

# 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

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**Abstract:** This review paper provides a comprehensive examination of recent developments in coordination chemistry, focusing on the synthesis and characterization of transition metal complexes incorporating 4-Amino-5-pyridyl-4H-1,2,4-triazole-3-thiol ligands. The investigation delves into the diverse methodologies employed for the synthesis of these complexes, encompassing various transition metals and reaction conditions. A detailed analysis of the structural features, spectroscopic properties, and potential applications of the synthesized complexes is presented. The paper aims to offer valuable insights into the design, synthesis, and understanding of the properties of these transition metal complexes, shedding light on their significance in the realm of coordination chemistry and their potential applications in catalysis, medicine, and materials science.

**Keywords:** Amino-5-(pyridyl)-4H-1, 2, 4-triazole-3-thiol Metal complexes, Spectral analysis, Nuclear Magnetic Resonance, Magnetic Susceptibility.

## I. INTRODUCTION

Heterocyclic chemistry, a distinct field with a rich history, plays a crucial role in contemporary society and holds promising prospects for the future. Nitrogen, oxygen, and sulphur are recognized as key hetero atoms. Among heterocyclic compounds, triazoles, specifically 1,2,3-triazoles and 1,2,4-triazoles, are noteworthy due to their relevance in drugs and industrial studies. Triazoles, comprising five members with the molecular formula C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>, have been extensively studied for their diverse applications. Notably, amine and thione-substituted triazoles exhibit anti-inflammatory and antimicrobial properties. Triazoles are esteemed as effective coordinating ligands, featuring both hard nitrogen and soft sulphur atoms. Their coordinating sites include the sulphur of thiol groups, nitrogen of primary amino groups, and two nitrogen atoms in the triazole ring system. This polydentate ligand forms stable five-membered rings through bidentate coordination to metal ions, leading to chelate complexes known for their enhanced stability.

The paper outlines the preparation and characterization of copper (II), nickel (II), zinc (II), cadmium (II), and tin (II) complexes with 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol.

## II. MATERIALS AND METHODS

All reagents, starting materials, and solvents were commercially purchased and used without additional purification. Melting points were determined using a Coslab melting point apparatus. Elemental analysis for carbon (C), hydrogen (H), nitrogen (N), and sulphur (S) was conducted with a Fison EA 1108 analyzer. Infrared (FTIR) spectra were recorded using an FTIR 8300 Shimadzu spectrophotometer with a CsI disc in the frequency range of 4000–200 cm<sup>-1</sup>. UV-visible (UV-VIS) spectra were obtained with a Shimadzu UV-VIS 160 A-Ultra-violet spectrophotometer in the range of 200–1100 nm. Magnetic susceptibility values were measured at room temperature using a Magnetic Susceptibility Balance from Johnson Matthey. Conductivity measurements were performed using a WTW conductivity meter. Atomic absorption measurements were acquired with a Shimadzu 680 cc-flame instrument. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Ultrashield 300 MHz in Jordan, utilizing deuterated DMSO-d<sub>6</sub> as the solvent and tetramethylsilane (TMS) as the internal standard.

### A. Synthesis of 4-Amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol (ligand)

A mixture containing 1 gram of is nicotinic acid (0.0072 mol) and 0.44 grams (0.008 mol) of potassium hydroxide dissolved in 10 ml of ethanol. After complete dissolution, 2 ml (0.014 mol) of carbon disulphide was slowly added. The reaction mixture

was stirred for 10 hours. To this, 10 ml of dry ether was added, resulting in a yellow precipitate, which was filtered, washed with ether, and dried. The obtained salt was nearly quantitatively yielded and used for the subsequent step. The yellow precipitate (potassium salt) was combined with an excess of hydrazine hydride (20 ml) and refluxed with stirring until the evolution of hydrogen sulphide ceased, confirmed by lead acetate paper. After cooling, the reaction mixture was filtered, and Hydrochloric acid was added for acidification, yielding a white precipitate (Siddiqui et al., 2010). The overall yield was 62%, and the melting point was in the range of 210–212 °C.

