

Synthesis, Physical, Chemical and DFT Properties of Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes with Polydentate Schiff Base Derived from 1,2,4-Triazole

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Abstract: The work describes the synthesis and spectral investigation of cobalt(II), nickel(II), copper(II), and zinc(II) complexes with (E)-4-((4-nitrobenzylidene)amino)-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazole-3-thiol (L). The new ligand was synthesized through three steps, first the preparation of 3,4,5-trimethoxyphenylhydrazide salt, the ring closure of potassium hydrazide salt with excess of hydrazine hydrate followed by condensation of the derivative 4-amino-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazole-3-thiol with 4-nitrobenzaldehyde in glacial acetic acid. The physical and spectroscopic properties of the ligand and its complexes were well investigated and theoretically studied. The experimental results were compatible with their expected compositions. Based on the spectral data, metal complexes with coordination numbers 6 and 4 were proposed, with L functioning as a bidentate ligand. The metal complexes displayed an octahedral geometry around bivalent cobalt, nickel, and zinc tetrahedral environment. Density functional theory calculations (DFT) were conducted to investigate the geometry optimization of the synthesized ligand L and its Co(II) complex and to confirm the structure of the ligand by comparing its experimental vibrational and NMR spectra with the corresponding DFT calculated spectra. The DFT results revealed the participation of nitrogen and sulfur atoms of imine and thione groups in coordination with the metal ions beside the good agreement with the experimental data of elemental analyses and spectroscopic measurements.

Keywords: 1,2,4-triazole complexes; DFT study; polydentate ligand

■ INTRODUCTION

1,2,4-Triazole derivatives have attracted great attention in the last decade due to their unique properties [1]. The triazole ring is easily formed and many of these functionalized compounds are readily accessible, thus they are talented, rich, and flexible in coordination chemistry. The triazole rings contain π -conjugated systems with easy coordination abilities to metal ions, as well as their ability to exhibit phosphorescence properties.

The nitrogen atoms act as hydrogen bond acceptors and aromatic systems, which correspond to π - π stacking [2]. The 1,2,4-triazole moiety contains three atoms of nitrogen in a five-membered aromatic ring, each two atoms are adjacent which provides stability and high solubility in water. It is able to get two isomers of tautomerism, 1H-isomer, and 4H-isomer. The derivatives of 1,2,4-triazole have gained wide applications in coordination chemistry due to the

capacity of active sites of imine and thiol functional groups [1-3]. They exhibited a variety of bioactivities, such as an antimicrobial [4], antitubercular [5], anticancer [6], anticonvulsant [7], and anti-inflammatory agents [8].

It has been documented that Schiff bases, a significant class of organic compounds, have a broad spectrum of activities. Schiff base derived from 1,2,4-triazoles have highly significant biological activities such as anti-inflammatory, antibacterial, antioxidant, antifungal, anticancer, antimonial, and anticonvulsant [9]. Furthermore, the thiol-thione tautomers of 1,2,4-triazoles or 1,2,4 triazole derivatives based on thiol form are less frequent than Mannich bases-thiol form [10-11]. The ligand derived from bis(4-amino-5-mercapto-1,2,4-triazol-3-yl)alkanes are good tetradentate coordinators to the metal ions through sulfur and amine group [12].

The coordination behavior of a Schiff base with SNO donation sites, derived from 4-amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol and salicylaldehyde condensation, was studied against certain bi- and tri-valent metal ions, namely manganese(II), cobalt(II), copper(II), zinc(II), chromium(III), and iron(III). The chelates showed octahedral, trigonal bipyramidal, and tetrahedral structures [13]. Thus, these types of polydentate involving thione and imine functional groups that are complexed with 1,2,4-triazole ligands are called chelate complexes.

Recently, Schiff base ligands containing 1,2,4-triazole moiety showed remarkable physicochemical properties in medicinal chemistry. The diverse range of substituted triazoles has been established as optimistic scaffold in biology as well as material science [14]. The therapeutic importance of 1,2,4-triazole derivatives has been recognized as antibacterial, anticancer, antifungal, antituberculosis, antithyroid, antitumor, antimicrobial, antidiabetic, antioxidant, and anti-urease agents [14-15]. Herein, a novel Schiff base ligand derived from condensation of 4-amino-5-(3,4,5-trimethoxyphenyl)-4*H*-1,2,4-triazole-3-thiol with 4-nitrobenzaldehyde and its metal complexes of Co(II), Cu(II), Ni(II), and Zn(II) were synthesized and well characterized using NMR, FTIR, MS spectra, and C.H.N.S micro-elemental analyses.

■ EXPERIMENTAL SECTION

Materials

Chemicals such as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and ZnCl_2 were procured by Sigma-Aldrich and Fluka Companies. The 3,4,5-trimethoxybenzohydrazide was supplied from Santa Cruze Biotechnology Quaternary Group, Amman, Jordan (98% purity). Carbon disulfide, hydrazine hydrate (80% purity) and 4-nitrobenzaldehyde were supplied from Merck and used without purification.

