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Synthesis of Binuclear Complexes of Cu (II), Ni (II) and Cr (III) Metal Ions Derived from Di-Imine Compound as Biterminal Binding Site Ligand

Safa Ismaiel Mahjoub Muslah[1,*], Ammar J. Alabdali[1] and Nasser D. Shaalan[2]

[1]Department of Chemistry, College of Sciences, Al-Nahrain University, Baghdad, Iraq
[2]Department of Chemistry, College of Science for women, University of Baghdad, Baghdad, Iraq

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Abstract

The research is concerning synthesis of two di-imine ligands derived from thiadiazole heterocyclic compounds. 1, 3, 4-thiadiazole-2, 5-dihydrazino is considered as ligand (L_1) and starting essential compound that used as precursor to synthesize the new ligand (2, 2'-(((1,3,4-thiadiazole-2,5-diyl)bis (hydrazin-2yl1ylidene))bis (methaneylylide)) diphenol (L_2). Six new complexes were derived from the ligands using some transition metal ions like Cu(II), Ni(II), and Cr(III). The synthesized compounds characterized by infra-red, ultra-violet-visible and gas chromatography-mass spectroscopy, conductivity, and thermal analysis. The coordination modes were suggested to be N_2 from two terminals to form binuclear complexes.

The mentioned characterization methods showed that the prepared complexes may have chelation pattern (bidentate or tridentate) depending on the suggested geometry (square planer or octahedral) and the type of ligand.

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*Corresponding author: Greencity30@yahoo.com

1. Introduction

Imines are compounds of carbon-nitrogen double bond $R_1R_2C=N–R_3$, where R = hydrogen, aliphatic, aromatic group. Hugo Schiff was the first one to synthesize this compound in 1864 from simple condensation between aldehydes or ketones with primary amines [1]. Schiff's bases have several applications, including: electrochemistry, bio-inorganic chemistry, separation processes, photo degradation, pharmacy, anti-microbial and dyes [2,3]. Schiff's bases have the ability to form stable complexes, due to the nitrogen atom that gives the electron pair the ability to synthesize so many complexes with metal ions [4-8]. Schiff base ligands containing more than one donor sites are extensively used for the preparation of metal complexes with interesting properties due to the chelating effect [9]. 1,3,4-Thiodiazole was one of the most popular isomer in the industrial and the pharmaceutical fields compared to other species. It’s considered a strong aromatic and high stability circular system and with lack of toxicity or harmful risks for humans [10].The thiadiazole and substitutes have different biological activities, such as: Anti-fungal, [11] Anti-pyretic [12], Anti-convulsive [13], Anti-viral [14]and Anti-inflammatory [15]. The aim of this work is to study the behavior of the ligands toward metal ions according to the available donor atoms and to suggest the ability of extracting metal ions from factory’s by product to determine the amount photometrical.

