Preparation and Characterization of New Tetra-Dentate N_2O_2 Schiff Base with Some of Metal Ions Complexes

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Abstract: *This study describes the preparation of a new series tetra-dentate N_2O_2 dinuclear complexes Cr(III), Co(II)and Cu(II) of the Schiff base 2-[5-(2-hydroxy-phenyl)-1,3,4-thiadiazol-2-ylimino]-methyl-naphthalen-1-ol], (LH_2) derived from 1-hydroxy-naphthalene-2-carbaldehyde with 2-amino-5-(2-hydroxy-phenyl)-1,3,4-thiadiazole. These ligands were characterized by FT-IR, UV-Vis, Mass spectra, elemental analysis, and ^{1}H-NMR. All prepared complexes have been characterized by conductance measurement, magnetic susceptibility, electronic spectra, infrared spectrum, thermal Analysis (TGA), and metal analysis by atomic absorption. The stoichiometry of metal to ligand, magnetic susceptibility, and electronic spectra measurements show an octahedral geometry for all (Cr^{3+}, Co^{2+}, Cu^{2+}) complexes. Conductivity measurement shows that the prepared Co^{2+} and Cu^{2+} complexes were nonelectrolytes except for Cr^{3+}. Studying the extraction efficiency such as ligand concentration, temperature and incubation time, centrifuge time, amount of surfactant were evaluated and optimized. The linear range of ions Cr(III), Co(II) and Cu(II) with ligand is 0.2–3, 0.2–4, 0.2–3, μg mL^{-1}, with the relative standard deviation of 0.15%, 0.34%, 0.46%, respectively. The successful method was applied for the determination of trace metal ions in the wastewater.*

Keywords: *tetradentate N_2O_2; naphthaldehyde; thiadiazole; cloud point*

INTRODUCTION

Multiple or tetra-dentate Schiff bases contain N_2O_2 coordination, and their mineral complexes have gained significant interest due to their excellent complexity. They are used in extracting many metallic ions from water due to their ability to form stable metal chelates complexes. They are widely studied in coordination chemistry, especially those which contains heterocyclic compounds with the azomethene group, as it has basic properties due to the presence of an electron pair on the nitrogen atom azomethene (–C=N) and often pentagonal or hexagonal rings with the metal ion [1-3]. Heavy metal pollutions are released into the environment by industrial activities affecting the ecosystem. The metal content determination is necessary for controlling purposes because there is an active procedure for simultaneous enrichment and separation species from matrices of various analytical applications and separation procedures [4]. Cloud point extraction has become one of the most popular methods used to separate and enrich metal ions. Due to their low cost, simplicity, safety, and high capacity for pre-concentration, the metals can be collected in small volumes (0.2–0.5 mL) of the surfactant phase [5-6]. Cloud point extraction has been used for extractive pre-concentration, separation, and/or purification of metallic species, metal chelates, biomaterials, and organic compounds [7]. The present study describes the coordination behavior of Schiff base (LH2) towards some transition elements, and we report on the results obtained in a study of the CPE of Cr(III), Co(II), and Cu(II) after the formation of a complex with (LH_2) using

Triton X-114 as surfactant followed by analysis by UV-Vis.

■ EXPERIMENTAL SECTION

Materials

All chemicals were obtained from Sigma- Aldrich companies such as phosphorus(V) oxide chloride 99%, thiosemicarbazide 98%, salicylic acid 99%, 1-hydroxy-naphthalene-2-carbaldehyde technical grade, potassium hydroxide 90%, $CrCl_3{\cdot}6H_2O$ 98%, $CoCl_2{\cdot}6H_2O$ 99%, and $CuCl_2{\cdot}2H_2O$ 99%.

Instrumentation

The electronic spectra were collected by using Shimadzu 160 A- Spectrophotometer. Mass analysis of ligand has been performed with LC-Mass 100P Shimadzu. The IR spectra of ligand and complexes have been obtained using the KBr method in the range of 4000–400 cm^{-1}. Using the Faraday Method, a Bruker BM6 device was used to conduct magnetic sensitivity measurements at room temperature. Thermal analysis studies of the compounds were performed on the Mettler instrument TGA. Conductivity measurements were performed with a conductivity meter of Model PCM 3 - JENWAY. The analysis of CHN was carried out using analyzer model 5500 Carlo-Erba. AAS. Spectrophotometer model Double-beam atomic Absorption spectrometer, model: AA400 Analytic Jeana. Centrifuge model PLC-03, Electro-thermal bath model AA-00267.