Instrumentation

The ^1H - and ^{13}C -NMR spectra of A1, A2 derivatives, and the new Schiff base (L) were measured on a 400 MHz Bruker NMR spectrometer at Basra University, Iraq. The FTIR spectra of the prepared ligand and complexes were recorded in the 4000–400 cm^{-1} region using an IR Affinity-1-Shimadzu IR spectrometer at Chemistry Department, College of Science, Mustansiriyah University Baghdad, Iraq. The UV-visible spectra of the ligand and metal complexes solutions in absolute ethanol and DMSO solvents (0.001 M concentration) were carried out on 860-Shimadzu UV spectrometer. The micro-analyses (C.H.N.S) of the synthesized ligand and its complexes were determined using Vario ELV5 CHNS Elemental analyzer model 11086109, Germany. The molar conductivity of the complex solutions in DMSO was recorded on a WTW-740 conductivity meter apparatus with a platinum electrode as the working electrode at the instrumental analysis laboratory, Department of Chemistry, College of Science, Mustansiriyah University. The readings of magnetic susceptibility of the solid complexes were determined at room temperature on Sherewood Magnetic balance apparatus with the Pascal's constants for diamagnetic corrections at Chemistry Department, College of Science, Mustansiriyah University.

Computational Studies

Geometry optimization and vibrational analysis were carried out by performing the DFT calculations at

the B3LYP level of theory [16] with the 6-311+G(2d,p) basis set, utilizing the Gaussian 03 software package [17]. Additionally, the $^1\text{H-NMR}$ chemical shifts were calculated using the Gauge-Independent Atomic Orbital (GIAO) method [18] at the same level of theory in the gas phase, with TMS as the reference compound.

Procedure

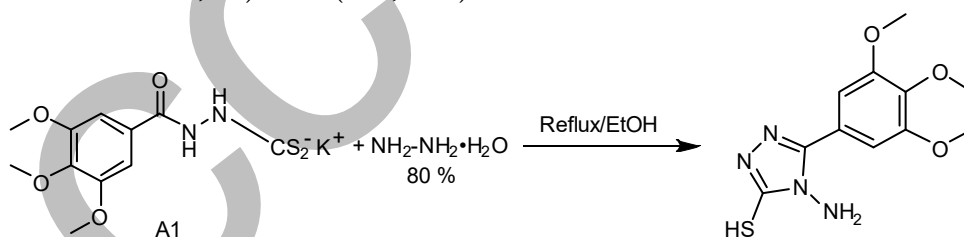
Synthesis of 4-amino-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazole-3-thione (A2)

The precursor of 1,2,4-triazole was prepared according to the previous method [14] with a modification. A mixture of potassium hydrazide salt, A1 (3.74 g, 0.011 mol) in excess amount of hydrazine hydrate (about 13 mL) was heated under reflux for 6 h. Color change of mixture from black green into light yellow due to the release of hydrogen sulfide by changing the $(\text{CH}_3\text{COO})_2\text{Pb}$ sheet from black to white. The reaction was controlled using thin-layer chromatography (TLC). The cooled mixture was poured into 15 mL ice-water and gradually acidified with 2 mL of 36.5% HCl to pH around 2–3. The off-white precipitate was filtered, washed with deionized water, and dried by air. The recrystallization from hot ethanol afforded grey crystal of A2 derivative as shown in Scheme 1. Yield 65%, m.p. 212–214 °C, M.wt 282.2 g/mol, $R_f = 0.66$ (ethylacetate:chloroform, 1:2). FTIR (KBr, cm^{-1}):

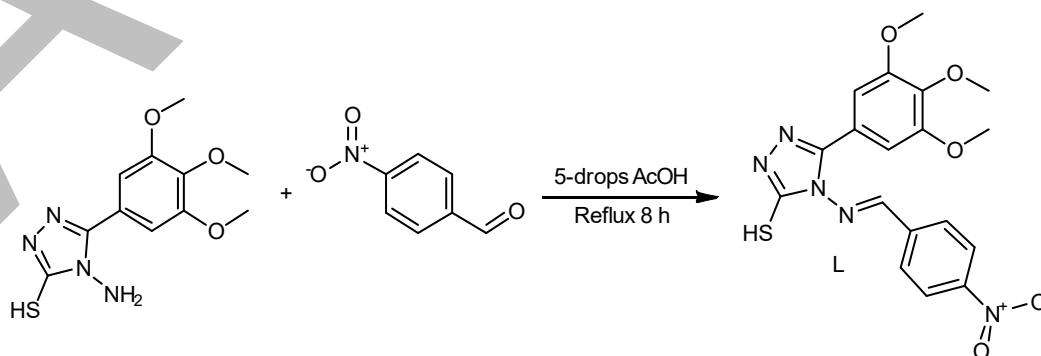
$\nu(\text{NH}_2)$ asym. and sym. (3200 and 3180), $\nu(\text{NH})$ (3100), $\nu(\text{S-H})$ (2690), $\nu(\text{C=S})$ (1095). $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ ppm): 10.45 (s, weak, SH), 7.46 (s, 2H, aromatic), 4.89 (s, broad, NH_2), 3.9 (s, 6H, 2OCH_3), and 3.8 (s, 3H, OCH_3). $^{13}\text{C-NMR}$ (100 MHz, DMSO) 56.60, 56.65, 60.64, 105.77, 121.43, 139.88, 153.28, and 167.09. MS (m/z): 282.0 [M^+].