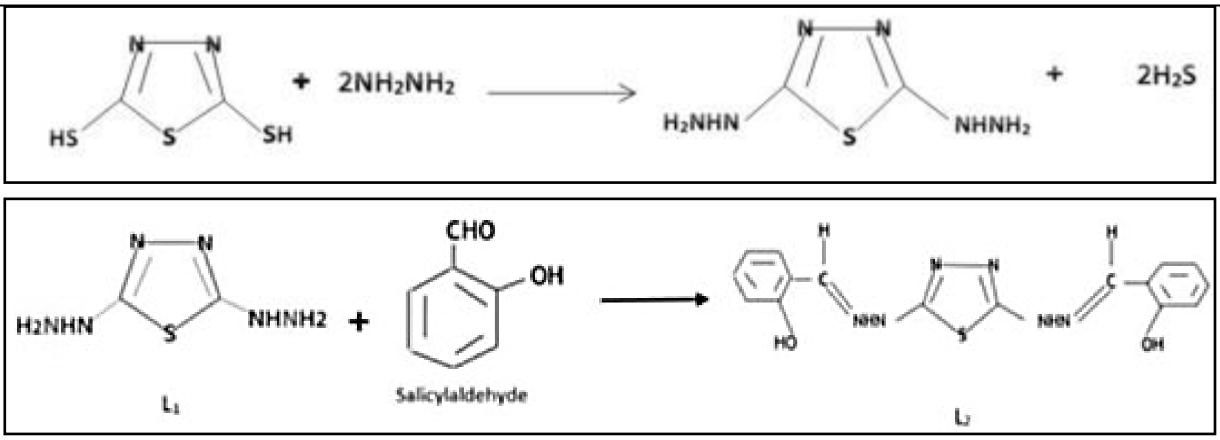
2. Experimental

General methods and instruments

All the prepared ligands and complexes characterized by infrared spectra were recorded by using FTIR 8300 Shimadzu Spectrophotometer frequency range of 4000-200 cm^{-1}, ultraviolet–visible (UV-Vis) spectra were recorded by using a Shimadzu U.V-Vis. 160 A-Ultra-violet Spectrophotometer in the range of 200-1100 nm, conductivity measurements were carried out by using a WTW conductivity meter, The Atomic Absorption Spectrophotometer (A.A.S) type: Double-beam, model: AA400 and thermal analysis and GC-Mass spectroscopy. The melting points were recorded by "Digital melting-point apparatus by placing it in the capillary tube.

Synthesis methods of (L_1, L_2), (A_1-A_3) and (B_1-B_3) compounds

Ligands and complexes were synthesized according to general methods mentioned in literatures. Scheme 1 showed the synthesis reaction of L_1 and L_2.



Scheme 1. The synthesis of L_1 and L_2 compounds.

Synthesis of 1,3,4-thiadiazole-2,5-dihydrazine (L_1)

A solution of 1, 3, 4 -thiadiazole-2, 5-dithiol (0.01 mole) dissolved in 200 ml of absolute ethanol was mixed with anhydrous hydrazine (0.02 mole) with stirring and when addition completed (drop wisely) the mixture will reflux with constant stirring for 5 hours. After reaction completed (monitored by litmus paper) the solvent is then removed by rotary evaporator where the output separated, which is a desired precipitate. The crystallization occurred by washing the products with ether [16].

The physical data of the prepared compounds are shown in Table 1.

Synthesis of 1,3,4-thiadiazole-2,5-bis-N-*o*-hydroxy phenyl imine (L_2)

0.01 mole of L_1 reacted with 0.02 mole of salicyldehyde in 20 ml absolute ethanol in the presence of some drops of glacial acetic acid. The reaction mixtures were refluxed with stirring for 4 hours, a precipitate will be formed indeed. The product filtered and washed with ether then dried. The physical data of the prepared compounds are shown in Table 1.

Synthesis of (A_1-A_3) and (B_1-B_3) complexes

A solution of L_1 or L_2 (0.01 Mole) dissolved in 5 ml acetone were added to metal ion $CuCl_2.2H_2O$, $NiCl_2.6H_2O$ or $CrCl_3.6H_2O$ (0.02 mole) dissolved in 5 ml alcoholic medium individually, after 24 hours of reflux and stirring the colour changed to derive (A_1-A_3) and (B_1-B_3) complexes respectively. The precipitate filtered and washed by ether then dried [17]. The physical data of the prepared compounds are shown in Table 1.

Table 1. The physical properties of the prepared compounds.

