Synthesis and Characterization of a Novel Azo-Dye Schiff Base and Its Metal Ion Complexes Based on 1,2,4-Triazole Derivatives

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Abstract: *The study focused on producing and examining the properties of the 2-(((3-mercapto-5-(4-nitrophenyl)-4*H*-1,2,4-triazol-4-yl)imino)methyl)-4-(((4-mercaptophenyl) diazenyl)phenol) ligand (L) and its complexes with three transition metal ions, namely Ni(II), Co(II), and Cu(II). The ligand was formed through diazotization and coupling reactions between 4-aminobenzenethiol and a coupling Schiff base derived from 1,2,4-triazole. The characterization of the ligand and its metal ion complexes was carried out using analytical techniques such as FTIR, ^{1}H- and ^{13}C-NMR, UV-visible spectroscopy, and thermal analysis (TGA and DTG). Various physical methods were employed to synthesize and analyze the properties of the three mononuclear Co(II), Ni(II), and Cu(II) complexes with the azo-dye Schiff's base ligand. Based on the microanalysis and spectroscopic results, it was determined that the coordination between the azo Schiff base ligand and the central metal ion occurred through the NOS-donating atoms of the ligand. The analysis of the electronic spectra revealed that the synthesized Co(II) and Ni(II) complexes exhibited an octahedral geometry, while the Cu(II) complex had a distorted octahedral geometry. The implications of the finding regarding the octahedral and distorted-octahedral geometries include expanding the structural diversity in coordination chemistry, providing insights into ligand-metal interactions, and understanding the influence of geometry on properties.*

Keywords: *azo-dye; Schiff base; metal ion complex; triazol*

■ INTRODUCTION

The field of coordination chemistry has captivated the interest of chemists and researchers due to its potential for the development of pharmaco-therapeutic fields [1]. Azo-Schiff bases could be created by combining azo-dyes and Schiff-bases with the azo-methine-C=N linkage [2]. The incorporation of two complex chromophores in one compound has been shown to enhance the biological and physicochemical properties of this versatile family of ligands and related metal complexes. There are many novel synthetic azo dyes, including 1,2,4-triazoles, which are particularly interesting for several reasons. The chemistry of 1,2,4-triazoles is complex and well-known, and they are stable substances [3]. The isolation of a variety of different macro-acyclic ligands has been made easier by the addition of 1,2,4-triazole compounds of transition metals with intriguing magnetic and electrochemical characteristics [4]. Azo compounds have been widely used for dyeing textile fibers, coloring various materials, and in biological-medical research, among other applications, making them the most commonly used class of dyes for many years [5].

In addition, Schiff bases are one of the most flexible and multidimensional classes of ligands [6]. Heterocyclic azo-dyes have been used as histological stains for anatomical research and as indicators in conventional analytical processes [3]. A –OH group increases the reactivity of Schiff bases substantially, especially when it is in the -*ortho* position. Bi-, tri-, and tetradentate metal complexes with a number of transition and inner-transition metals. In biological systems, Schiff bases with transport donor atoms of nitrogen, oxygen, or sulfur are important [7]. Due to their outstanding coordination potential and wide range of pharmacological effects, including antibacterial, antifungal, and anticancer activities, transition metal complexes with a 1,2,4-triazole substituted moiety have attracted a lot of attention [8-9]. We reported herein the syntheses and structural characterization of novel azo containing Schiff bases derivative ligand (2-(((3-mercapto-5-(4-nitrophenyl)-4*H*-1,2,4-triazol-4-yl)imino)methyl)-4-((4-mercaptophenyl)diazenyl)-6-methoxyphenol) (*L*) and its complexes with Co(II), Ni(II), and Cu(II) ions. The synthesized compounds have been characterized by Fourier-transform infrared spectroscopy (FTIR), proton- (^{1}H-NMR) and carbon-nuclear magnetic resonance (^{13}C-NMR), UV-vis spectroscopy, thermogravimetric analysis (TGA), and differential thermal analysis (DTA).

■ EXPERIMENTAL SECTION

Materials

Chemicals used in the research included *p*-nitrobenzoic acid (Fluka, Germany), sulfuric acid (H_2SO_4), absolute ethanol (C_2H_6O), methanol (CH_3OH), and dichloromethane (CH_2Cl_2) from Merck. Sodium bicarbonate ($NaHCO_3$, Fluka), anhydrous magnesium sulphate ($MgSO_4$, BDH), hydrazine hydrate (N_2H_4, 80%), and carbon disulphide (CS_2) were obtained from CDH. Potassium hydroxide (KOH), hydrochloric acid (HCl, 35%), and 2-hydroxy benzaldehyde were obtained from Merck. Sodium nitrate ($NaNO_3$, Fluka), *p*-aminothiophenol (Merck), cobalt acetate tetrahydrate ($(CH_3COO)_2Co{\cdot}4H_2O$), nickel acetate tetrahydrate ($Ni(OCOCH_3)_2{\cdot}4H_2O$), and copper acetate dihydrate ($C_4H_{10}CuO_6$) were obtained from BDH.

Instrumentation

The FTIR measurements of the prepared compounds were performed at 4000–400 cm^{-1} using a KBr disc with an 8400 FTIR Shimadzu spectrophotometer. The UV-vis spectra were measured on a UV-1700 Shimadzu spectrophotometer in the range of 300–800 nm. The thermal analysis of the ligand and complex was conducted by using TGA on DTG-60. The melting point was conducted using Stuart SMP30 (UK). The produced compounds were measured by NMR at 400 MHz (Germany) at Isfahan University of Technology (IUT, Iran).