Procedure

Preparation of compound [A] [8]

The melting point (M.p.), yield, and CHNO analysis are listed in Table 1.

Synthesis of 2-[5-(2-Hydroxy-phenyl)-1,3,4-thiadiazol-2-ylimino]-methyl-naphthalen-1-ol] LH_2 [9-10]. A mixture with the same stoichiometric (0.02 mol) ratio of compound [A] with 1-hydroxy-naphthalene-2-carbaldehyde was added in a crucible. It was then put in microwave irradiation of 230 W for 3 min. After the reaction was complete, the obtained solid was recrystallized by absolute ethanol. Some properties of the product are listed in Table 1.

Preparation of metal complexes

A stoichiometric reaction of the corresponding LH_2 ligand (0.02 mol in 20 mL methanol) was added to a few drops of Triethylamine before mixing in 50 mL round bottom flask with (0.02 mol) metal(II) chlorides molar ratio (M:L) of 1:1. The mixture was put in an ultrasonic bath at 60 °C. After 60 min, crystalline-colored precipitates formed after cooling at room temperature. The resulting solids were filtered off, washed with distilled water and ether, and then dried in a desiccator. Some properties are summarized in Table 1.

Stoichiometric determination of complexes [11]

The continuous variation (JOB) method ensured the correlation ratio between ions and ligand in equilibrium media.

Analytical procedure

Metal ions Cr(III), Co(II), Cu(II) Chloride (3×10^{-4} mol L^{-1}) and LH_2 (3×10^{-4} mol L^{-1}) were put in 10 mL centrifuge tubes containing Triton X-114 (10% w/v) each individually. The mixture was shacked for 3 min then put and heated in an oil bath at 65 °C for 20 min. After that, heating was transferred to centrifuged late at 20 min and then cooled in an ice bath for 10 min. The

Table 1. LH_2 and metal yield percentages and CHNO analysis

Compound	Yield%	Analysis (calculated)					
		C%	H%	N%	O	Cl	M
LH_2 $C_{19}H_{13}N_3O_2S$	67%	65.45 (65.69)	3.82 (3.77)	12.24 (12.10)	19.27 (9.21)	--	--
$[Cr_2\,(LH_2)_2\,(H_2O)_4]Cl$	%73	48.83 (48.67)	3.18 (3.22)	8.83 (8.96)	13.55 (13.65)	7.63 (7.56)	10.97 (11.09)
$[Co_2\,(LH_2)_2(H_2O)_4]$	%77	51.69 (51.82)	3.49 (3.43)	9.67 (9.54)	14.65 (14.53)	--	13.23 (13.38)
$[Cu_2\,(LH_2)_2(H_2O)_4]$	%71	51.13 (51.29)	3.47 (3.40)	9.53 (9.44)	14.29 (14.38)	--	14.45 (14.28)

final step was taking the Triton X-114 rich phase and diluting it in 1 mL of ethanol. The eluent solution was transferred to a UV-VIS device, and the absorbance was measured. Titrations were performed using different solutions for any of the solutions Cr(III), Co(II), and Cu(II). The same method was used to determine the metal ions Cr(III), Co(II), and Cu(II) in the wastewater.

■ RESULTS AND DISCUSSION

FT-IR Spectra of LH_2

The method for synthesis of LH_2 is illustrated in Scheme 1. The FT-IR spectra of the ligand showed the emergence of new beams, which are the bundles of the right group (C=N). The absorption beams of the imine group of the prepared ligand were in the range of 1623 cm^{-1}, which belongs to the azomethene group, and the frequencies of the thiadiazole ring appeared at 1053–1239 cm^{-1} [10]. Fig. 1 and Table 2 contain the values of the infrared spectra of the prepared ligand.

