Zn(Ligand)2	2.1	4.1
Cd(Ligand)2	2.3	1.98
Sn(Ligand)2	0.8	11.88

IV. INFERENCE

The ligand5-pyridyl 4-Amino-3-thiol -4H-1, 2,4-triazole was effectively produced and utilized to form complexes with different metal ions. The coordination process involved the interaction of both the amino, thiol clusters of the ligand, foremost to the creation of a 5-membered chelate ring. It is proposed that the copper complex adopts a square planar geometry, whereas the other metal complexes are believed to have a tetrahedral -geometry.

REFERENCES

[1] Haddad, Raghad, Emad Yousif, and Ahmed " Synthesis *and characterization of transition metal complexes of 4-Amino-5-pyridyl-4H-1, 2, 4-triazole-3-thiol*." SpringerPlus , 2013, pp. 1-6.

[2] Acheson R, "*An introduction to the chemistry of heterocyclic compound"* Wiley, New York, 3, 1989, pp. 122–129

[3] Al-Maydama H, Al-Ansi T, Jamil Y, Ali A "*Biheterocyclic ligands: synthesis, characterization and coordinating properties of bis(4-amino-5-mercapto-1,2,4-triazol-3-yl) alkanes with transition metal ions and their thermo kinetic and biological studies*" 1989, Ecl Quim 33(3):29–42

[4] Awad I, Abdel-Rahman A, Bakite "*4-[(E)-(3-Methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)iminomethyl] benzonitrile*" J Chem Technol Biotechno 2008, pp. 483–486

[5] Bele D, Singhvi I "*A review on1, 2, 4- triazole. Asian J of Biochem and Pharmaceutical Res*" 2011, (1): pp. 88–100

[6] Bruice P , Organic Chemistry, 2nd edn. Viacom Company, 1998, New Jersey

[7] Carey F Organic Chemistry. McGraw-Hill Inc, 1980, America

[8] Cheremisina M, Khlystunova E, Varand V "*IR spectra of complexes of certain metals with thio and selenourea in the region of the metal-ligand vibrations*" Bulletin of the Academy of Sciences of the USSR, division of chemical science. 1972, 21(12):pp. 2604–2606

[9] Chohan Z , "*Antibacterial dimeric copper (II) complexes with chromone derived compounds Trans*" Met Chem 34: 2009, pp. 153–161

[10] Clayden J, Greeves N, Warren S, Wothers P Organic Chemistry. New York, Oxford University, 2001, pp 798–799

[11] Cos-kun A "*The synthesis of 4-phenoxyphenylglyoxime and 4,4-oxybis(phenylglyoxime) and their complexes with Cu(II), Ni(II) and Co(II)* " Turk J Chem 2006, (30): pp. 461–469

[12] Davari M, Bahrami H, Haghighi Z, Zahedi M (2010) "*Quantum chemical investigation of intramolecular thione-thiol tautomerism of 1,2,4-triazole-3-thione and its disubstituted derivatives*" J Mol Model 2010, 16(5):pp.841–855

[13] Figgis B , "*Ligand Field Theory and its Applications*", 1st ed. John-Wiley, New YorkFlifel I, Kadhim, 2000.