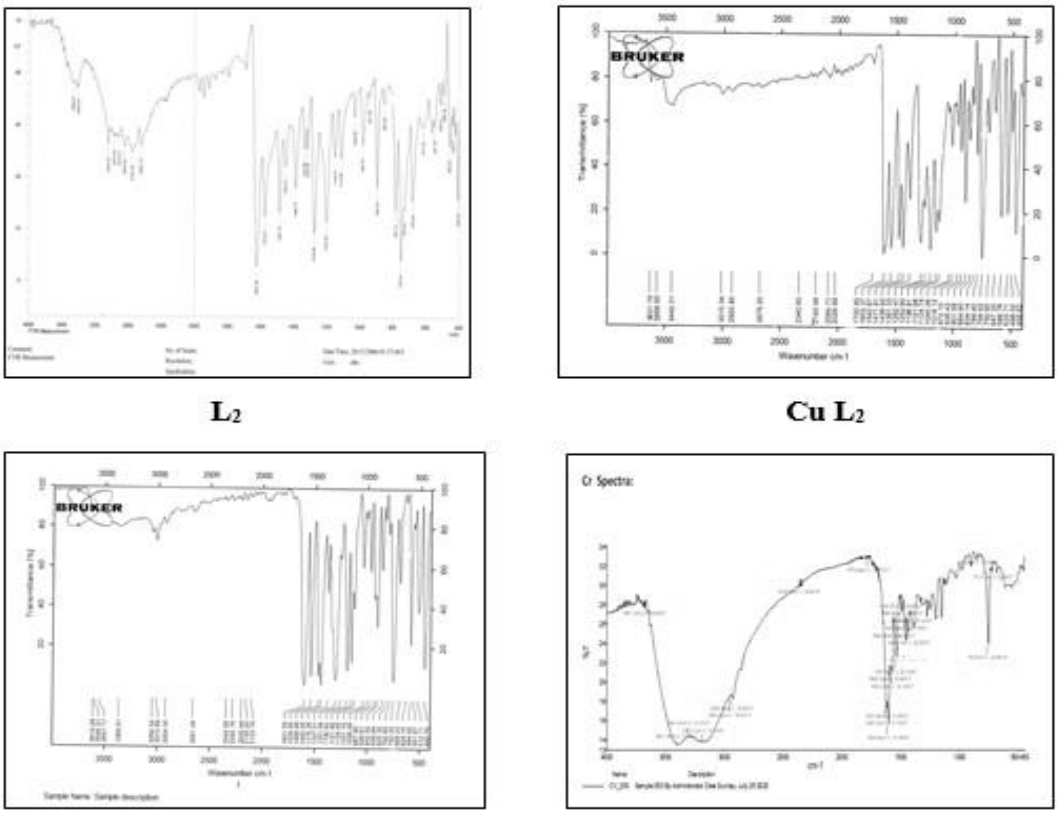
Symbol	Formula	M.p.°C	Color	Yield %
L_1	$C_2H_6N_6S$	226-228	Pale-yellow	85.71
A_1	$[Cu_2L_1(Cl)_2(H_2O)_2]Cl_2.2H_2O$	253-255	Pale-brown	46.53
A_2	$[Ni_2L_1(Cl)_2(H_2O)_2]Cl_2$	290 d	Dark-brown	76.19
A_3	$[Cr_2L_1(Cl)_4(H_2O)_4]Cl_2$	237-240	Olive	57.84
L_2	$C_{16}H_{14}N_6O_2S$	223-225	Yellow	83.69
B_1	$[Cu_2L_2(Cl)_2(H_2O)_2]Cl_2$	285-287	Brown-orange (Rusty)	85.50
B_2	$[Ni_2L_2(Cl)_4].3H_2O$	268-270	Brown	72.96
B_3	$[Cr_2L_2(Cl)_2(H_2O)_4]Cl_2.2H_2O$	235-237	Yellowish-green	63.22

3. Results and Discussion

A- Infra-red spectra of (L_1, L_2), (A_1-A_3) and (B_1-B_3) complexes

The absorption bands of infra-red (IR) spectra of the ligands and complexes are shown in Table 2, were L_1 and L_2 showed strong bands at 1620 cm^{-1} and 1624 cm^{-1} respectively, which could be attributed to azomethine group (imine) [18,19].

IR spectra of the prepared complexes were measured to determine the coordination mode of each ligand with metal ions. This can be achieved through the shifting in frequencies of the involved groups in coordination clearly at the spectrum; imine group of L_1 and L_2 was shifted to low frequency by (19-23) cm^{-1} and (21-23) cm^{-1} respectively for Cu (II), Ni (II) and Cr (III) complexes. Figure 1 shows the infrared spectra of L_2 and its complexes.



L₂ **Cu L₂**

Ni L₂ **Cr L₂**

Figure 1. Infrared spectra of L_2 and its complexes.