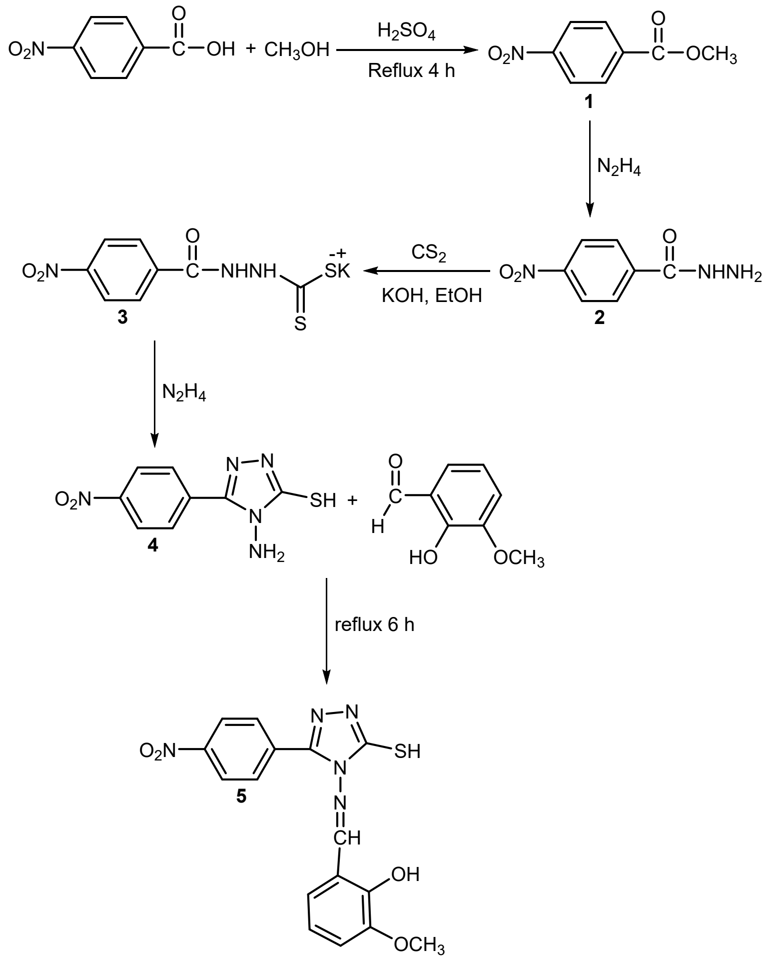
Procedure

Synthesis of methyl 4-nitrobenzoate compound (1)

In a 250 mL round bottom flask, 10 g (0.059 mol) of 4-nitrobenzoic acid was dissolved in 50 mL of methanol and added with 4 mL of concentrated sulfuric acid (Scheme 1). The reaction mixture was heated under a reflux for 6 h. After the reaction was finished, the extra alcohol was evaporated using a rotary evaporator. A separating funnel held 250 mL of water, and the residue was emptied. The separating funnel was filled with dichloromethane (20 mL), and the mixture was agitated briskly. The methyl 4-nitrobenzoate in the dichloromethane separated when the solution was let to stand and collected at the bottom of the separating funnel. The upper aqueous layer was excluded after the lower layer had been thoroughly removed. To eliminate all of the free acid, the methyl 4-nitrobenzoate was put back into the funnel and agitated with a strong sodium bicarbonate solution. In a little dry conical flask with 2 g of anhydrous magnesium sulphate, methyl 4-nitrobenzoate was dried after being rinsed with water once. Five minutes of shaking was followed by 1 h of standing. A small piece of fluted filter paper was used to funnel the methyl 4-nitrobenzoate solution into a distillation flask. The flask was equipped with a condenser, a 360-degree thermometer, and a receiving flask. The methyl 4-nitrobenzoate was extracted from the flask following the distillation of dichloromethane at 40 °C. For the recrystallization of the ester, ethanol was used as a solvent [10].

Synthesis of p*-nitrobenzohydrazide compound (2)*

The synthesized *p*-nitrobenzohydrazide as shown in Scheme 1 was prepared by dissolving methyl 4-nitrobenzoate (6 g, 0.023 mol) in 50 mL of ethanol and then hydrazine hydrate (80%, 22 mL) was added to the solution. The mixture was then heated through reflux for 10 h. Finally, after letting the mixture cool, a solid was extracted and then filtered, washed with ice water, dried, and then re-crystallized with ethanol [11].



Scheme 1. The synthesized scheme for Schiff base 5 in this work

Synthesis of potassium salt of hydrazide compound (3)

Absolute ethanol was used to dissolve KOH (4 g, 0.021 mol) and compound 2 (4 g, 0.021 mol) in 100 mL and the mixture was placed in an ice bath. Carbon disulfide (20 mL) was added dropwise and the reaction mixture was continually stirred for 6 h. Then, anhydrous ether was used to dilute it. After precipitation, the resulting potassium dithiocarbamate was isolated by filtration. The precipitate was washed with 100 mL of anhydrous ether and subsequently vacuum-dried. The obtained potassium salt was in quantitative yield and was not subjected to further purification as it was utilized in the subsequent step [12].

Synthesized of 3-mercapto-4-amino-5-(4′-nitrophenyl)-1,2,4-triazole (4)

A solution containing 3 g (0.01 mol) of compound 3 and excess hydrazine hydrate was refluxed for 30 min in 25 mL of water. As the reaction proceeded, hydrogen sulfide gas evolved, and the mixture turned green. A homogeneous reaction mixture was obtained throughout the process. After diluting the reaction mixture with 150 mL of water, it was cooled to room temperature. Upon acidification with hydrochloric acid, the necessary triazole precipitated out and was washed with cold water, then recrystallized from ethanol [13].

