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Synthesis and Thermal Studies of Some Metal azo Complexes Derived from Hydroxy coumarin

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Abstract

In the current study, of two azo dyes made from coumarin and procaine (T1) and coumarin and Sulfa guanidine (T2)were synthesized. The dyes were characterized by IR, CHN, ^{1}H-NMR, ^{13}C-NMR and MS spectroscopic techniques. .

To make azo metal(II) complexes, these novel legands were combined with acetate salts of copper(II) and nickel(II) in a 1:2 molar ratio.The metal to ligand ratio [M:L] in all complexes, according to analytical data, is (1:2).This ligand behaves as a bidentate chelating, according to spectral and analytical data.Thermo gravimetric (TGA) analysis was used to study the thermal behavior of these substances. These chemicals' thermal breakdown is a multi-stage process

1. Introduction

Azo compounds play a critical part in the dye and printing market's governance

.These dyes are made using a simple diazotization and coupling technique To get the appropriate color characteristics, yield, and particle size of the dye for better dispersibility, many approaches and modifications are used[1]. Aside from their negative effects on humans and aquatic life, azo dyes have prompted urgent calls for the treatment of effluents containing azo dyes in order to eradicate or convert them into useful and safe products, utilized in a range of applications, notably as antiseptics.[2] Antimicrobials[3] antidiabetics[4] antineoplstics[5] antiulcerative[6] and antitumor[7] Coumarins are benzopyrones with a wide range of structural properties as well as biological and pharmacological effects[8].Several chemicals in this class have antibacterial, antifungal, and antiviral properties. antifungal [9]. Numerous coumarins have also been investigated for their diverse biological activity as anticoagulants [10], antithrombotics [11] and HIV inhibitors [12], On the other hand Sulfanilamide and its derivatives have been studied for various reasons such as pharmacological screening of its substituted derivatives [13], evaluation of its ciprofloxacin conjugates [14], as antimicrobial drugs [15], biological evaluation as antimicrobial agents [16], sorption to soil organic sorbents [17], characterization and spectral study [18], pharmacological screening of its substituted derivatives [13], pharmacological screening of its ciprofloxacin conjugates [14]

Metal coordination complexes have grown in importance in medicinal chemistry, owing to their physicochemical characteristics, various oxidation states, and stereochemistry, which make them ideal candidates for the development of new metal-based therapeutic medicines. Furthermore, depending on the structure of the ligand, the biological effects and reactivity of metal-based medications can be easily modified. [19]

Metal complexes of coumarins have been studied for a wide range of therapeutic applications. Metal complexes obtained in some cases had higher biological activity than their ligands [20-22], We recently established that metal complexation has a favorable effect on the nonlinear optical characteristics of some electroactive ligands.[23-26]

The goal of this research was to learn more about the synthesis and characterisation of two azo dyes made from coumarin and Sulfa guanidine (L1) and coumarin and procaine (L2), as well as their Cu(II), Co(II), and Ni(II) complexes. Various analytical methods have been used to investigate the coordination behavior of these azo compounds towards Cu and Ni ions. Its biological activity is also examined.

2-EXPERIMENTAL

2-1 .Material and instrumentation

All compounds employed in this study were analytical grade.TLC was used to assess the purity of the compounds. Using KBr pellets, the produced products were analyzed using FT-IR (on an ashimadzu 8400 FT-IR spectrophotometer.Using a Euro EA elemental analyzer, element analysis (C.H.N) was performed, and (C, H, N) analysis revealed that the calculated and found values were within permissible limits.

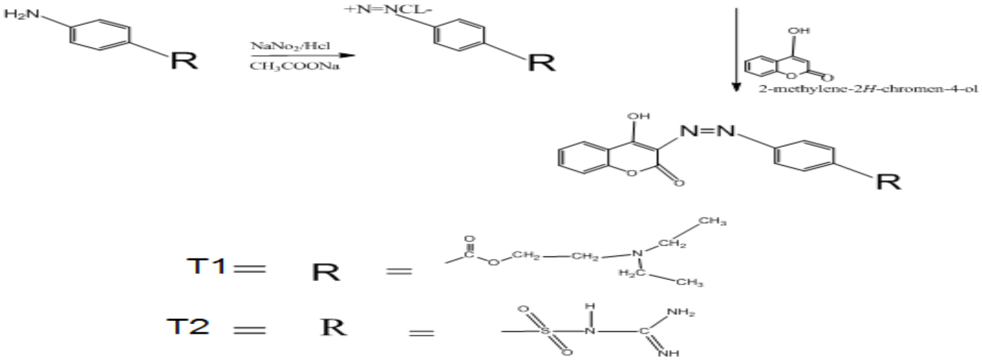
On a Bruker -500 MHz spectrophotometer, the 1 H NMR spectra of ligand were obtained in DMSO-d6 as the solvent, with TMS [Si(CH3)4] as the internal standard.The chelate complexes' conductivity was measured in a Jenway Pcm3 Conductivity meter in DMF (10-3M) at room temperature.