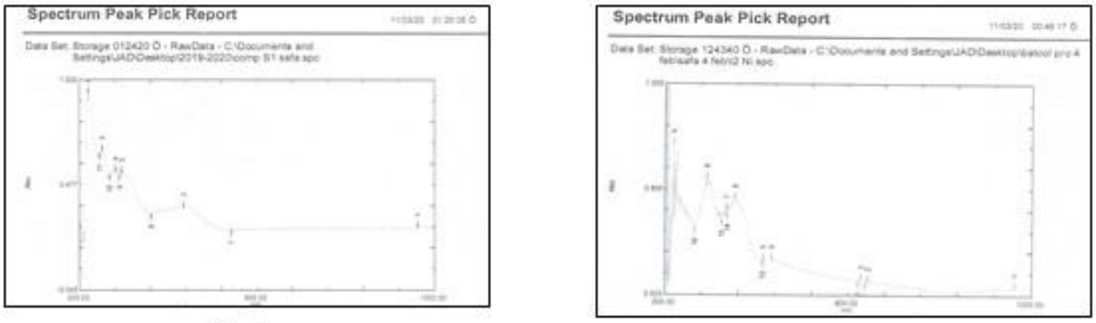
Table 2. The characteristic absorption bands of the ligands and complexes.

Compound	(O–H)	(N–H)	(C–H) aromatic	(C=N)	(C–H) aromaticity	ortho-Subs.
L_1	–	3410 3248 3143	–	1620	–	–
L_2	3520	3406	3043	1624	1573 1485	752
A_1	3401(br)	3158	3052	1601	–	–
A_2	3352(br)	Obscure	3028	1605	–	–
A_3	3401(br)	3402	–	1605	–	–
B_1	3568 3631	3442	3010	1603	1542 1471	759
B_2	Obscure	Obscure	3032	1601	1531 1460	752
B_3	3571	3442	–	1604	–	763

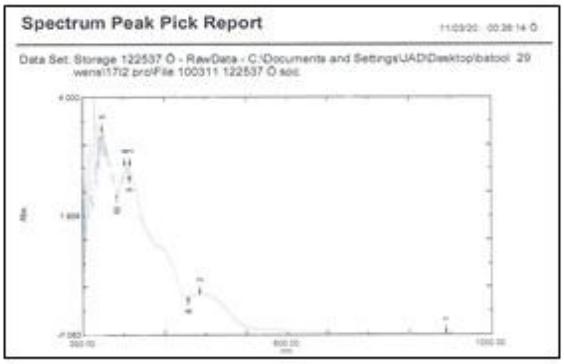
B- Electronic transitions spectra of metal complexes

The absorption spectrum of the ligands consisted variable peaks in the range 200 nm to 350 nm due to the presence of different atoms possess n → π* and π → π* transitions. The electronic spectra of the Cu (II) complexes appeared electronic transitions in the visible region as broad peak belong to d-d transition [20].

The electronic spectra of the Cr (III) complexes showed different bands at visible region which may be attributed to ($^4A_2g \rightarrow {}^4T_2g$), ($^4A_2g \rightarrow {}^4T_1g$) and ($^4A_2g \rightarrow {}^4T_1g$ (P)). The Ni (II) complexes showed two broad bands appeared in the range and (15,000-27,000) cm^{-1}, which suggested geometry to these complexes as square planer. Table 3 shows the absorption band and assignments of these complexes. Figure 2 included U.V-Vis. spectra of L_2 and its complexes.



Cu L_2 **Ni L_2**



Cr L_2

Figure 2. U.V-Vis. spectra of L_2 and its complexes.

Table 3. The electronic transitions and assignments of (A_1-A_3) and (B_1-B_3) complexes.