Mass Spectral Data and^{1}H-NMR

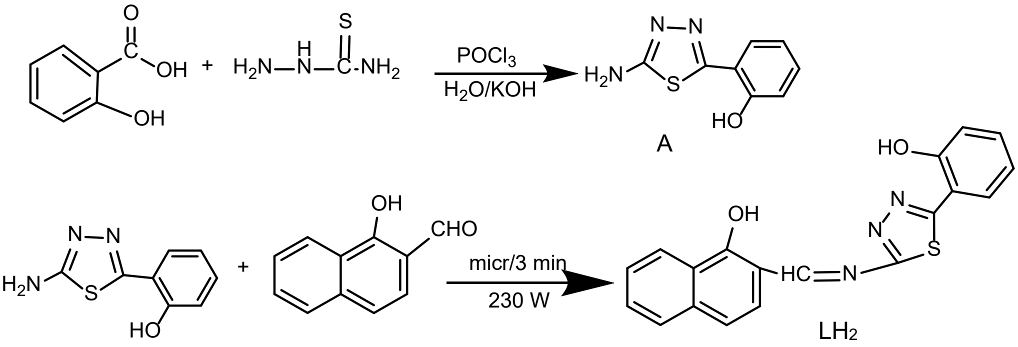
The mass spectral data of Schiff base ligand have been observed to give molecular ion peaks at *m/z* 348.0 (M+), which is in good agreement with the expected values at *m/z* = 347.39. This value refers to ($C_{19}H_{13}N_3O_2S$), *m/z* = 191 ($C_8H_5N_3OS$), *m/z* = 156 ($C_{11}H_8O$), and *m/z* = 94 (C_6H_6O).

^{1}H-NMR Spectroscopy

The peaks of the ^{1}H-NMR spectra of ligand are shown in Fig. 2. ^{1}H-NMR ($CDCl_3$ – 400 MHz) of LH_2 exhibited two singlet peaks at 13.687 and 11.506 ppm corresponding to OH proton. The signals at 8.756 ppm were attributed to the azomethine proton peak (CH=N). The doublets and multiplets were observed in the range of 6.155–7.504 ppm due to benzene rings' aryl protons.

FT-IR Spectra of Complexes

The all FT-IR spectra bands assignment of the compounds are presented in Table 2. The imine group ν(C=N) band in the LH_2 (1623) cm^{-1} complexes shifted to lower frequencies in all the complexes. The shifting indicates linked by the nitrogen atom of C=N in coordination with the metal [12]. As shown in the tables, the disappearance of the bands in the range 3419–3481 cm^{-1} belonging to the hydroxyl phenolic (O) complexes is evidence of its chelation by the phenolic oxygen atom [13]. The bending (Wagging and twisting) of the coordination water complexes appears by about 623–757 cm^{-1} [14]. The linked nitrogen atom of thiadiazol



Scheme 1. Synthesis of ligand

Table 2. FT-IR data of ligand and its metal complexes (cm^{-1})

Compound	ν(C=N)	ν(H-O)	ν(C-N=N-C)	Wagging ν H_2O	Twisting ν H_2O	ν(H_2O)	ν(M-N)	ν(M-O)
LH_2	1623(s)	3419–3481	1156–1354	-	-	3441	-	-
$[Cr_2 (LH_2)_2 (H_2O)_4] Cl_2$	1606(s)	-	1155–1301	623	757	3375	493	586
$[Co_2 (LH_2)_2(H_2O)_4]$	1598(s)	-	1159–1311	683	748	3345	458	590
$[Cu_2 (LH_2)_2(H_2O)_4]$	1613(s)	-	1117–1299	692	749	3387	495	587