Synthesized of Schiff base of [1,2,4]-triazole-3-thiol derivative (5)

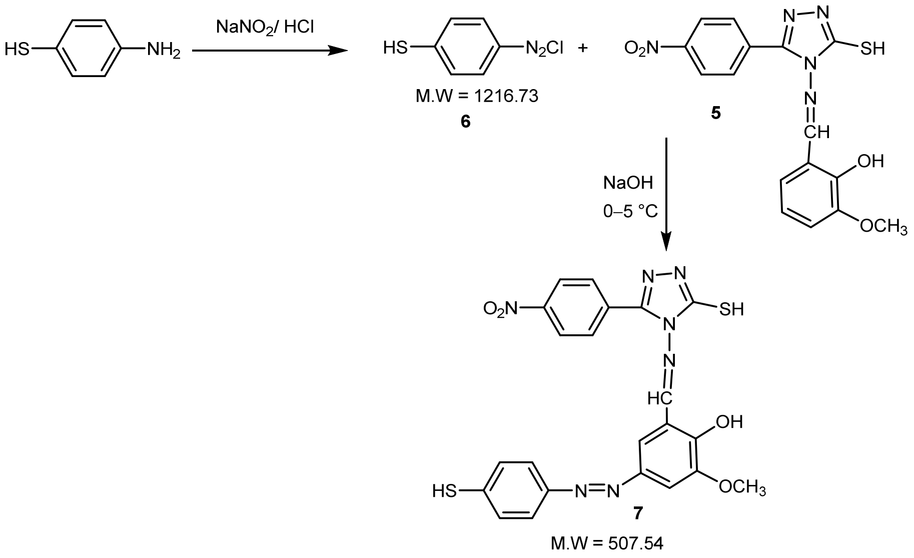
In 50 mL of absolute ethanol, 1.9 g (0.012 mmol) of 2-hydroxy-3-methoxybenzaldehyde was dissolved, and 3 g of (0.012 mol) compound 4 was added. The reaction mixture was refluxed for 6 h. The resulting solid was filtered, washed with cold ethanol, and recrystallized by ethanol [14].

Synthesized azo-dye Schiff base ligand (6)

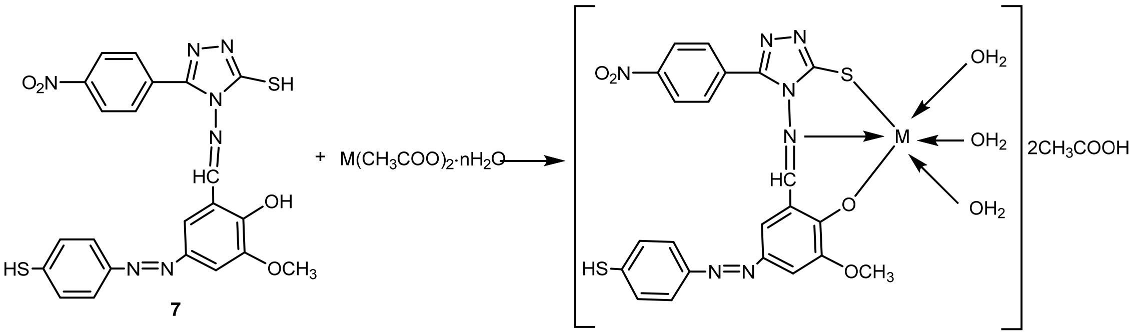
To a solution of *p*-aminothiophenol (1 g, 0.008 mol) in 10 mL water, concentrated hydrochloric acid (10 mL) was gradually added with stirring (Scheme 2). The clear solution was added to an ice water mixture that had been diazotized for 20 min at 0 to 5 °C with sodium nitrite (0.6 g, 0.008 mol) and 5 mL of water. During 30 min period at a temperature between 0–5 °C, the cold diazo solution was gradually added to a solution of the Schiff base compound (3 g, 0.008 mol) in water (50 mL) containing sodium hydroxide (1 g) and sodium carbonate (10 g). The reaction mixture was shaken for 1 h in an ice bath, the filtration was collected and recrystallized from ethanol with water [1,15].

Synthesized metal ion complexes (Co$_{(1)}$ to Co$_{(3)}$)

Metal ion complexes were synthesized by adding hot ethanolic metal ion solutions $M(CH_3COO)_2 \cdot nH_2O$ to a hot ethanolic ligand solution (0.50 g, 0.01 mol/L) at a 1:1 molar ratio of metal:ligand (Scheme 3). After refluxing for 3 h, colored precipitates formed, which were filtered and recrystallized using ethanol. Table 1 shows the metal salt quantities in the resulting complexes [16].



Scheme 2. The synthesized scheme for Schiff base 6



Scheme 3. The synthesized scheme for metal ion complexes

Table 1. Amount of metal salt quantities in the resulting complexes

Symbol compound	Suggested formula	Metal ion salts	Mass (g)
Co$_{(1)}$	$[Co(L)(H_2O)_3]_2CH_3COOH$	$Co(OAc)_2 \cdot 4H_2O$	0.245
Co$_{(2)}$	$[Ni(L)(H_2O)_3]_2CH_3COOH$	$Ni(OAc)_2 \cdot 4H_2O$	0.245
Co$_{(3)}$	$[Cu(L)(H_2O)_2]_2CH_3COOH$	$Cu(OAc)_2 \cdot 2H_2O$	0.196

■ RESULTS AND DISCUSSION

^{1}H-NMR for Azo-Dye Schiff Base (Ligand 6)

Fig. 1 displays the ^{1}H-NMR peaks of ligand (azo-dye Schiff base) in DMSO while Table 2 lists the peak assignments. Methyl protons were detected as a singlet peak at δ 3.8 ppm [17]. DMSO peak was found at 2.5 ppm. At 6.69–7.51 ppm, broad multiplets were found and identified as aromatic protons. Signals at 9.10, 10.28, and 3.70 ppm represented the CH=N proton, OH, S–H thiophenol and S–H tetrazole, respectively [18].

^{13}C-NMR Data for Ligand 6

The ^{13}C-NMR spectrum of azo dye-Schiff base is shown in Fig. 2. The spectral measurements from ^{13}C-NMR provided additional support for the synthesized ligand. In accordance with the findings from the chemical shift's spectrum, the L molecular structure can be seen in Table 3 [19].