### B. Synthesis of Complexes

To synthesize complexes of this ligand, an ethanolic solution containing suitable metal salts [Copper (II) acetate, Tin (II) Chloride, Zinc (II) acetate dihydrate, Cadmium (II) acetate, and Nickel (II) acetate] was combined with an ethanolic solution of 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol in a 1:2 (metal:ligand) molar ratio. The mixture was refluxed for two hours, resulting in the formation of crystalline-colored precipitates at room temperature. The obtained solids were washed with hot methanol, allowed to dry, and then recrystallized from ethanol (Majeed et al., 2004).

## III. RESULTS AND DISCUSSION

### A. Elements analysis

The melting points and physical properties of all the compounds under investigation are presented in Table 1. CHNS data were obtained using the flame atomic absorption technique, and the calculated values align well with the experimental results. The physical analytical data, including melting points and elemental analysis, for the ligand (L) and its complexes are summarized in Table 1.

TABLE I  
PHYSICAL DATA OF PREPARED COMPLEXES

Complexes	Colour	M.P.	Elemental analysis theoretical (Experimental)				
			% C	% H	% N	% S	% M
L	White	212–214	45.91(46.23)	5.30(5.75)	33.47(33.82)	15.32(14.98)	--
Ni(L)2 1	Green	240–242	40.01(39.22)	5.25(4.11)	29.16(30.01)	13.35(13.73)	12.22(12.28)
Cu(L)2 2	Dark green	222–224	39.61(40.21)	5.19(5.89)	28.87(29.32)	13.22(13.58)	13.10(16.02)
Zn(L)2 3	Off white	178–180	39.46(40.05)	5.17(6.13)	28.76(29.30)	13.17(13.52)	13.43(17.28)
Cd(L)2 4	White	255–257	35.99(40.25)	4.72(5.25)	29.23(28.88)	12.01(12.52)	21.05(23.85)
Sn(L)2 5	Yellow	230–232	35.57(35.12)	4.66(4.85)	25.93(25.54)	21.97(21.55)	21.97(6.152)

### B. Infrared Spectroscopy

The FTIR spectrum of the ligand (L) displayed characteristic stretching bands at 3250 and 3213 (NH<sub>2</sub>), 2736 (S-H), 1645 (C = N of triazole ring), and 673 (stretching of C-S bond). Similar bands were observed in complexes 1-5, as reported in various studies. The triazole structure may exist in a tautomeric form (see Figure 1). Deprotonation before complexation is indicated by the complete disappearance of the band related to  $\nu$ (S-H) in complex spectra. After deprotonation, the ligand can bind with the metal ion either through N or S of the thioamide group. Bonding at S is favored, forming a stable five-membered chelate.

An exception is observed in the  $\nu$ (C = N) bands of complexes 1-5, which shift to a lower wavelength compared to the ligand (L), suggesting coordination via the nitrogen atom of the ligand. The NH<sub>2</sub> bands also shift due to complexation. The disappearance of the S-H band and the shift of C-S and C = N bands indicate changes in bond orders and complexation through sulphate. New bands appear, supporting the frequencies of M-S, M-N bonds. The significant IR bands and their likely assignments are summarized in Table 2 (Flifel and Kadhim, 2012; Cheremisina et al., 1972; Qurban, 2011; Yousif et al., 2004)

TABLE II  
KEY INFRARED DATA OF L AND COMPLEXES 1–5

Complexes	NH <sub>2</sub>	-S-H	C = N	C-S	M-N	M-S
L	3250, 3213	2736	1645	673	-	-
Ni(L)2 1	3280, 3228	-	1643	690	530	459
Cu(L)2 2	3321, 3286	-	1620	694	532	428
Zn(L)2 3	3329, 3286	-	1640	694	529	432
Cd(L)2 4	3440, 3391	-	1639	693	528	451
Sn(L)2 5	3200, 3165	-	1643	690	528	451