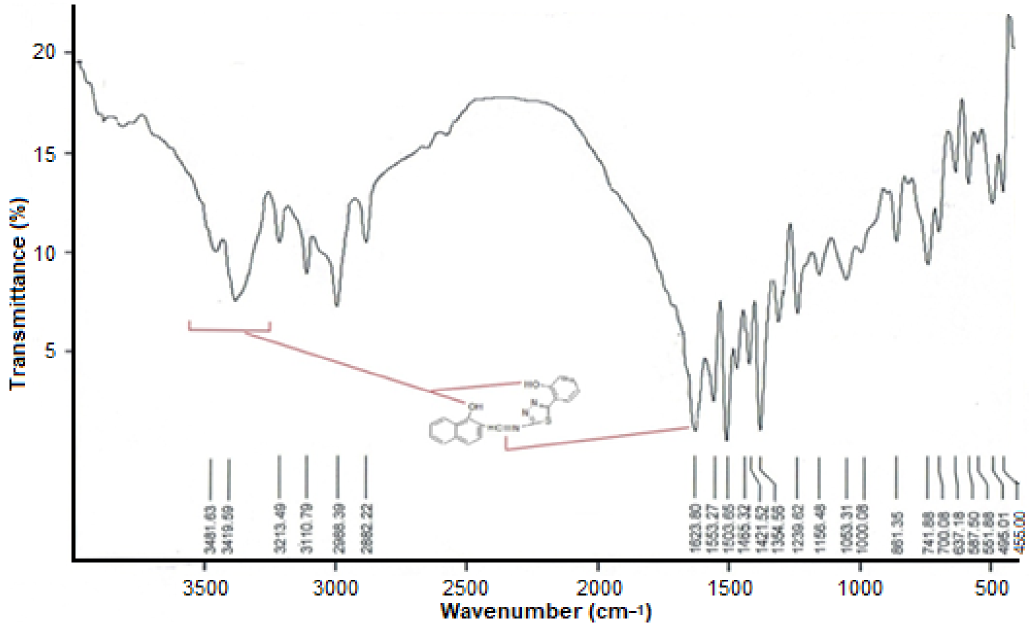


Fig 1. FT-IR for LH_2 ligand

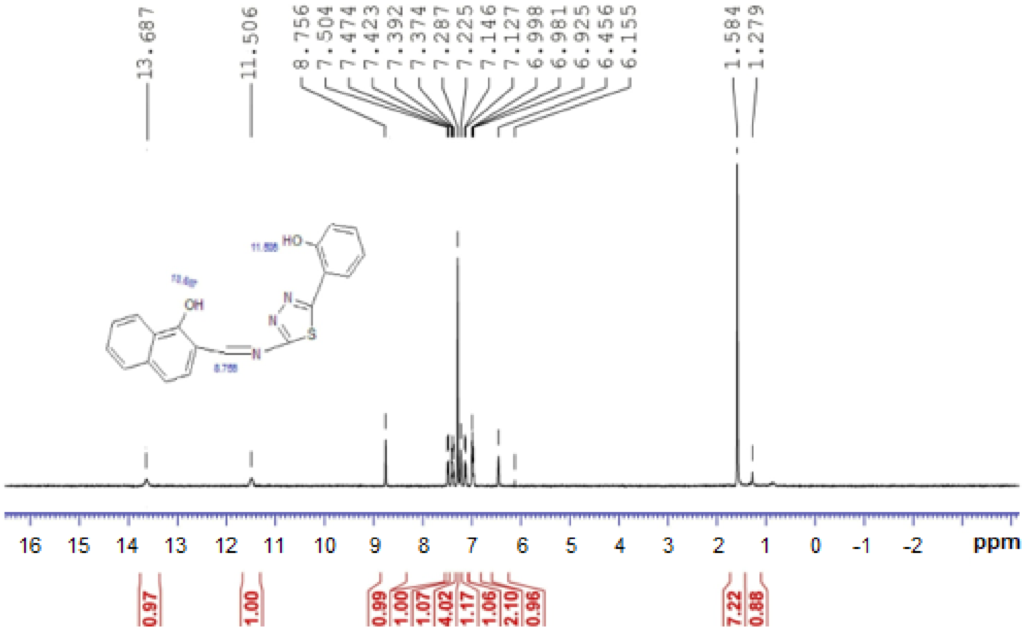


Fig 2. ^{1}H-NMR for LH_2 ligand

ring shows shifted absorption bands of ligand at 1174–1303 cm^{-1} in complexes confirming the metal's binding to the by group =N–N= [15]. For all complexes, a new beam appeared in the range of 586–590 cm^{-1} due to the vibrations of the group stretch (M–O) [16] and showed a stretching of the group (M–N) of the prepared complexes in the bounded region between 458 and 495 cm^{-1}. This confirms the metal's association via the N atom [17]. All the infrared spectrum values for the complexes are shown in Table 2.

Electronic Spectra, Magnetic Moments, and Molar Conductance of Complexes

Most of the complexes of the transition elements show absorbance at certain wavelengths of the spectrum because most of these complexes are colored. The electronic spectrum of the prepared complexes was recorded in the range of 200–1100 nm using DMF solvent [18].