FTIR Spectra of Ligand

To identify the active group of complexes, the KBr disc was used to compare the IR spectra of ligands with

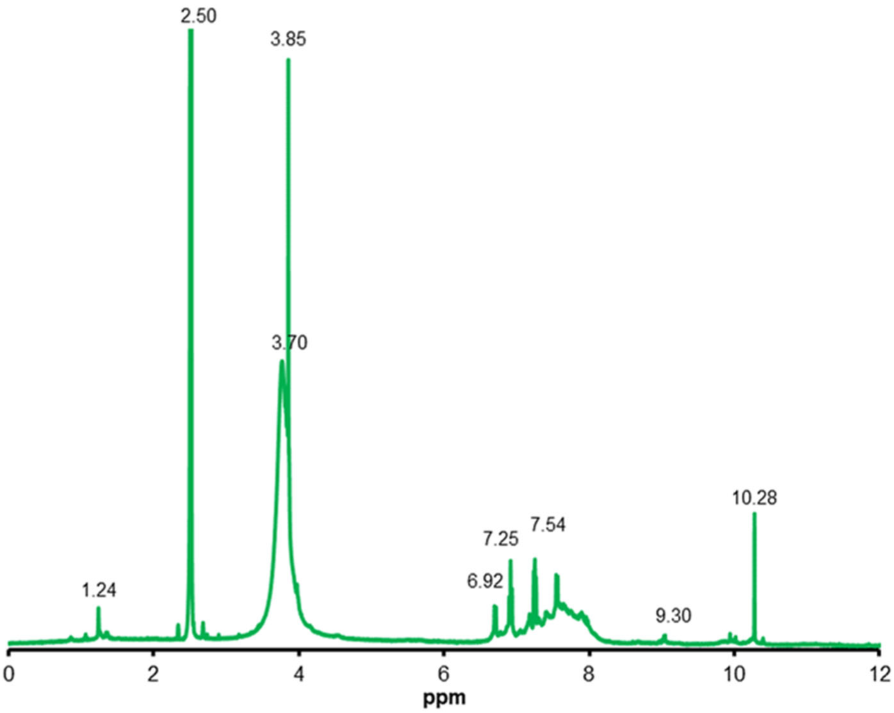


Fig 1. ^{1}H-NMR spectrum for ligand L

Table 2. ^{1}H-NMR data for ligand

Compound	Assignment ligand	Chemical shift
Ligand		δ DMSO (2.50 ppm) δ –OCH_3 (3.80 ppm) δ aromatic rings (6.69–7.51 ppm) δ CH=N (9.10 ppm) δ O–H (10.20 ppm) δ S–H (3.70 ppm)

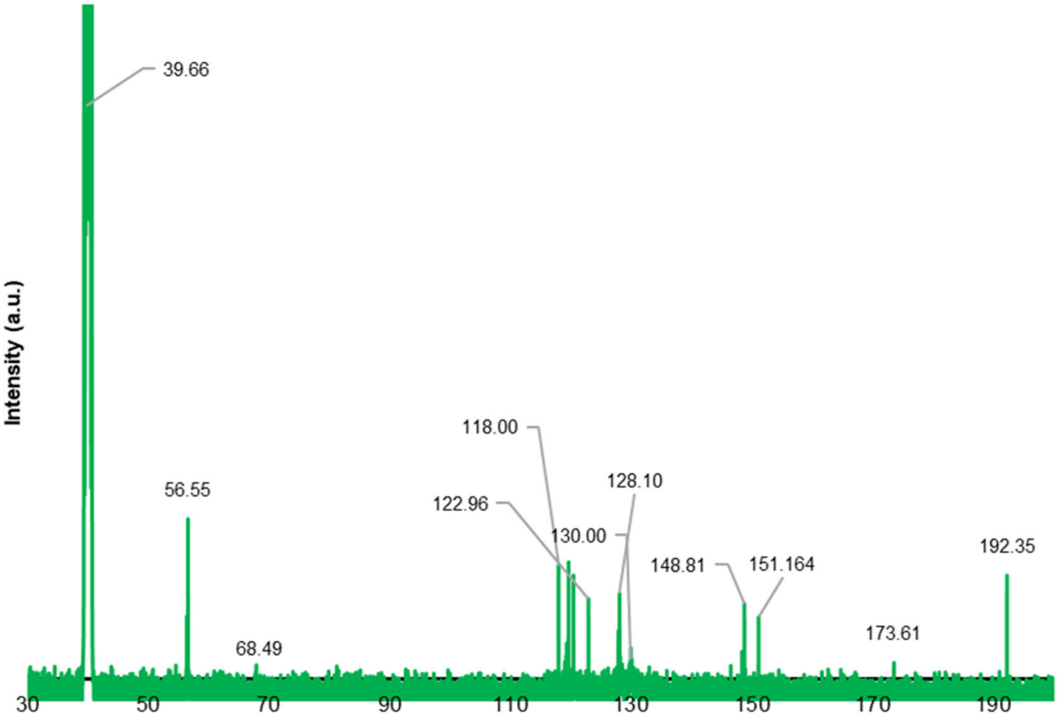


Fig 2. ^{13}C-NMR spectrum for ligand L

Table 3. ^{13}C-NMR data for ligand

Chemical shifts (ppm)	Assignments
118.12	C-aromatic
148.00	C–N=N
151.16	C=N tetrazole
130.00	C–SH thiophenol
173.00	C=N Schiff base
162.00	SH-tetrazole

their complex IR spectra in the range of 4000 to 400 cm^{-1}. This method was also used to identify the inorganic active site of the two ligands that bound to the metal ions at wave numbers between 4000 and 400 cm^{-1}. The FTIR spectra of the essential components used in synthesis must be mentioned before diving into the spectrum of the ligand L.

FTIR of 3-mercapto-4-amino-5-(4′-nitrophenyl)-1,2,4-triazole

The FTIR spectra of this compound are illustrated in Fig. 3 with two bands at 3275 and 3360 cm^{-1}, respectively, corresponding to the two weak bands of stretch asymmetric and symmetric NH_2 group. At 1090 and 2550 cm^{-1}, respectively, two medium-intensity bands are attributed to C=S and S–H vibrations [20].