Synthesis of the Schiff base (E)-2-(((3-mercapto-5-(3,4,5-trimethoxyphenyl)-4H-1,2,4-triazol-4-yl)imino)nitrobenzen) (L)

A solution of A2 derivative (2.82 g, 0.01 mol) in 25 mL hot absolute ethanol was added gradually with stirring to a solution of 4-nitrobenzaldehyde (1.51 g, 0.01 mol) in 25 mL hot absolute ethanol then 5 drops of glacial acetic acid was added and refluxed the mixture on heating for 10 h then allowed to settle the crude precipitate at room temperature for 30 min. A yellow-colored precipitate was filtered off, washed three times with ethanol and diethyl ether and dried in air and then in oven at 75–80 °C. Recrystallization from hot methanol afforded yellow crystals of ligand as shown in Scheme 2. Yield 88%, m.p. 228–230 °C, M.wt 415.10 g/mol, $R_f = 0.75$ (ethylacetate:chloroform, 1:2). FTIR (KBr, cm^{-1}): $\nu(\text{NO}_2^-)$ (1450), $\nu(\text{C=S})$ (1075), $\nu(\text{C=N})$ (1645). $^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$, δ ppm): 10.55 (s, 1H, NH),



Scheme 1. Preparation of A2 derivative



Scheme 2. Preparation of Schiff base L

9.79 (s, 1H, CH=N), 7.10 (s, 2H, aromatic), 6.75 (d, 1H, aromatic), 7.45 (d, 1H, aromatic), 6.95 (d, 2H, aromatic), 7.66 (d, 2H, aromatic), 3.83 (s, 6H, 2OCH₃), and 3.75 (s, 3H, OCH₃).

Synthesis of the solid metal complexes

The metallic complexes of L were synthesized by mixing 0.410 g of L (1 mmol) in 20 mL hot solution of methanol with a solution of CuCl₂·2H₂O (0.171 g, 1 mmol) in 10 mL ethanol. The mixture was stirred in water bath at 70–80 °C for about 30 min and allowed to cool at room temperature to get an olive precipitate of [CuLCl₂(H₂O)₂].H₂O complex. Similarly, the complexes of cobalt(II), nickel(II), and zinc(II) were isolated under heated reflux for 2–3 h.

RESULTS AND DISCUSSION

Physical Properties and Elemental Analysis

Table 1 shows the molecular formula of the prepared ligand with its metal complexes and their results of elemental micro-analyses. The observed C.H.N.S data were in good agreement with the calculated data which supported the predicted chemical structure. FAAS data approved the expected metal contents and confirmed the chemical formula with 1:1 mol ratio. All the metal complexes were stable in air and had higher melting points compared with the free L. All the metal complexes were insoluble in common organic solvents. However,

they were sparingly soluble in hot methanol, acetonitrile, DMSO, and DMF solvents. The molar conductivity of complexes in DMSO solvent showed low values in the region 15–22 ohm⁻¹ cm² mol⁻¹ confirming no counter ion of chloride in the structure of all the synthesized metal complexes then they behave as neutral complexes [14,19].

The mass spectrum of the A1, A2, L, and CoL complexes are represented in Fig. S1. The A1 showed molecular ion at 340 corresponding to its chemical formula and expected molecular weight. The molecular ion (*m/z*) of 282.2 for the A2 derivative, confirmed the ring closure of excess hydrazine hydrate with A1. The mass spectrum of L showed a high intensity peak at *m/z* of 415 in good agreement with its molecular weight and chemical formula (C₁₈H₁₇N₅O₅S). The mass fragmentations of methoxy moieties resulted in peaks at 368 and 331, whereas the peaks at 390 and 385 may be attributed to cleavage of HS and –NO₂ groups, respectively.

The molecular weight of cobalt(II) complex is confirmed with the help of mass spectrum. The molecular ion (*m/z*) of 582 and 581 are remarkably associated with the suggested chemical formula of [CoL(H₂O)₂Cl₂], which supports the coordination of one mole of L to one mole of cobalt(II) chloride hexahydrate besides the presence of water molecules.