Compounds	λ nm	cm^{-1}	Assignments	Suggested structure
A_1	647 629 280 266	15,455 15,898 35,714 37,593	$^{2}B_{1}g \rightarrow {}^{2}Bg$ $^{2}B_{1}g \rightarrow {}^{2}A_{1}g$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Square planer
A_2	816 318 284 224	12,254 31,446 35,211 44,642	$^{1}A_{1}g \rightarrow {}^{1}A_{2}g$ $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Square planer
A_3	629 485 319 265	15.898 20.618 31,347 37,735	$^{4}A_{2}g \rightarrow {}^{4}T_{2}g$ $^{4}A_{2}g \rightarrow {}^{4}T_{1}g$ C.T $\pi \rightarrow \pi^*$	Octahedral
B_1	434 295 288 252	23,041 33,898 34,722 39,682	$^{2}B_{1}g \rightarrow {}^{2}Bg$ $^{2}B_{1}g \rightarrow {}^{2}A_{1}g$ $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	Square planer
B_2	628 433 415 352 291	15,923 23,094 24,096 28,409 34,364	$^{1}A_{1}g \rightarrow {}^{1}A_{2}g$ $^{1}A_{1}g \rightarrow {}^{1}B_{1}g$ C.T $n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	square planer
B_3	620 498 393 265	16,129 20,080 25,445 37,735	$^{4}A_{2}g \rightarrow {}^{4}T_{2}g$ $^{4}A_{2}g \rightarrow {}^{4}T_{1}g$ $n \rightarrow \pi^*$, C.T $\pi \rightarrow \pi^*$	octahedral

GC-Mass spectroscopy

Mass spectrometry is the study of system generating the formation of gaseous ions, with or without fragmentation; which are then characterized by their mass to charge ratios (m/z) and relative abundances.

In measuring of L_1, the ligand appeared fragment that represent this structure (CH=NH–O) was lose 43 M.wt from the compound, considering the (HN–N=CH–CH) as intermediate state during this loss [21].

When the electronic bombardment of complexes the hydrogen sulfide molecule has been lost from the heterocyclic compound and the reason for this is due to that is very stable molecule and considered as driving force (H_2S).the disruption of the benzene ring which converted to five membered ring (69 M.wt) which considered one of the important peaks. Finally the most important peak is of the charged molecular weight at 352 M.wt after losing two terminal hydrogen atoms. Table 4 included the most important peaks and the suggested fragments of L_2 compound depending on GC-Mass spectrum that shown in Figure 3.

Table 4. The fragmentation and suggested molecular weights of L_1.

Suggested lost and observed fragments			
Lost fragment	**M.wt.**	**Chemical formula**	**M.wt.**
H_2	2	$C_{16}H_{12}N_6O_2S_1$	352
O_2	32	$C_{16}H_{12}N_6S_1$	320
$2(C_6H_4^+)$	76	$C_4H_4N_6S_1$	168
2(CH=NH–NH)	43	$C_{14}H_8N_2S_1$	236
$2(C_6H_6N)^+$	92	$C_4H_1N_4S_1$	137
2(CH)	13	$C_2N_4S_1$	111
N_2	14	$C_2N_2S_1$	83
(N)	14	$C_2N_1S_1$	69
(CH_2)	14	$C_2N_1S_1$	55