FTIR spectra of Schiff base 5

Fig. 3 shows the FTIR spectrum of Schiff base compound, the band at 1640 cm^{-1} due to ν(C=N), the broad band corresponding to ν(O–H) and ν(CH_2) appearance at 2940 cm^{-1} [21].

FTIR spectra of azo-dye Schiff base (ligand 6)

The FTIR spectra for the ligand compound are listed in Table 4. Table 4 shows new bands observed and changes in intensity. The new band at 1480 cm^{-1} due to ν(N=N), 1643 cm^{-1} corresponding to ν(C=N) and ν(S–H) at 2550 cm^{-1}. Comparing the spectra of the free ligand L sites involved in chelation with their complexes makes it easy to determine the structure of the complexes. The imine group of the ligand in each complex shifted to a lower wavenumber due to the coordinated interaction between the ligand L imine group (C=N) and the metal via the nitrogen atom. The spectra of the complexes indicated the formation of stable five-membered chelate rings by coordinating

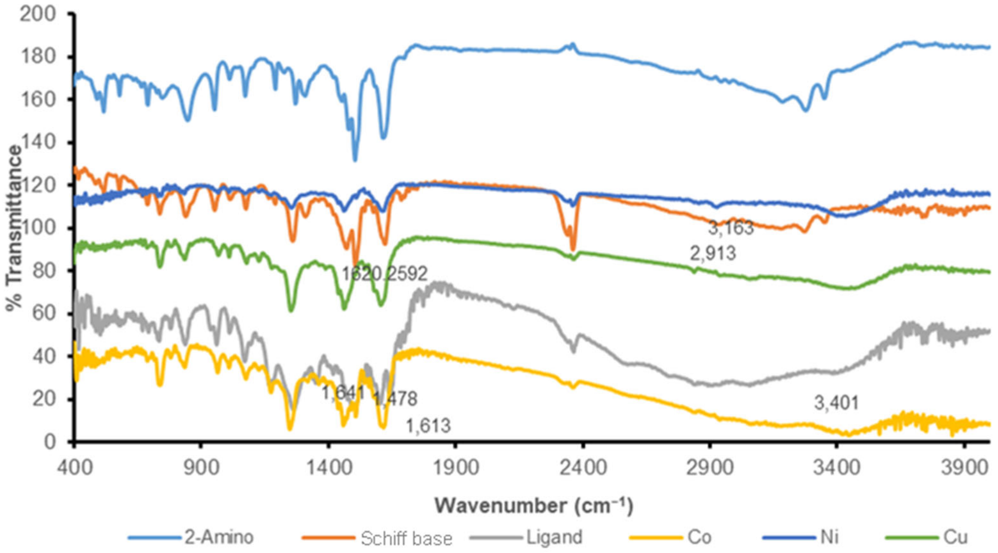


Fig 3. FTIR spectra for ligand and their metal ion complexes

Table 4. List the primary FTIR spectra of the ligand L and their complex

Compound	ν(NH_2) (cm^{-1})	ν(C=N) cyclic ν(C=N) (cm^{-1})	ν(OH) (cm^{-1})	ν(CH_2) (cm^{-1})	ν(SH) (cm^{-1})
1,2,4-triazole derivative	3275, 3260	1624			2550
Schiff base		1621 1640	3190	2940	2550
Azo-dye Schiff base (L)		1622 1643	3390	2950	2550
[Co(L)] complex		1620	3200		2545
[Ni(L)] complex		1612	3200		2540
[Cu(L)] complex		1612	3250		2543

metal ions with nitrogen atoms from imine groups, oxygen atoms from hydroxy groups, and sulfur atoms from thiol groups. However, they also displayed changes such as the transition to higher frequencies or the appearance of multiple bands with varying shapes and reduced intensities [22].

Electronic Spectra of Ligand and Their Metal Complexes

Two bands at 280 nm (35,714 cm^{-1}) and 320 nm (31,250 cm^{-1}) were identified in the UV-vis absorption spectrum of the ligand L in ethanol and were attributed to the n→π* and π→π* transitions shown in Fig. 4 and summarized in Table 5. Two spin-allowed bands in the visible range of the electronic spectrum of L1Co, show that peaks at 420 (15,337 cm^{-1}) and 595 nm (23,810 cm^{-1}) in Fig. 4 may correspond to the transitions $^4T_1g \rightarrow ^4A_2g_{(F)}$ (ν3) and $^4T_1g \rightarrow ^4T_1g_{(P)}$ (ν2), respectively. The bands' positions are consistent with those reported for an octahedral geometry. In Fig. 4, three bands at 15337, 21231, and 30769 cm^{-1}, corresponding to the $^3A_2g \rightarrow ^3T_2g$, $^3A_2g \rightarrow ^3T_1g_{(F)}$, and $^3A_2g \rightarrow ^3T_1g_{(P)}$ transitions, are visible in the electronic spectra of the Ni(II) complex. These bands suggest an octahedral geometry surrounding the Ni(II) ion, and the absence of the frequency at 20000 cm^{-1} indicates that the complex was excluded from the square planer. Additionally, a weak band that was observed at 9803 cm^{-1} may also suggest the presence of octahedral geometry in the complex. The spectra should be viewed similarly to how the spectra of the d4 ion and the 2D term of the free ion are predicted to divide in a crystal field. The LCu complex spectrum in DMF exhibits a