Table 1. Analytical data of the ligand L1 and its metal complexes C1-C4

No.	General formula	M.Wt (g/mol)	Micro elemental analysis - Found (calc.)				Metal content – Found (calc.)
		Chemical formula	C%	N%	H%	S%	
A	A2	282.2	(46.80)	(19.85)	(5.00)	(11.36)	-
		C ₁₁ H ₁₄ N ₄ O ₃ S	45.55	19.23	4.56	11.89	
L	L	415.10	(52.04)	(16.86)	(4.12)	(7.72)	-
		C ₁₈ H ₁₇ N ₅ O ₅ S	51.66	15.50	3.38	7.02	
C1	[Co(L)(H ₂ O) ₂ Cl ₂]	582.35	(37.23)	(12.05)	(3.69)	(5.50)	(10.12)
		C ₁₈ H ₂₁ Cl ₂ CoN ₅ O ₇ S	36.66	12.22	3.450	5.33	9.74
C2	[Ni(L)(H ₂ O) ₂ Cl ₂]	580.97	(37.35)	(12.16)	(3.62)	(5.60)	(10.23)
		C ₁₈ H ₂₁ Cl ₂ N ₅ NiO ₇ S	37.25	13.00	3.02	5.07	9.75
C3	[Cu(L)Cl ₂ (H ₂ O) ₂]	603.1	(36.90)	(11.95)	(3.62)	(5.47)	(10.06)
		C ₁₈ H ₂₃ Cl ₂ CuN ₅ O ₈ S	35.88	12.22	2.99	5.11	9.01
C4	[Zn(L)Cl ₂]	551.35	(39.22)	(12.71)	(3.10)	(8.79)	(11.80)
		C ₁₈ H ₁₇ Cl ₂ N ₅ O ₅ SZn	40.37	13.22	2.89	8.04	11.22

FTIR Spectra

FTIR spectra of the newly synthesized ligand as well as its all the metal complexes were recorded in the range 4000–400 cm^{-1} are presented in Fig. S2. A1 formed upon the addition reaction of carbon disulfide solution in potassium hydroxide 0.01 M to 3,4,5-trimethoxybenzoic hydrazide showed strong absorptions at 1672, 1647, and 1257 cm^{-1} which were consistent with stretching frequencies of carbonyl of HN-C=O moiety and thiol moiety of $-\text{CS}_2\text{-K}^+$. The formation of the ligand was confirmed by the FTIR spectra, which strong absorptions at around 1649, 1582, and 1396 cm^{-1} assigned to HC=N , C=N (triazole ring), and C-N moieties, respectively [18–19]. These results confirmed a successful condensation of the amine group of the ligand. The stretching mode at 2755 cm^{-1} was observed due to the thiol (S-H) group of L. This spectral data has also confirmed a successful coordination of the metal ion and the ligand. For metal complexes, the band value of HC=N shifted downwards by 15 to 30 cm^{-1} referring to the bonding of ligand to metal *via* N atom of azomethine group [20]. Also, the disappearance of the band at 2755 cm^{-1} in the spectra of metal complexes and the appearance of the new band in the range of 404–410 cm^{-1} ascertained the bonding *via* S atom of thiol and formation of M-S bond in the metal complexes [21]. The presence of peak at 825–832 cm^{-1} showed the coordinated water molecules in the coordination sphere of metal complexes except for $\text{Cu}(1:2)$ and $\text{Pd}(1:2)$. Broad absorption in 3362–3387 cm^{-1} range was assigned to $\text{H}_2\text{O}/\text{OH}$ and appearance of a new band in the range 475–487 cm^{-1} evinced the metal–N bonding in the metal complexes [22].

NMR Spectra

The ^1H - and ^{13}C -NMR data of A1, A2, and L are presented in Fig. S3. The ^1H -NMR of A1 displayed small intensity peaks at 9.73 and 10.33 ppm assigned to the nuclear spin of amide proton $\text{H}_2\text{N-HN-C=O}$, which linked directly to CS_2^- moiety of potassium hydrazide salt. The absorptions located at 3.63–4.02 ppm were resulted from nuclear spin of aliphatic methoxy groups ($-\text{OCH}_3$) at C3, C4 and C5 of aromatic ring. The aromatic protons were resonated at 7.05–7.22 ppm [12,15]. The A2

derivative formed from the ring closure of A1 with hydrazine hydrate showed peaks at 11.85, 9.50, and 5.72 ppm which are associated with S-H , HN-C=S , and NH_2 protons of 1,2,4-triazole derivative. The peak appeared at around 3.61–4.02 ppm and 7.10–7.32 ppm assigned to $-\text{OCH}_3$ and aromatic (Ar-H) protons, respectively. The absorptions at 167–165 ppm and 153.87–153.21 ppm of A2 confirmed the formation of 1,2,4-triazole ring with $-\text{C=N-}$ and $-\text{C-SH}$ moieties respectively. The aromatic carbon atoms of 3,4,5-trimethoxy phenyl were resonated at around 141.53, 139.75, 125.63, 121.35, and 117.98 ppm, respectively, and aliphatic carbon atoms of the three OCH_3 groups were resonated at 56.60 and 60.63 ppm which confirmed A2 structure [22]. In addition, a singlet peak at 13.90 ppm corresponded to thiol proton (triazole-SH) [18] and a sharp distinct singlet at 8.39 ppm was due to the proton of the azomethine ($-\text{CH=N-}$). The doublet of doublet seen in the region 7.79–7.33 ppm may be designated to the 1,4-disubstituted aromatic protons in the ^1H -NMR spectrum of L [21,23]. The singlet peaks observed at 3.56–4.05 ppm were due to the protons of methoxy groups present in C3, C4, and C5 of the phenyl ring attached at C3 of triazole ring.