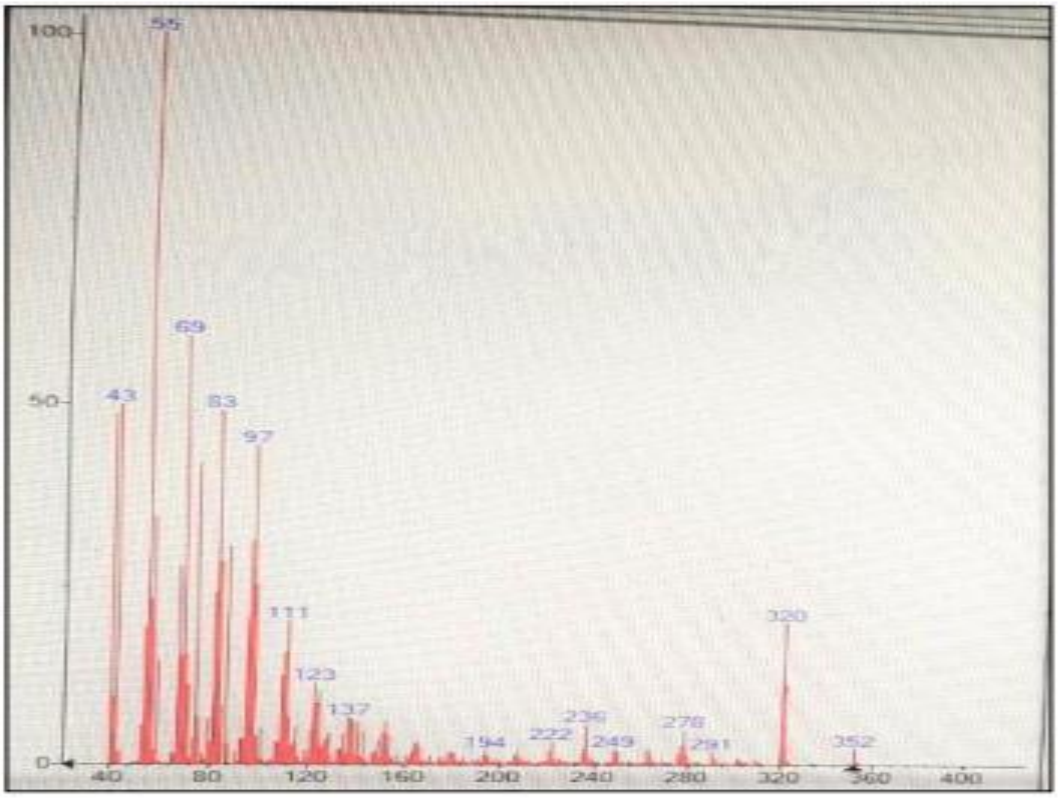


Figure 3. GC-Mass spectrum of the synthesized L_2 ligand.

Molar Conductance

The complexes are dissolved naturally with DMF, which must be non-reactive toward the measured compound and have reasonably high electrical stability and low viscosity to be electrical compound [22]. The molar conductance of the complexes was measured and all complexes are electrolytic except complex B_2 was non-electrolytic. Table 5 included the conductivity measurements of the complexes in 10^{-3} M.

Table 5. Theconductivity measurements of complexes in DMF.

Complexes	Conductivity (MS/cm)	Electrolytic property
Ligand	–	–
A_1	141.1 M.s/cm	Electrolytic
A_2	133.8 M.s/cm	Electrolytic
A_3	165.4 M.s/cm	Electrolytic
B_1	137.8 M.s/cm	Electrolytic
B_2	22.5 M.s/cm	Non-electrolytic
B_3	137.0 M.s/cm	Electrolytic

Atomic Absorption Spectrometry

The atomic absorption technique is based on the absorption of light by free metal ions to determine the concentration of chemical elements (a specific element) in a sample of the complexes created. It can measure more than 70 elements by absorbing the optical beam (light) of free atoms in the gaseous state [23].

The calculated and found values showed in Table 6 and both values are in good agreements.

Table 6. The atomic absorption values of the synthesized complexes (A_1-A_3) and (B_1-B_3).

Complexes	Chemical formula	M.wt. (g/mol)	Calculated Values	Experimental Values
A_1	$[Cu_2L_1(Cl)_2(H_2O)_2]Cl_2.2H_2O$	469	27.1 %	26.89%
A_2	$[Ni_2L_1(Cl)_2(H_2O)_2]Cl_2$	441	26.5 %	25.5 %
A_3	$[Cr_2L_1(Cl)_4(H_2O)_4]Cl_2$	535	19.4%	17.3 %
B_1	$[Cu_2L_2(Cl)_2(H_2O)_2]Cl_2$	659	19.2%	18.98 %
B_2	$[Ni_2L_2(Cl)_4].3H_2O$	667	17.5%	16.4 %
B_3	$[Cr_2L_2(Cl)_2(H_2O)_4]Cl_2.2H_2O$	708	14.6%	13.3 %

Thermal Analysis

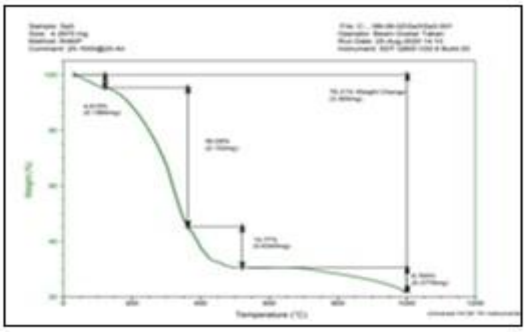
This technique is concerned with thermal analysis of inorganic and organic compounds, whether solid, semi-solid or liquid. All thermal analysis techniques simply measure the change of a specific property of a substance as a function of temperature and access to required information related to chemical compounds, including dynamic and thermal equilibrium.