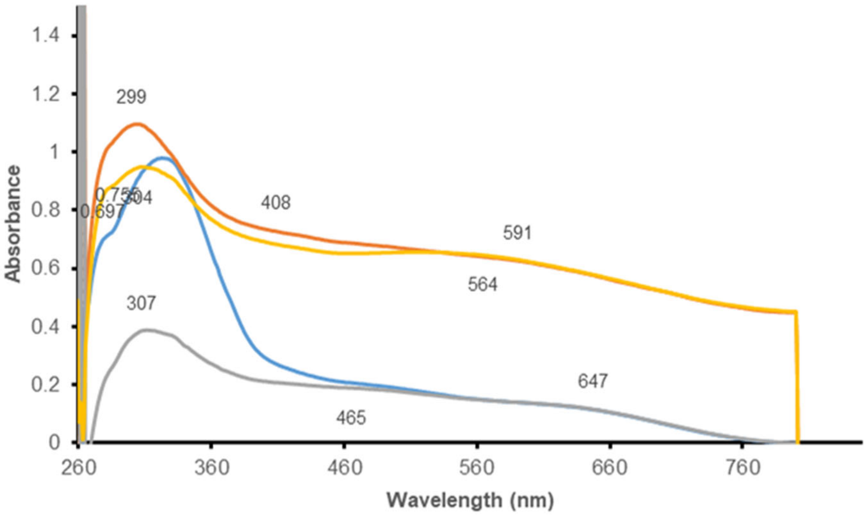


Fig 4. UV-vis spectra for ligand and their metal complex

Table 5. Electronic spectral data for ligand and their metal ion complexes

Compounds	Maximum absorption ν_{max} (cm^{-1})	Band assignment	Suggested geometry
Ligand	35,714	n→π*	-
	31,250	π→π*	
Co(L) complex	15,337	$^4T_1g \rightarrow {}^4A_2g_{(F)}$	Octahedral geometry
	23,810	$^4T_1g \rightarrow {}^4T_1g_{(P)}$	
Ni(L) complex	15,337	$^3A_2g \rightarrow {}^3T_2g$,	Octahedral geometry
	21,231	$^3A_2g \rightarrow {}^3T_1g_{(F)}$,	
	30,769	$^3A_2g \rightarrow {}^3T_1g_{(P)}$	
Cu(L) complex	18,518	$^2B_1g \rightarrow {}^2A_1g$	Distorted octahedral geometry
	30,303	$^2B_1g \rightarrow {}^2B_2g + {}^2Eg$	

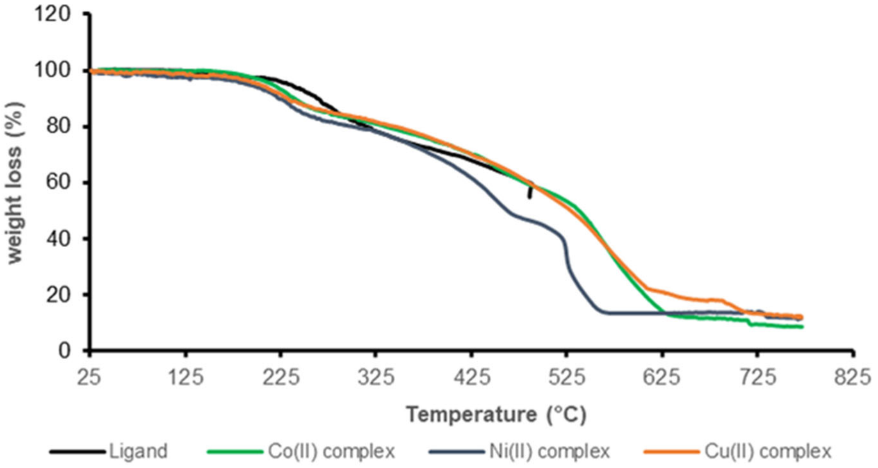


Fig 5. TG curves of the ligand and its metal ion complexes

broad band at (540 nm, 18,518 cm^{-1}), which corresponds to the $^2B_1g \rightarrow {}^2A_1g$ (ν1) transition and a shoulder band at (330 nm, 30,303 cm^{-1}) that corresponds to the $^2B_1g \rightarrow {}^2B_2g$ + ^2Eg (ν2) transitions. The position of these bands is consistent with highly distorted octahedral geometry [23-25].

Thermal Analysis

Fig. 5 and 6 show the thermal degradation process, TGA was conducted on both azo-linked Schiff base ligands and their metal complexes over a temperature range of 30–800 °C. Table 6 contains the thermal stability data. The findings from the TG study made it abundantly evident that the complexes decompose in four steps for the complexes of Co(II) and Ni(II), or three steps for the complex of Cu(II). Between 50 and 300 °C, water molecules were lost, and at temperatures above 600 °C, complexes of the elements Co(II), Ni(II), and Cu(II) formed metal oxides. Meanwhile, 600 °C was the temperature at which all compounds completely decomposed [26-27].

■ CONCLUSION

The study involved synthesizing a novel azo dye-Schiff base ligand and forming complexes with Co(II), Ni(II), and Cu(II) metals. The structures of these complexes were confirmed through various spectroscopic