The spectra of the chromium complex observed two (428 nm, 608 nm) in Table 3, attributed to the allowed transfer $^4A_2g \rightarrow {}^4T_1g$ (F) and $^4A_2g \rightarrow {}^4T_1g$ (F) respectively [19]. It has been observed that the electron spectrum is complex cobalt(II) low spin octahedral ($t_2g^6eg^1$), one permissible transition 500 nm, which is $^2Eg\ {}^2T_2g$ (20). The spectrum of the copper(II) complexes showed an absorption peak at the region of 722 nm, as shown in Table 3, which attributed to$^2B_1g \rightarrow {}^2B_2g$. It agrees with the published research in this regard [21].

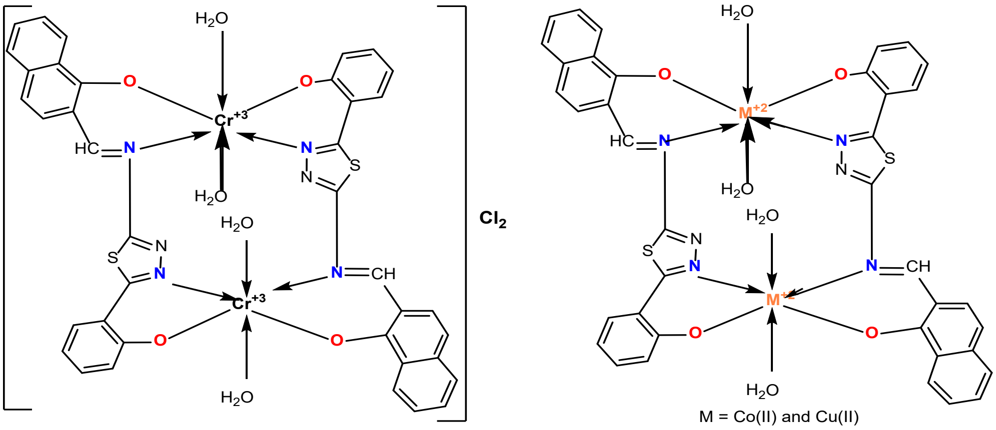
The UV–Vis spectra of a ligand with complexes show a displacement in the range between 5 and 20 nm. There is a difference between the spectra of the ligand and the metal ion solution and the clear difference in the colors of the mixing solutions from the solutions of the ligand and the metal ion before mixing, which is clear evidence of coordination between them [22]. Table 3 gives the prepared compounds' electronic spectral, magnetic moments, and Molar Conductance data. The magnetic susceptibility results gave values for the magnetic moment, which correspond to the suggested shape. From the electronic spectra, infrared spectrum, and magnetic measurements, it indicates that most of Cr(III), Co(II), and Cu(II) complexes contain hexacoordinate and have octahedral geometry, as illustrated in Scheme 2.

Continuous Variation Method

The absorbance of the complexes was measured at λ_{max} = 483, 500, and 413 nm. The stoichiometric ratio between the Cr(III), Co(II), Cu(II) and ligand was 1:1.

Table 3. Some physical data electronic spectra for LH_2 and complexes in DMF

Compound	Dec. Point °C	Conductivity ohm^{-1} cm^2 mol^{-1} 25 °C	Magnetic Moment (B.M)	Color	Absorption Bands (nm)	Assigned Transition
LH_2	206–207	8	-	Yellow	235	$\pi \rightarrow \pi^*$
					345	$N \rightarrow \pi^*$
$[Cr_2 (LH_2)_2 (H_2O)_4]Cl_2$	268d	142	3.9	Violet	608	$^4A_2g \rightarrow {}^4T_2g$ (F)
					452	$^4A_2g \rightarrow {}^4T_1g$ (F)
					374	Charge Transfer
$[Co_2 (LH_2)_2(H_2O)_4]$	281	19	2.39	Dark brown	500	$^2E_1g \rightarrow {}^2T_2g$
					375	Charge Transfer
$[Cu_2 (LH_2)_2(H_2O)_4]$	255d	23	1.89	brown	722	$^2B_1g \rightarrow {}^2B_2g$
					483	Charge Transfer



Scheme 2. Suggested structure for complexes

Extraction Metal Ions in Water Sample

The spectrum of ligand LH_2 and complexes

The general relative standard deviation was the absorbance of Cr(III), Co(II), and Cu(II) complexes' highest absorption. Surfactant-rich phases against blank prepared under similar conditions were recorded. Triton X-114 was good as an extracting agent [23].