The ^{13}C -NMR spectrum of L in $\text{DMSO-}d_6$ solvent displayed absorptions at 166.87, 165.48, 153.87–153.21, and 149.62 ppm, which assigned to the nuclear spin of C-S , C=N (triazole ring), and CH=N isomethine moiety, respectively. Furthermore, the absorptions located at 141.53, 139.75, 125.63, 121.35, and 117.98 ppm were associated with aromatic carbon atoms of 4-nitrophenyl, whereas the absorptions at 106.21, 105.82, and 103.78 ppm were attributed to the aromatic carbon of 3,4,5-trimethoxyphenyl ring. However, the nuclear spin of OCH_3 moiety observed at 60.63 and 56.60 ppm was consistent well with the predicted structure of the prepared ligand.

Electronic and Magnetic Studies

The electronic spectra of ligand and its complexes are summarized in Table 2. The electronic spectra of metal complexes supported the geometries of the metal in the synthesized complexes. At room temperature,

UV-vis spectra were recorded for all the complexes along with L in their respective DMF solutions in the range of 250–800 nm. The yellow solution of L in absolute ethanol exhibited three absorption bands, two bands at 210 (47619 cm⁻¹) and 252 nm (39682 cm⁻¹) were assigned to $\pi\text{-}\pi^*$ transition and a band at 335 nm (29850 cm⁻¹) assigned to $n\text{-}\pi^*$ transition [20]. Some variation between these absorptions was noted in complexes, which indicated successful mixing of ligand with metal chlorides.

The olive solution of CoL in DMF displayed weak intense bands in the regions 728 (13736 cm⁻¹), 675 (14814 cm⁻¹), and 520 nm (19230 cm⁻¹) which are attributed to the transition ${}^4T_{1g}\rightarrow{}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}\rightarrow{}^4A_{2g}(F)$ (ν_2), and ${}^4T_{1g}\rightarrow{}^4T_{1g}(P)$ (ν_3), respectively. The strong absorptions at around 390 (25641 cm⁻¹) and 284 nm (35211 cm⁻¹) are assigned to charge-transfer (CT) and $\pi\text{-}\pi^*$ transition, respectively. The three spin-allowed transitions in the visible region for CoL investigate the high-spin octahedral of CoL with ground term 4F , which mainly splits to three microstates from the stable ground ${}^4T_{1g}(F)$, therefore the application of Tanabe-Sugano (T-S) diagram leads to intercepts γ_1, γ_2 at $E_1/B', E_2/B'$ to provide Racah parameter (B') which was found to be 650 cm⁻¹ and

the crystal field splitting energy 10Dq found to be 13,500 cm⁻¹, indicating the high spin octahedral environment around Co(II) ion [22-23]. The covalence parameter (β) was calculated and found to be 0.72 indicating the high degree of interaction between s, p and d -orbitals of ligand and metal ions with synergetic effect, hence inter electronic repulsion has been decreased during the process of chelation.

The green solution of NiL complex in DMF showed three spin-allowed transitions at around 789 (12674 cm⁻¹), 694 (14409 cm⁻¹), and 549 nm (18214 cm⁻¹) which are associated with ${}^3A_{2g}\rightarrow{}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2), and ${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$ (ν_3) transitions, respectively. The application of T-S diagram on UV-visible spectrum of C2 through the ratio ν_2/ν_1 found to be 1.23 which results in the values of γ_1, γ_2, x_1 intercepts at $E_1/B', E_2/B'$ and Dq/B' was found to be 22, 18, and 23, respectively. The calculation refer B' equal to 695 cm⁻¹ and 10Dq equal to 15,300 cm⁻¹ indicating octahedral environment around nickel(II) ion [23-24]. Electron-electron repulsion in d^8 configuration was decreased through overlapping with thione (C=S) and imine (C=N) groups, this was confirmed from nephelauxetic effect found to be 0.70.

Table 2. Electronic spectra of ligand and its complexes

Symbol	Bands, λ nm (cm ⁻¹)	Band assignment	Geometry	Molar conductivity (S/mol)	Magnetic moment, μ (BM)
L	210 (47619)	$\pi\rightarrow\pi^*$	-	-	-
	252 (39682)	$\pi\rightarrow\pi^*$			
	335 (29850)	$n\rightarrow\pi^*$			
C1	728 (13736)	${}^4T_{1g}\rightarrow{}^4T_{2g}(F)$	Octahedral	22	4.65
	675 (14804)	${}^4T_{1g}\rightarrow{}^4A_{2g}(F)$			
	520 (19230)	${}^4T_{1g}\rightarrow{}^4T_{1g}(P)$			
	390 (25641)	CT			
C2	789, (12674)	${}^3A_{2g}\rightarrow{}^3T_{2g}(F)$	Octahedral	18	2.83
	694 (14409)	${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$			
	549(18215)	${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$			
	380 (26500)	CT			
C3	585 (17094)	${}^2E_g\rightarrow{}^2T_{2g}$	Distorted octahedral	17	1.73
	350 (28571)	CT			
	287 (34843)	$\pi\rightarrow\pi^*$			
	351 (28490)	$Cl\rightarrow Zn^{2+}$			
C4	339 (29498)	$n\rightarrow\pi^*$	Tetrahedral	15	0.00
	289 (34602)	$\pi\rightarrow\pi^*$			

The solid NiL complex recorded effective magnetic moment of 3.45 BM which is associated with the two unpaired electrons (t_{2g}^6, e_g^2) being greater than the spin-only value (2.83 BM) and in good agreement of its octahedral geometry with orbital contribution to the magnetic moment.