This technique calculates the lost weights of vehicles in several steps, after gradually increasing temperatures from −150 °C up to 2400 °C [24].

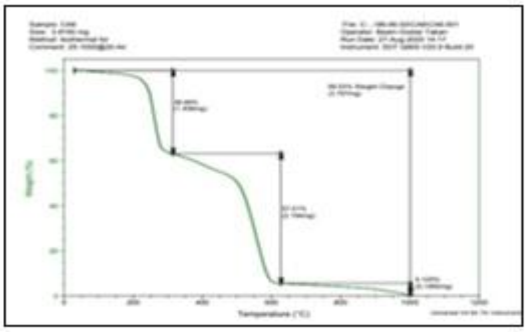
As there is an initial loss of water molecules and gases, then partial loss of the compounds occurs by breaking them down by high temperature. Thus, we obtain metal oxides [25] as a final step of the thermal decomposition process for these processed complexes. The Table 7 described assignments of the complexes for thermal gravimetric analysis. Figure 4 shows thermal graphic analysis of the synthesized complexes (A_1-A_3) and (B_2-B_3).

Table 7. The lost parts at temperature ranges of (A_1-A_3) and (B_2, B_3) complexes.

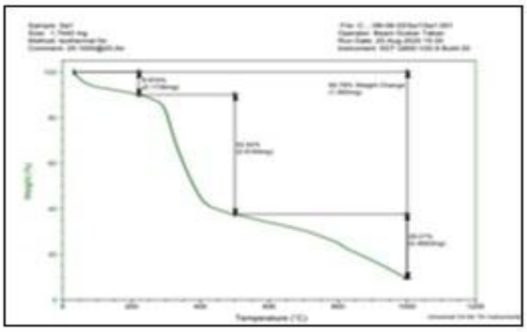
Complexes	**TGA range °C**	**Mass lose %**	**Theoretical**	**Assignments**
A_1	0 – 135	4.6%	3.8%	Loss of one (H_2O) lattice molecule.
	135 - 360	50.09%	52.0%	Loss of $2Cl_2$, $2(H_2O)$ and $2(NH_2NH_2)$.
	360 – 530	14.77%	17.9%	Loss of C2N2S.
	> 620	31.7%	33.9%	Removal 2(CuO) residue.
A_2	0 – 320	36.8%	40.3%	Loss 2 H_2O and 2 Cl_2.
	> 620	57.5%	59.6%	Loss of L_1 and Ni_2 metal.
		5.6%	–	Not found residue (99.53)
A_3	0 – 230	9.97	13.2%	Loss of Cl_2
	230 – 500	52.52	51.9%	Loss of $2Cl_2$,$4H_2O$ coordinate water molecule and $2NH_2NH_2$
	> 620	28.2%	25.9%	Loss of Cr metal and C_2N_2S
		9.3%	14.2%	Loss of ½ Cr_2O_3
B_2	0 – 325	8.3%	8.0%	Loss of ($3H_2O$) lattice molecule.
	325 – 480	47.8%	49.1%	Loss of $2CL_2$, $2(C_6H_5OH)$ molecule.
	480 – 590	31.2%	33.9%	Loss of $C_4H_4N_6S$ molecule
	> 620	12.5%	11.1%	Removal NiO metal oxide.
B_3	0 – 190	20.4%	15.1%	Loss of $2H_2O$ Lattice water and Cl_2
	190 – 350	18.2%	20.1%	Removal Cl_2 and $4H_2O$ coordinate.
	350 – 610	54.53%	57.3%	Loss L_2 and Cr metal
	> 610	12. 2%	14.1%	Remove CrO_3