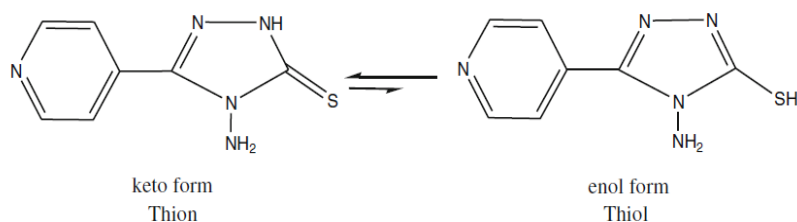


Fig.1. Tautomerism form in triazole

### C. Nuclear Magnetic Resonance

The <sup>1</sup>H NMR and <sup>13</sup>C NMR data for 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol and its complexes showed good solubility in DMSO. The proton nuclear magnetic resonance spectra provided additional confirmation of the complex compositions. The observed changes in the spectra indicate that complexation has occurred, as the chemical shift of a compound is strongly influenced by its electronic environment (Yousif et al., 2010; Ibraheem et al., 2010; Cos-kun, 2006).

#### i. Ligand

The <sup>1</sup>H NMR data (ppm) for the ligand in DMSO-d<sub>6</sub> at 300 MHz reveals signals at 5.301 (2H, s, NH<sub>2</sub>), 8.014, 8.025-8.744, 8.755 (4H, d, d, CH aromatic ring), and 10.189 (1H, s, SH). The <sup>13</sup>C NMR shows chemical shifts at 121.564 (carbon a), 150.133 (carbon b), 132.891 (carbon c), 147.308 (carbon d), and 167.551 (carbon e) (See Figure 2).

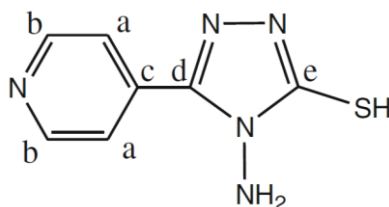


Fig.2. The structure of ligand

#### ii. Complex 1

The <sup>1</sup>H NMR data (ppm) for Complex 1 in DMSO-d<sub>6</sub> at 300 MHz reveals signals at 3.314 (2H, s, NH<sub>2</sub>) – this peak is shifted to a lower field due to its attachment to the zinc atom, 7.945, 8.014-8.739, 8.678 (4H, d, d, CH aromatic ring), and 11.099 (1H, s, NH). The <sup>13</sup>C NMR shows chemical shifts at 125.001 (carbon a), 149.583 (carbon b), 134.991 (carbon c), 155.683 (carbon d), and 183.548 (carbon e) (See Figure 3)

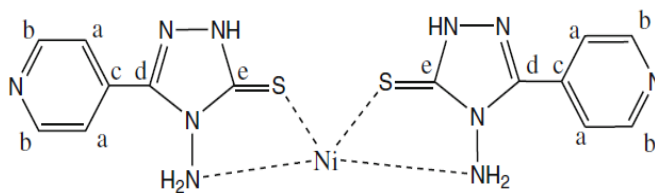
Fig.3. The structure of complex 1 Ni(L)<sub>2</sub>

TABLE III  
<sup>1</sup>H NMR DATA OF L AND METAL COMPLEXES 1,3 AND 4 IN DMSO-D<sub>6</sub> COMPLEXES  
 (C-H AROMATIC, NH<sub>2</sub>, S-H N-H)

L	(8.014,8.025-8.744,8.755)d,d(5.301)s (10.189)s
Ni(L) <sub>2</sub>	(7.945,8.014-8.739,8.678)d,d(3.314)s -(11.099)s
Zn(L) <sub>2</sub>	(8.024-8.702)m (3.354)s- (10.012)s
Cd(L) <sub>2</sub>	(7.901,7.952-8,625,8.690)d,d(3.270)s- (11.101)s

#### iii. Complex 2

In the <sup>1</sup>H NMR data (ppm) for Complex 3 in DMSO-d<sub>6</sub> at 300 MHz, signals appear at 3.354 (2H, s, NH<sub>2</sub>) – this peak is shifted due to its attachment to the metal atom, 8.024-8.702 (4H, m, CH aromatic ring), and 10.012 (1H, s, NH). The <sup>13</sup>C NMR shows

chemical shifts at 121.705 (carbon a), 149.322 (carbon b), 134.035 (carbon c), 158.297 (carbon d), and 180.114 (carbon e) (See Figure 4).