The greenish-yellow solution CuL in DMF showed one weak shoulder band at 585 nm ($17,094\text{ cm}^{-1}$) which is ascribed to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, as well as the high intense peaks at 350 ($28,571\text{ cm}^{-1}$) and 287 nm ($34,843\text{ cm}^{-1}$) are assigned to CT and $\pi-\pi^*$ bands, respectively. The Cu(II) ion with the electronic configuration d^9 has one unpaired electron in the $3d$ -orbital. Therefore, its spin-only magnetic moment value should be 1.73 B.M. However, the C3 complex at room temperature recorded an effective magnetic moment value of 1.88 BM, indicating the z-out elongation with octahedral geometry [25-26].

The Zn(II) complex having a d^{10} configuration favors the formation of complexes with tetrahedral geometry. The electronic spectrum of C4 displayed three high intensity bands at 351 (28490 cm^{-1}), 339 (29498 cm^{-1}), and 289 nm (34602 cm^{-1}) assigning to $Cl \rightarrow Zn^{2+}$ and $\pi-\pi^*$ transitions, respectively [27].

Geometry Optimization

The potential energy surface (PES) scan and the fully optimized structure, complete with atom numbering, is depicted in Fig. 1. Conformational analysis was carried out to determine the most stable conformer of the ligand

L. The PES scan involved varying the dihedral angles N7-C1-C8-C9 and C4-N6-N31-C32 from 0° to 360° in increments of 24° . This process resulted in the generation of 256 conformers for the ligand L.

The most stable conformation of the ligand L underwent geometry optimization through DFT calculations at the B3LYP/6-311+G(2d,p) level of theory. A summary of selected bond distances and bond angles is provided in Table 3. Notably, the C32=N31 bond exhibited a length of 1.2967 \AA , indicating a double bond character between the C and N atoms [28]. Furthermore, the 1,2,4-triazole-3-thione group displayed an *E* conformation relative to the C32=N31 bond, while the β -nitrogen was *cis* to the thioketone sulfur in relation to the C4-N6 bond. The ligand was found to exist in the thione tautomeric form, and the near planarity of its atoms, except for the trimethoxyphenyl ring, suggested the presence of electron delocalization within the ligand. Additionally, the calculated bond lengths and bond angles fell within typical ranges, aligning with similar structures reported in the literature [29].

To represent the prepared complexes, geometry optimization of the CoL was conducted through DFT calculations at the B3LYP/LANL2DZ level of theory. The fully optimized structure, complete with atom numbering, is illustrated in Fig. 2. The ligand L is coordinated to the Co(II) metal ion via the azomethine nitrogen (N31) and the thioketone sulfur (S5) atoms. The Co(II) metal atom adopted a distorted octahedral

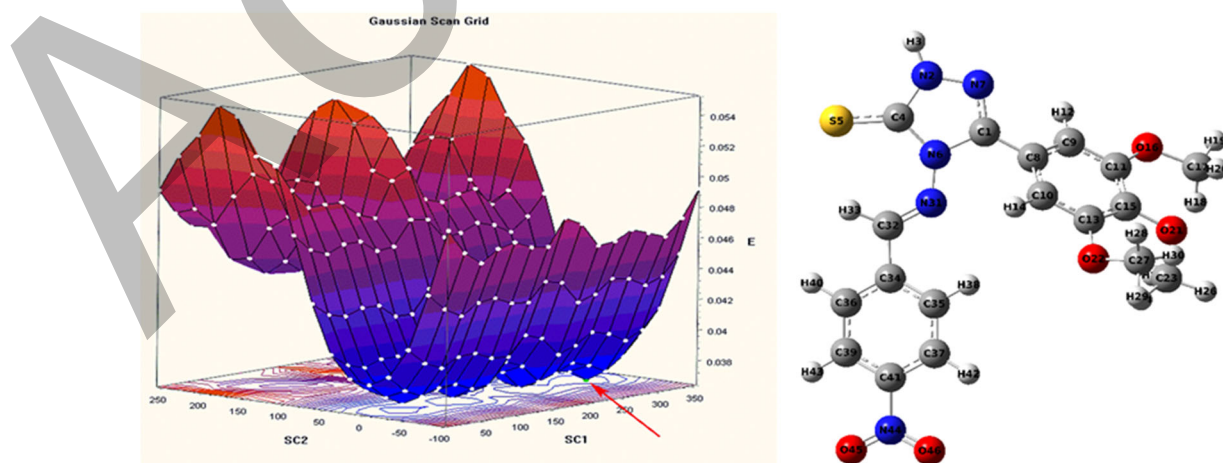
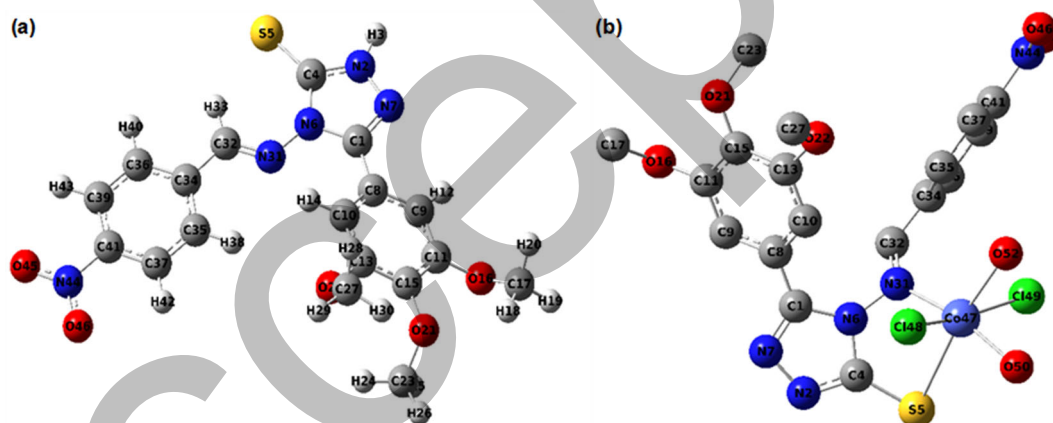