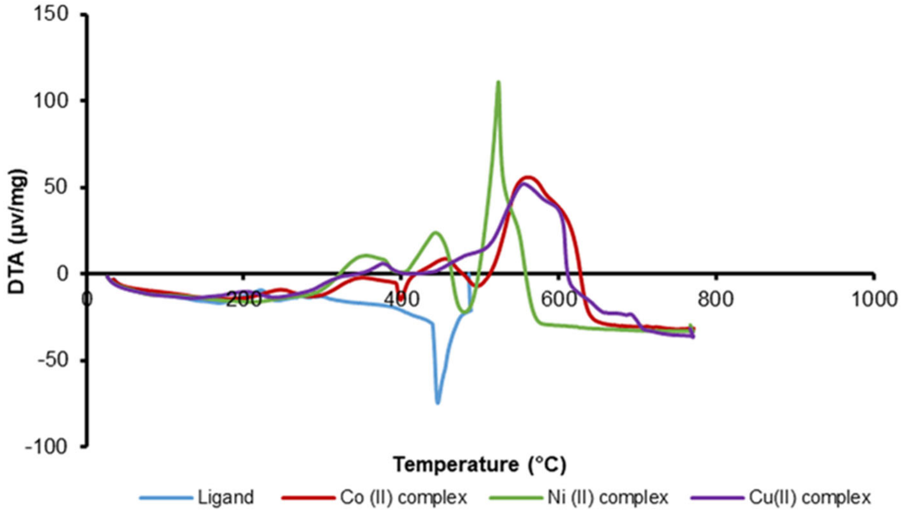


Fig 6. DTA curves of the ligand and its metal ion complexes

Table 6. Thermal decomposition TGA data for azo-dye (ligand) and their metal ion

Compound	Molecular formula	Molecular weight	Step	Temperature range of the decomposition (°C)	Mass (%)
Ligand (L)	$C_{22}H_{17}N_7O_4S_2$	507.54	1	33–409	30.705
			2	409–488	10.069
			3	488–498	5.166
				>500 (Residue)	
[Co(L)]	$[Co(C_{22}H_{17}N_7O_4S_2)(H_2O)_3]_2CH_3COOH$	740.57	1	33–320	17.990
			2	320–506	24.341
			3	506–630	45.000
			4	>630 (Residue)	
[Ni(L)]	$[Ni(C_{22}H_{17}N_7O_4S_2)(H_2O)_3]_2CH_3COOH$	740.57	1	38–306	27.081
			2	306–490	33.616
			3	490-568	32.029
			4	>570 (Residue)	
[Cu(L)]	$[Cu(C_{22}H_{17}N_7O_4S_2)(H_2O)_2]_2CH_3COOH$	727.04	1	33–305	15.875
			2	305-606	61.610
			3	606–766	10.051
			4	>770 (Residue)	

techniques such as FTIR, UV-vis, ^{1}H-NMR, ^{13}C-NMR, and TG-DTA. The metal ions in the complexes were bonded to the ligand via the azomethine nitrogen and thiol sulfur groups, forming five-membered chelate rings. The results indicated that the suggested structures of the complexes had an octahedral geometry. Furthermore, the thermal degradation profiles of metal complexes were examined using TG/DTA in an inert atmosphere. The major components of the $Co_{(1)}$ and $Co_{(2)}$ complexes were degraded in two phases, while those of the $Co_{(3)}$ complex were degraded in a single step. These results could be helpful in predicting organisms' biological activities and behavior. The findings provide a promising avenue for the discovery of new compounds with diverse and potentially valuable properties.

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■ AUTHOR CONTRIBUTIONS

Conceptualization: Nada Ahmed Rasheed Al-qasii, Ali Talib Bader, and Zaied Mosaa. Synthesis and data curation: Nada Ahmed Rasheed Al-qasii and Ali Talib Bader; measurements and assignment data analysis: Zaied Mosaa. The manuscript and the supporting information were written and reviewed with Nada Ahmed Rasheed Al-qasii and Ali Talib Bader. All authors have read and agreed to the published version of the manuscript.

■ REFERENCES

[1] İspir, E., 2009, The synthesis, characterization, electrochemical character, catalytic and antimicrobial activity of novel, azo-containing Schiff bases and their metal complexes, *Dyes Pigm.*, 82 (1), 13–19.

[2] Alghool, S., Abd El-Halim, H.F., and Dahshan, A., 2010, Synthesis, spectroscopic thermal and biological activity studies on azo-containing Schiff base dye and its cobalt(II), chromium(III) and strontium(II) complexes, *J. Mol. Struct.*, 983 (1-3), 32–38.

[3] Sancak, K., Er, M., Ünver, Y., Yildirim, M., Degirmencioglu, I., and Serbest, K., 2007, Cu(II), Ni(II) and Fe(II) complexes with a new substituted [1,2,4] triazole Schiff base derived from 4-amino-5-(thien-2-yl ethyl)-2,4-dihydro-3*H*-1,2,4-triazol-3-one and 2-hydroxy-1-naphthaldehyde: Synthesis, characterization and a comparison of theoretical and experimental results by *Ab initio* calculation, *Transition Met. Chem.*, 32 (1), 16–22.

[4] Klingele, M.H., Noble, A., Boyd, P.D.W., and Brooker, S., 2007, Synthesis and X-ray crystal structures of some mononuclear and dinuclear complexes of 4-isobutyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole, *Polyhedron*, 26 (2), 479–485.

[5] Gouda, M.A., Eldien, H.F., Girges, M.M., and Berghot, M.A., 2016, Synthesis and antitumor evaluation of thiophene based azo dyes incorporating pyrazolone moiety, *J. Saudi Chem. Soc.*, 20 (2), 151–157.

[6] Yaman, M., İpek Dirin, E., Kaplan, G., Seferoğlu, N., and Seferoğlu, Z., 2022, The synthesis, photophysical properties, DFT study and textile applications of fluorescent azo dyes bearing coumarin-thiazole, *J. Mol. Liq.*, 368, 120718.

[7] Kumari, S., Maddipoti, K., Das, B., and Ray, S., 2019, Palladium–Schiff base complexes encapsulated in zeolite-Y host: Functionality controlled by the structure of a guest complex, *Inorg. Chem.*, 58 (2), 1527–1540.

[8] Diaz-Ortiz, A., Prieto, P., Carrillo, J.R., Martin, R., and Torres, I., 2015, Applications of metal-free 1,2,4-triazole derivatives in materials science, *Curr. Org. Chem.*, 19 (7), 568–584.

[9] Bazhina, E.S., Bovkunova, A.A., Shmelev, M.A., Korlyukov, A.A., Pavlov, A.A., Hochvaldová, L., Kvítek, L., Panáček, A., Kopel, P., Eremenko, I., and Kiskin, M.A., 2023, Zinc(II) and copper(II) complexes with *N*-substituted imines derived from 4-amino-1,2,4-triazole: Synthesis, crystal structure, and biological activity, *Inorg. Chim. Acta*, 547, 121359.