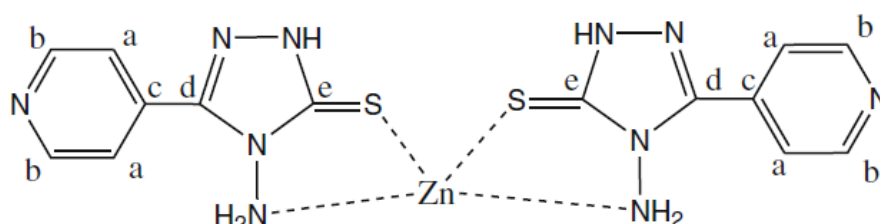


Fig. 4. The structure of complex 3 Zn(L)<sub>2</sub>

#### iv. Complex 3

In the <sup>1</sup>H NMR data (ppm) for Complex 4 in DMSO-d<sub>6</sub> at 300 MHz, signals are observed at 3.270 (2H, s, NH<sub>2</sub>) – for the reason mentioned above, 7.901, 7.952-8.625, 8.690 (4H, d, d, CH aromatic ring), and 11.101 (1H, s, NH). The <sup>13</sup>C NMR shows chemical shifts at 120.992 (carbon a), 149.603 (carbon b), 134.036 (carbon c), 150.297 (carbon d), and 187.329 (carbon e) (See Figure 5).

Tables 3 and 4 provide the <sup>1</sup>H NMR and <sup>13</sup>C NMR data for L and metal complexes 1, 3, and 4 in DMSO-d<sub>6</sub>, including chemical shift,  $\delta$  (ppm).

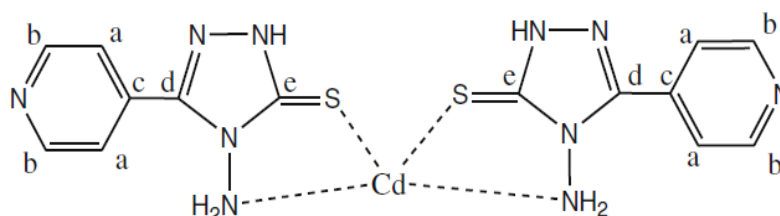


Fig.5. The structure of complex 4 Cd(L)<sub>2</sub>

TABLE IV

<sup>13</sup>C NMR DATA OF L AND METAL COMPLEXES 1, 3 AND 4 IN DMSO-D<sub>6</sub> CHEMICAL SHIFT,  $\delta$  (PPM)

L	121.564 150.133 132.891 147.308 167.551
Ni(L) <sub>2</sub>	125.001 149.583 134.991 155.683 183.548
Zn(L) <sub>2</sub>	121.705 149.322 134.035 158.297 180.114
Cd(L) <sub>2</sub>	120.992 149.603 134.036 150.297 187.329

#### D. Ultraviolet-visible Spectroscopy

The absorption spectra of the ligand (L) and its complexes were recorded in DMSO solvent within the range of 250–900 nm. The electronic spectra of (L) and its complexes are summarized in Table 5. The ligand's electronic spectra display three bands at 263, 302, and 309, corresponding to intraligand transitions ( $\pi$ - $\pi^*$ ), ( $\pi$ - $\pi^*$ ), and ( $n$ - $\pi^*$ ) electronic transitions, respectively. Complexes 1–5 also exhibit similar electronic transitions with shifts compared to the ligand (L).

For complexes 1 and 2, additional electronic transitions of metal d orbitals (d-d electronic transitions) were observed in the visible region for Ni(II) and Cu(II). In Ni(II), the d-d electronic transition appeared at 620 nm, assigned to the  $3\ T_1(F) \rightarrow 3\ T_1(P)$  and  $3\ T_1(F) \rightarrow 3A_2(F)$  transitions. For Cu(II), bands at 280, 300, 312, and 451 nm were attributed to ( $\pi$ - $\pi^*$ ), ( $n$ - $\pi^*$ ), charge transfer, and  $2\ T_2 \rightarrow 2E_2$  transitions, respectively. However, complexes 4, 5, and 6 were diamagnetic, as expected for d<sup>10</sup> ions, with no (d-d) transition expected in the visible region (Chohan, 2009).