Fig 1. The potential energy surface (PES) scan (a) and the initial optimized structure (b) of the ligand L

Table 3. Selected bond distances (Å), angles (°), and natural charges (e) for the ligand L and its Co(II) complex

Bond distances (Å)			Angles (°)			Natural charges (e)		
	L	Co(II) complex		L	Co(II) complex		Co(II) complex	
Co-S5	-	2.8172	N31-Co-S5	-	79.10	C1	0.3228	0.1394
Co-N31	-	2.0222	N31-Co-Cl48	-	90.89	N2	-0.5435	-0.3280
Co-Cl48	-	2.3621	N31-Co-Cl49	-	95.41	C4	0.2784	-0.1396
Co-Cl49	-	2.3769	N31-Co-O52	-	108.52	N6	-0.6421	-0.1730
Co-O50	-	1.9795	S5-Co-Cl48	-	96.25	N7	-0.1613	-0.0215
Co-O52	-	2.2011	S5-Co-Cl49	-	96.50	C8	0.0595	0.4475
C1-N6	1.4149	1.4130	S5-Co-O50	-	88.43	C32	0.0195	-0.1971
C1-N7	1.3196	1.3290	O50-Co-O52	-	83.99	N31	-0.1542	-0.0878
C4-N6	1.4110	1.3986	N6-C1-N7	109.75	109.24	S5	-0.0652	0.0741
C4-N2	1.3591	1.3712	C1-N6-C4	108.63	109.80	Co47	-	0.1907
N2-N7	1.3889	1.4037	N2-C4-N6	102.07	102.02	Cl48	-	-0.4116
C4-S5	1.7148	1.7104	C4-N2-N7	114.68	113.98	Cl49	-	-0.4138
N6-N31	1.3840	1.4207	C1-N7-N2	104.86	104.77	O50	-	-0.6433
C32-N31	1.2967	1.3098	C1-N6-N31	119.62	128.90	O52	-	-0.6746
-	-	-	N6-N31-C32	122.09	113.41	-	-	-
-	-	-	N31-C32-C34	119.22	124.28	-	-	-

**Fig 2.** Optimized structures of the (a) ligand L and its (b) Co(II) complex, H atoms were omitted in (b) for clarity

geometry, with bond angles falling between 79.10° to 96.25° . Notably, the charge on the Co(II) atom was found to be $+0.191e$, which was a reduction from the formal charge of $+2$. This decrease in charge was attributed to electron-density acceptance from the ligand's donating atoms.

Structural Characterization

To validate the structure of the newly synthesized ligand, its experimental FTIR and NMR spectra were compared to the corresponding calculated spectra. The experimental FTIR spectrum was aligned with the

corresponding calculated spectrum in a gas phase using the B3LYP/6-311+G(2d,p) level of theory as presented in Fig. 3. An overall good agreement was observed between the observed and calculated spectra, with particularly strong alignment in the lower wavelength regions. However, in the higher wavelength region ($4000\text{--}2000\text{ cm}^{-1}$), the predicted frequencies were computed at higher wavenumbers than the observed frequencies. This discrepancy in the higher wavelength region can be attributed to several factors, including the treatment of electron correlation, anharmonicity effects, limitations in the basis set, and the absence of considerations for