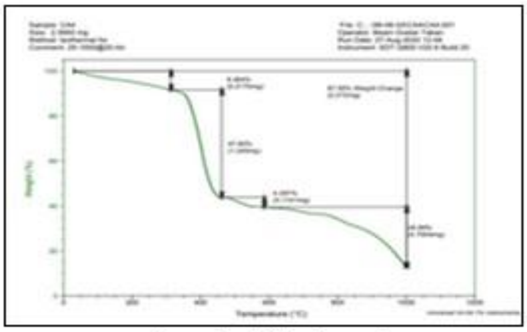
Thermal analysis for A$_1$ complex



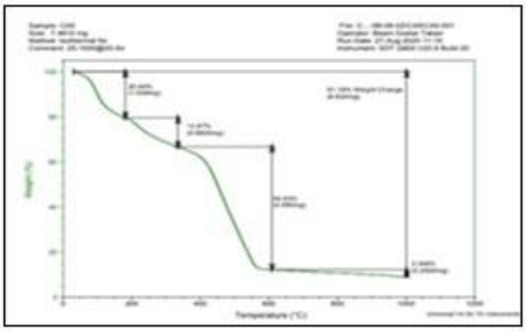
Thermal analysis for A$_2$ complex



Thermal analysis for A$_3$ complex



Thermal analysis for B$_2$ complex

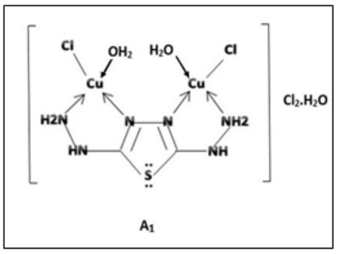


Thermal analysis for B$_3$ complex

Figure 4. Thermal graphic analysis of the synthesized complexes (A$_1$-A$_3$) and (B$_2$-B$_3$).

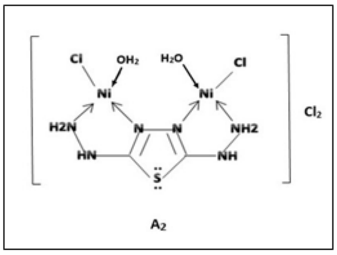
4. Conclusion

In complexes of L$_1$ the coordination pattern is N$_2$-bidentate chelation forming stable 5-membered ring for the three metal ions, in complexes of L$_2$ the presence of hydroxyl group assisted to form tridentate coordination pattern of N$_2$O of facial geometry using 6-membered ring in chromium complex and not the other. Therefore; according to the previous results the suggested structures and chemical formula for all complexes are shown below:



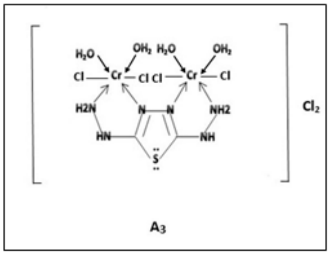
A1

$[Cu_2L_1(Cl)_2(H_2O)_2]Cl_2.2H_2O$



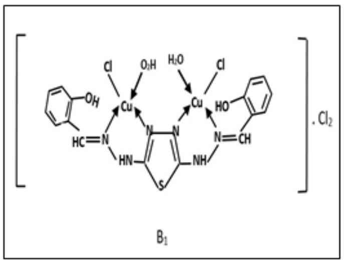
A2

$[Ni_2L_1(Cl)_2(H_2O)_2]Cl_2$



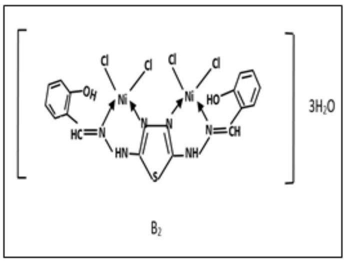
A3

$[Cr_2L_1(Cl)_4(H_2O)_4]Cl_2$



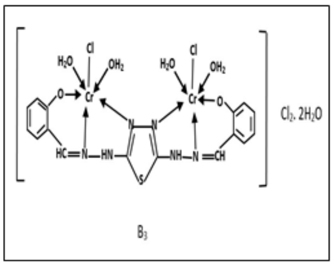
B1

$[Cu_2L_2(Cl)_2(H_2O)_2]Cl_2$



B2

$[Ni_2L_2(Cl)_4].3H_2O$



B3

$[Cr_2L_2(Cl)_2(H_2O)_4]Cl_2.2H_2O$

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