TABLE V  
ELECTRONIC SPECTRA OF PREPARED COMPOUNDS

Complexes	Absorption Transition
L	263, 302, 309 ( $\pi-\pi^*$ ), ( $\pi-\pi^*$ ), ( $n-\pi^*$ )
Ni(L) <sub>2</sub>	262, , 610 ( $\pi-\pi^*$ ), 3 T1(F) $\rightarrow$ 3 T1(P)
Cu(L) <sub>2</sub>	280, 300, 312, 451 ( $\pi-\pi^*$ ), ( $n-\pi^*$ ), L $\rightarrow$ Cu(CT), 2 T2 $\rightarrow$ 2E2
Zn(L) <sub>2</sub>	264, 300, 310 ( $\pi-\pi^*$ ), ( $\pi-\pi^*$ ), ( $n-\pi^*$ )
Cd(L) <sub>2</sub>	262, 310 ( $\pi-\pi^*$ ), ( $n-\pi^*$ )
Sn(L) <sub>2</sub>	265, 310 ( $\pi-\pi^*$ ), ( $n-\pi^*$ )

Here (\*) symbol means the excited states

### E. Magnetic Susceptibility and Conductivity Measurements

Magnetic measurements are commonly used to study transition metal complexes, where the presence of unpaired electrons in the partially filled d-orbitals contributes to their magnetic properties. Complex 1 exhibited a magnetic moment value of 1.09 B.M., indicating paramagnetic. Complex 2, with a magnetic moment value of 0.7 B.M., is believed to have a copper (II) metal moiety with distorted square planar geometry (Win et al., 2011). Complexes 3–5 are diamagnetic, with no recorded magnetic moment in this study (Chohan, 2009).

Conductivity measurements were conducted on these complexes in ethanol solvent to determine if the solutions were electrolytes. Table 6 presents the molar conductivity measurements of complexes 1–5, revealing that all the prepared complexes are non-electrolytes (Majeed et al., 2010).

According to the spectral study, complexes 1–5 exhibit distorted tetrahedral geometry, except for complex 2, which has a distorted square planar structure (Foo et al., 2013). The proposed structures of complexes 1–5 are illustrated below (See Figure 6).

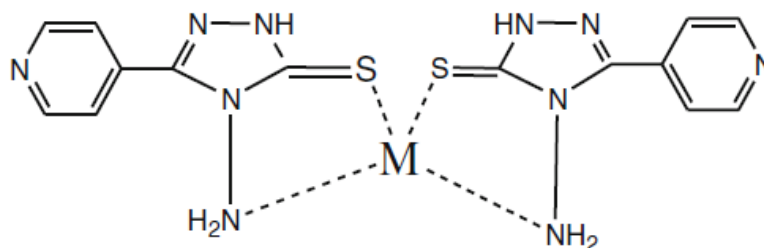


Fig. 6. The proposed structure of complexes 1–5

(Where M=Ni(II), Cu(II), Zn(II), Cd(II) and Sn(II))

TABLE VI  
CONDUCTIVITY MEASUREMENT AND MAGNETIC MOMENT OF LAND ITS COMPLEXES

Complexes	Conductivity ( $\mu\text{S}/\text{cm}$ )	Magnetic moment
L	-	-
Ni(L) <sub>2</sub>	3	1.09
Cu(L) <sub>2</sub>	1	0.7
Zn(L) <sub>2</sub>	3	4.0
Cd(L) <sub>2</sub>	2	2.0
Sn(L) <sub>2</sub>	1	12.0

## IV. CONCLUSION

The synthesis of the ligand 4-amino-5-(pyridyl)-4H-1,2,4-triazole-3-thiol was successful, and it was used to form complexes with various metal ions. The coordination of the ligand involved both amino and thiol groups, resulting in the creation of a five-membered ring chelate. The copper complex was suggested to have a square planar geometry, while the other complexes were proposed to exhibit a tetrahedral geometry.

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