Effect of ligand amount

As shown in Fig. 3, increasing the concentration of LH2 inclines the absorbance of the complexes, but at a higher concentration, the absorbance declines for all metal ions investigated. The ligand concentration of 3 × 10^{-4} mol L^{-1} was chosen as the optimum condition for other variables. The effects of the ligand on relative standard deviation efficiency were investigated as 55 × 10^{-4} mol L^{-1}. Obaid et al. reported that the best ligand concentration for extracting metal ions from water by cloud point extraction (CPE) was 55 × 10^{-4} mol L^{-1}. At a higher concentration (excess of LH_2), competition with a complexing agent (Triton X-114) reduces the metal ion concentration in complexes and decreases absorbance [24].

Effect of surfactant

The correct choice of Triton X-114 as a surfactant is fundamental for obtaining an optimal extraction process, separating the metal-ligand complex from the aqueous phase surfactants, and assisting quantitative extraction of the metal chelate complex. Furthermore, among the nonionic surfactants used, Triton X-114 gave a higher absorbance value to the samples Cr(III), Co(II), and Cu(II) complexes (0.103, 0.198, 0.210) highest absorption when compared with other surfactants; hence, Triton X-114 was preferred as an extracting solvent [25].

Calibration graph

The linear calibration graph of Cr(III), Co(II), and Cu(II) with agent LH_2 ligand was obtained as given in Fig. 4 for each ion. The Beer law was obeyed over the concentration range of 0.2–3, 0.2–4, and 0.2–3 µg L^{-1}.

The methods were applied to the determination of Cr(III), Co(II), and Cu(II) ions in Water of Marshlands (Mesan/Iraq) and wastewater of Industrial sewage of Tannery Factories in Nahrawan (Bagdad /Iraq). It gave good accuracy and precision, as shown in Table 4. In addition, the good method was compared with other literature methods.

Thermal Analysis

As shown in Fig. 5, the complex showed three well-defined steps. The first step represents the loss of four

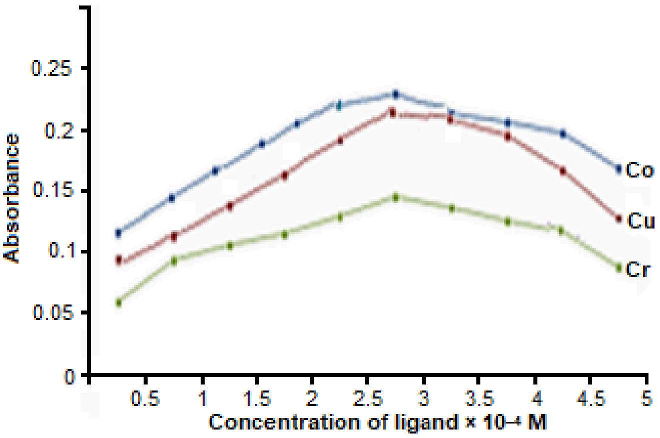


Fig 3. Effect of ligand concentration on complex absorbance; Cr(III), Co(II), Cu(II) = 3 × 10^{-4} mol L^{-1} (each 1 mL) and 10% (V/V) Triton X-114

Table 4. Application of the proposed method for determination of Cr(III), Co(II), and Cu(II) by LH_2

Metal ions	Real sample	Found	RSD%*	RSD% average	Recovery%	Recovery% Average
Cr^{+3}	Wastewater of Tannery Factories	2.95	0.49%	1.609%	99.3%	98.7%
	Water of Marshlands	1.92	0.110%	0.431%	97.2%	96.95%
Co^{+2}	Wastewater of Tannery Factories	3.979	0.82%	0.55%	99.3%	99.08%
	Water of Marshlands	2.81	0.16%	0.57%	96.2%	97.15%
Cu^{+2}	Wastewater of Tannery Factories	1.94	0.37%	0.41%	97.9%	97.65%
	Water of Marshlands	1.99	0.12%	0.62%	99.1%	97.44%