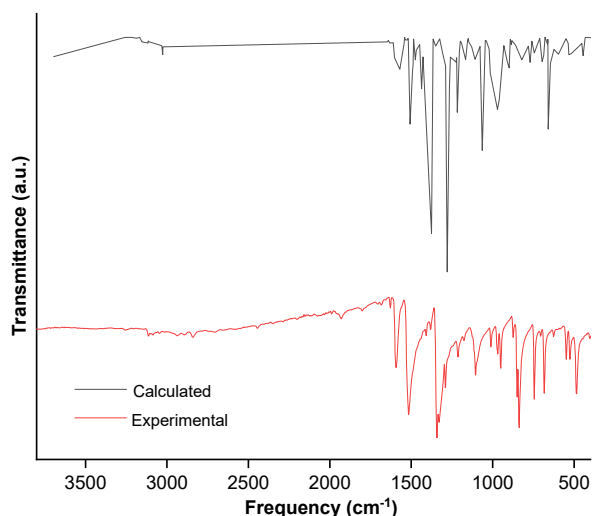


Fig 3. Experimental FTIR spectrum of the ligand L compared with the corresponding calculated one in the gas phase using the B3LYP/6-311+G(2d,p)

Table 4. Experimental and calculated ^1H chemical shifts (δ) for the synthesized ligand (numbering as in Fig. 2)

H atom	Calculated (ppm)	Experimental (ppm)
3-H (NH)	7.59	12
12-H (phenyl)	6.70	7.80
14-H (phenyl)	6.79	7.60
18-H (OCH ₃)	4.20	3.70
19-H (OCH ₃)	3.17	3.44
20-H (OCH ₃)	2.65	3.90
24-H (OCH ₃)	3.55	4.22
25-H (OCH ₃)	2.93	2.99
26-H (OCH ₃)	3.17	3.77
28-H (OCH ₃)	2.65	2.01
29-H (OCH ₃)	4.03	4.20
30-H (OCH ₃)	3.17	3.99
33-H (C-CH-N)	10.50	9.50
38-H (phenyl)	7.66	8.09
40-H (phenyl)	6.64	8.55
42-H (phenyl)	7.51	7.33
43-H (phenyl)	7.51	7.81
RMSD		8.77

crystalline packing interactions in the gas phase calculations. These factors contribute to the observed differences between the experimental and calculated spectra [22,25,30].

The calculated ^1H -NMR chemical shifts for the ligand

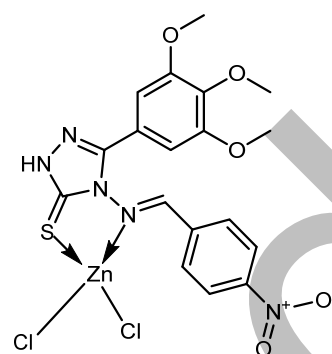


Fig 4. Tetrahedral structure of ZnLCl_2 complex

L were determined using the GIAO approach at the B3LYP/6-311+G(2d,p) level of theory in the gas phase, with TMS as the reference compound. These calculated values were then compared with the corresponding experimental values, as outlined in Table 4, by means of the RMSD values. The results of this comparison indicated that the calculated chemical shift values tended to be overestimated when compared to the experimental values. This overestimation may be attributed to the absence of solute-solvent interactions in the gas phase calculations and the potential influence of intermolecular hydrogen bonding interactions [27,29]. According to the results of FTIR, UV-vis, and magnetic susceptibility measurements, the octahedral geometry has adopted around cobalt(II), nickel(II), and copper(II) ions whereas the tetrahedral geometry was investigated for zinc(II) complex, as shown in Fig. 4.

CONCLUSION

A series of transition metal complexes of Schiff base L were synthesized. The data observed from NMR, FTIR, and MS spectra confirmed the bidentate behavior of Schiff base through C=N and C=S functional groups. The elemental micro-analyses, molar conductivity, and magnetic measurements investigated the octahedral environment around cobalt(II), copper(II), and nickel(II) ions whereas the Zn(II) complex was adopted as tetrahedral geometry. The fully optimized structure of ligand L was examined using DFT calculations at the B3LYP/6-311+G(d,2p) level of theory. The analysis revealed that the ligand exhibited coplanarity throughout its structure, except for the trimethoxyphenyl ring,

indicating the presence of electron delocalization within the molecule. Furthermore, the 1,2,4-triazole-3-thione group displayed an *E* conformation relative to the C32=N31 bond, and the β -nitrogen was *cis* to the thioketo sulfur concerning the C4–N6 bond. The ligand was determined to exist in the thione tautomeric form. The structure of the synthesized ligand was further corroborated through in-depth analyses, which involved comparing its experimental NMR and FTIR spectra with their corresponding theoretical counterparts. These comparisons exhibited very good correlations, confirming the accuracy of the ligand's structural characterization.

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■ CONFLICT OF INTEREST

There are no conflicts to declare.

■ AUTHOR CONTRIBUTIONS

Fatima Haitham Zuhair has conducted the experimental part of the study and wrote the first draft. Zahraa Salim Al-Garawi and Mahmoud Najim Al-jibouri have designed the study, analyzed data and the results, and revised the manuscript. Abanoub Mosaad Abdallah and Gehad Genidy Mohamed have performed the DFT and molecular study, wrote, and revised the final version of the manuscript. All authors agreed to the final version of this manuscript.

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