[10] Bader, A.T., Al-qasii, N.A.R., Shntaif, A.H., El Marouani, M., Majidi, M.I.H.A., Trif, L., and

Boulhaoua, M., 2022, Synthesis, structural analysis and thermal behavior of new 1,2,4-triazole derivative and its transition metal complexes, *Indones. J. Chem.*, 22 (1), 223–232.

[11] Nonkuntod, P., Senawong, T., Soikum, C., Chaveerach, P., Watwiangkham, A., Suthirakun, S., and Chaveerach, U., 2022, Copper(II) compounds of 4-nitrobenzohydrazide with different anions (ClO_4^-, NO_3^- and Br^-): Synthesis, characterization, DFT calculations, DNA interactions and cytotoxic properties, *Chem. Biodiversity*, 19 (3), e202100708.

[12] Bader, A.T., Rasheed, N.A., Aljeboree, M., and Alkaiml, A.F., 2020, Synthesis, characterization of new 5-(4-nitrophenyl)-4-((4-phenoxybenzylidene) amino)-4*H*-1,2,4-triazole-3-thiol metal complexes and study of the antibacterial activity, *J. Phys.: Conf. Ser.*, 1664, 012100.

[13] Beyzaei, H., Ghanbari Kudeyani, M., Samareh Delarami, H., and Aryan, R., 2020, Synthesis, antimicrobial and antioxidant evaluation, and molecular docking study of 4,5-disubstituted 1,2,4-triazole-3-thiones, *J. Mol. Struct.*, 1215, 128273.

[14] Oderinlo, O.O., Jordaan, A., Seldon, R., Isaacs, M., Hoppe, H.C., Warner, D.F., Tukulula, M., and Khanye, S.D., 2023, Hydrazone-tethered 5-(pyridin-4-yl)-4*H*-1,2,4-triazole-3-thiol hybrids: Synthesis, characterisation, *in silico* ADME studies, and *in vitro* antimycobacterial evaluation and cytotoxicity, *ChemMedChem*, 18 (6), e202200572.

[15] Almáši, M., Vilková, M., and Bednarčík, J., 2021, Synthesis, characterization and spectral properties of novel azo-azomethine-tetracarboxylic Schiff base ligand and its Co(II), Ni(II), Cu(II) and Pd(II) complexes, *Inorg. Chim. Acta*, 515, 120064.

[16] Alothman, A.A., Albaqami, M.D., and Alshgari, R.A., 2021, Synthesis, spectral characterization, quantum chemical calculations, thermal studies and biological screening of nitrogen and oxygen donor atoms containing Azo-dye Cu(II), Ni(II) and Co(II) complexes, *J. Mol. Struct.*, 1223, 128984.

[17] Piegat, A., Goszczyńska, A., Idzik, T., and Niemczyk, A., 2019, The importance of reaction conditions on the chemical structure of *N*,*O*-acylated chitosan derivatives, *Molecules*, 24 (17), 3047.

[18] Hari, S., Swaroop, T.R., Preetham, H.D., Mohan, C.D., Muddegowda, U., Basappa, S., Sethi, G., and Rangappa, K.S., 2020, Synthesis, cytotoxic and heparanase inhibition studies of 5-oxo-1-arylpyrrolidine-3-carboxamides of hydrazides and 4-amino-5-aryl-4*H*-1,2,4-triazole-3-thiol, *Curr. Org. Synth.*, 17 (3), 243–250.

[19] Aggarwal, R., Hooda, M., Kumar, P., and Sumran, G., 2022, Vision on synthetic and medicinal facets of 1,2,4-triazolo[3,4-b][1,3,4]thiadiazine scaffold, *Top. Curr. Chem.*, 380 (2), 10.

[20] Panda, K.C., Ravi Kumar, B.V.V., and Sahoo, B.M., 2022, Microwave induced synthesis of 1,2,4-triazole derivatives and study of their anthelmintic and anti-microbial activities, *Res. J. Pharm. Technol.*, 15 (12), 5746–5750.

[21] Xie, W., Zhang, H., He, J., Zhang, J., Yu, Q., Luo, C., and Li, S., 2017, Synthesis and biological evaluation of novel hydroxybenzaldehyde-based kojic acid analogues as inhibitors of mushroom tyrosinase, *Bioorg. Med. Chem. Lett.*, 27 (3), 530–532.

[22] Pavia, D.L., Lampman, G.M., Kriz, G.S., and Vyvyan, J.A., 2014, Introduction to Spectroscopy, 5th Ed., Cengage Learning, Stamford, CT, US.

[23] de Araújo, E.L., Barbosa, H.F.G., Dockal, E.R., and Cavalheiro, É.T.G., 2017, Synthesis, characterization and biological activity of Cu(II), Ni(II) and Zn(II) complexes of biopolymeric Schiff bases of salicylaldehydes and chitosan, *Int. J. Biol. Macromol.*, 95, 168–176.

[24] Abdel-Rahman, L.H., Abu-Dief, A.M., Moustafa, H., and Hamdan, S.K., 2017, Ni(II) and Cu(II) complexes with ONNO asymmetric tetradentate Schiff base ligand: Synthesis, spectroscopic characterization, theoretical calculations, DNA interaction and antimicrobial studies, *Appl. Organomet. Chem.*, 31 (2), e3555.

[25] Retnam, C.T.G., Rose, S.V., and Kumari, B.S., 2023, Synthesis, characterization, biological activity and molecular docking study of transition metal

complexes from heterocyclic ligand system, *J. Mol. Struct.*, 1282, 135162.

[26] Al Zoubi, W., Al-Hamdani, A.A.S., and Ko, Y.G., 2017, Schiff bases and their complexes: Recent progress in thermal analysis, *Sep. Sci. Technol.*, 52 (6), 1052–1069.

[27] Kavitha, N., and Anantha Lakshmi, P.V., 2017, Synthesis, characterization and thermogravimetric analysis of Co(II), Ni(II), Cu(II) and Zn(II) complexes supported by ONNO tetradentate Schiff base ligand derived from hydrazino benzoxazine, *J. Saudi Chem. Soc.*, 21, S457–S466.