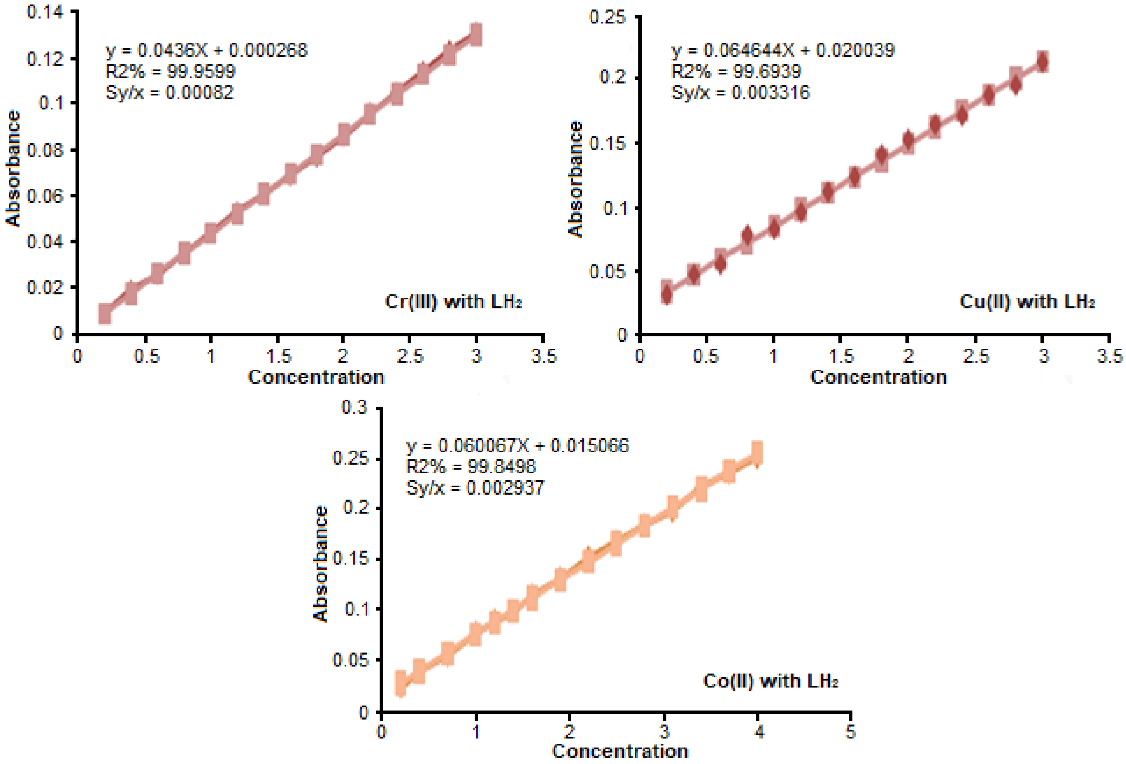


Fig 4. The calibration curves showing the correlation between absorbance and concentration of the complexes

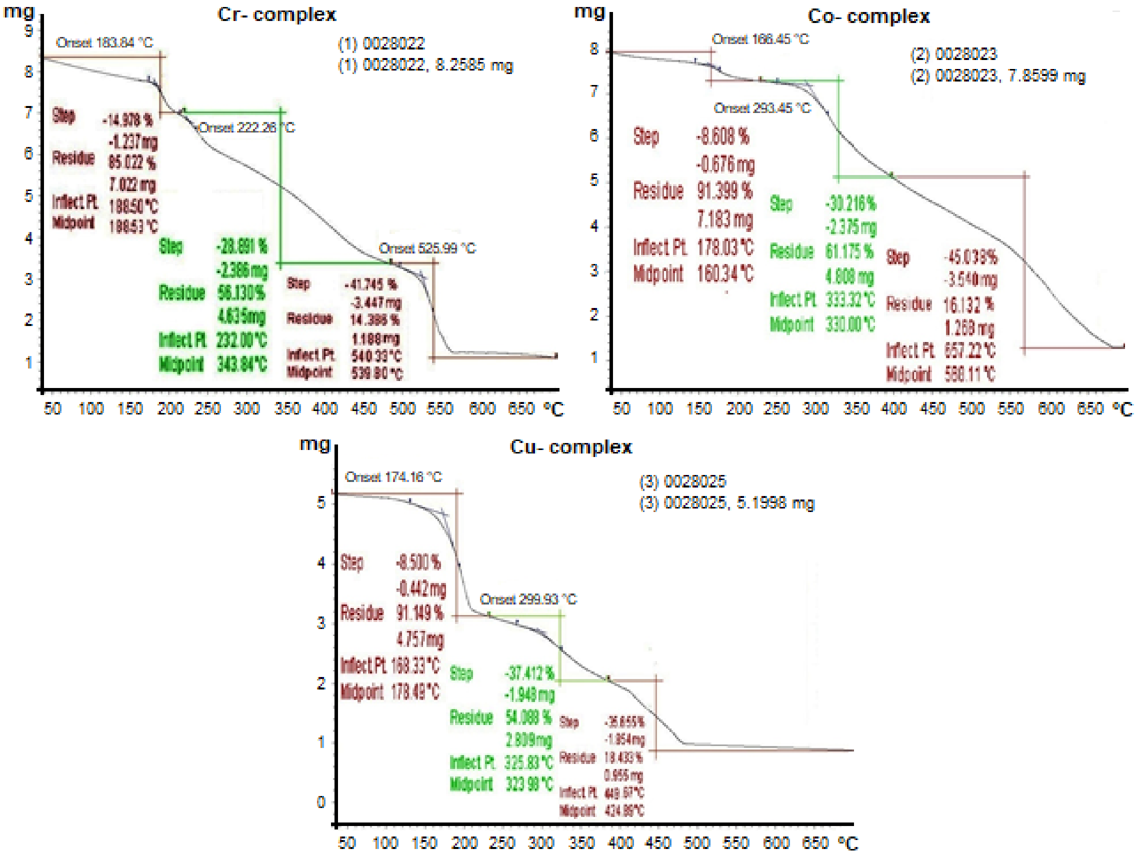


Fig 5. Thermal analysis of the complexes

Table 5. TGA analysis data of complexes

Sample (step)	T. range °C	Weight mass loss (calc) found%	Reaction
Cr(1)	37–188	(14.97) 15.26	($4H_2O$+2Cl)
Cr(2)	188–343	(29.980) 28.891	$C_{14}H_{10}O_2$
Cr(3)	343–540	(41.75) 40.95	$C_{16}H_{12}N_6O_2S_2$
Final residual		(14.50) 14.38	$2CrO^+$
Co(1)	37–178	(8.17) 8.60	$4H_2O$
Co(2)	140–272	(31.83) 30.22	$C_{20}H_{10}O_2$
Co(3)	272–462	(46.09) 45.04	$C_{18}H_{10}N_6O_2S_2$
Final residual		(17.84) 17.13	2CoO
Cu(1)	37–178	(8.10) 8.50	4H2O
Cu(2)	178–325	(38.02) 37.42	$C_{22}H_{14}N_2O_2$
Cu(3)	325–449	(35.10) 35.65	$C_{16}H_{12}N_4S_4$
Final residual		(17.87) 18.36	2CuO

H_2O molecules from Co(II) and Cu(II) but Cr(III) loses $2H_2O$ and 2Cl as evidence of the coordinated water molecules in complexes [26]. The second, third, and fourth steps are explained in Table 5. These steps are due to the loss of mass in the form of gases. The final step's large weight drop can be explained by considering that the residue is a 1:1 mixture of 2 (Metal oxide).

■ CONCLUSION

We have observed new ligand compounds and complexes from the first series of transitional metals by examining their physical properties using various analyses. The collected data demonstrated that the ligand behaves as a tetradentate ligand of N_2O_2 and forms binuclear stable complexes. Molar conductivity measurements indicate that complexes with the formula $[M_2(LH_2)_2(H_2O)_4]$ with M(II) = Co, Cu were neutral (a nonelectrolyte), while the other complexes with the formula $[Cr_2(LH_2)_2(H_2O)_4]Cl_2$ were electrostatic type (1:2). The determination trace of Cr(III), Co(II), and Cu(II) in water samples performed well by using cloud point extraction by applying Schiff (LH_2) as extracting reagent because it is a stable and selective complexing reagent. The cloud point extraction method is good, fast, and inexpensive to use compared to other methods for quantifying metal ions. The method gives a very low limit of detection and good relative standard deviation values.

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