The magnetic susceptibility of metal complexes was measured using the Faraday balance technique.The metal content of the complexes was determined using Phoenix-986 atomic absorption, and thermal analysis (TG) was performed using TGA Q500- V6.7 in a dynamic nitrogen environment (50 ml/min) with a heating rate of 10C/min.

The agar well diffusion method was used to assess in vitro antibacterial activity against various bacterial and fungal infections.

2-2. Azo dye ligand preparation

Azo ligands (**T1,T2)** were synthesized by dissolving 0.004 moles of each(procaine and sulfagundine) in 1.4 ml concentrated HCl and 20 ml distilled water, then drop by drop at - 5 ^{o}C, a stirring solution of (0.304 g sodium nitrite in 20 ml distilled water) was added to form diazonium salt.The above diazonium salt was added to an alkaline solution of 0.004mole of 4- hydroxycumarain in (1.2 percent w/v. NaOH).Then, by adding dilute HCl (to maintain a pH value of 6.5 – 7.5), convert the prepared dye from sodium to hydrogen.To remove any remaining un reacted substances.The product was purified by washing with distilled water and recrystallized by using ethanol as solvent and dried in a vacuum at 50°C for several hours(27) as shown in scheme 1



scheme 1

2. Preparation of nickel and copper azo complexes

Metal complexes were synthesized by mixing matching metal chlorides with an azo dye ligands (T1 or T2) in a 1:2 [M:L] molar ratio.An ethanolic solution (0.002 mol) was mixed in 50 mL of azo dye ligand(T1 or T2) , and (0.001 mol) of Fe(III), Co(III), Ni(II)and Cu(II chlorides were dissolved in 40 mL hot buffer solution (ammonium acetate) at pH = 7 .The solid metal complexes were separated, washed with a little amount of heated ethanol (5 mL) to eliminate any unreacted material, and then wished with distilled water.The metal complexes were then dried for several hours in a 60 °C oven and maintained under vacuum desiccators over fused CaCl2.The percent yield, molecular formula, molecular weight, color, and element analysis data (CHN) of azo dye ligands and their metal complexes. (28)

3. Results and Discussion

At room temperature, the novel two azo ligands and their complexes are stable in air. Most solvents [acetone, THF, DMSO, DMF, Methanol, Ethanol] are highly soluble in azo ligand, while it is only sparingly soluble in water. Thin layer chromatography (TLC) was used to confirm the ligand's purity. Metal:ligand complexes are found in a [1:2] ratio.
Table 1 summarizes the results of the elemental analysis and physical properties of the complexes, which are in good accord with a hypothesized molecular formula indicating that the ligand behaves bidentate in produced complexes.

Table 1: Analytical Data And Physical Properties Of Azo Legands And Their Complexes

Table 1: physical and analytical data of novel azo dye of ligand (T1 and T2) and its metal complexes

Compd	Molecular formula	m.p ºC	COLOR	C % Cal. (found)	H % Cal (found)	N % Cal (found)	M % Cal (found)
T1	$C_{22} H_{23} O_5 N_3$	d205	Yellow-orange	62.11 (61.10)	5.41 (5.01)	9.8 (9.6)	0
T2	$C_{16}H_{13}N_5O_5S$	198	yellow	49. 57 (49.56)	3.35 (3.35)	18.07 (18.07)	0

3.1- The FT-IR spectra

The FT-IR spectra data for azo dye ligands (T1and T2) and its chelates complexes with Cu(II), and CO(II) are given in Table.3. FT-IR spectrum of the chelates complexes and free ligand reveals a number of varied absorbance bands. These absorbance bands that appeared on the FT-IR spectrum were owing to active functional groups present [29-30]. Through this study shows that the shifts and change were occurred on absorbance bands at certainly wavenumber when these bands are compared with those that corresponding into free azo dye ligand and that it is pointing into formation a new shapes and coordination for metallic ions with of free azo ligand to created metallic chelates complexes and suggest the possible bonding modes in the complexes.. [31] The IR spectra of the free ligand reveals a medium band about 3400-3500cm-1,**t**he appearance of a broad band at (3200) attributed to (OH) and group due to stretching vibrations (NH) . A prominent intensity band in the region of 1150-1380cm-1 is seen due to the (C-N) in the azo ligands.Due to (C-N) in the azo ligands, there is a strong intensity band in the region of 1150-1307cm^{-1}. This band was shifted to lower frequency in metal complexes,indicating the imine nitrogen atom coordination to metal ions [32].

The azo spectrum displays the azo (-N=N-) group at 1481 cm^{-1},this group is changing to lower frequency at (1417-1516)cm-1,suggests its participation inbonding with metal ions [31]

The stretching vibration of N=N bond gives rise to a band at 1460 – 1428 cm -1 while the bending vibration band of the OH group appears at 1230 – 1216 cm $^{-1}$.[32]

The out-of-plane deformation vibration of the hydrogen atoms contained in the ring is responsible for the majority of the strong bands seen in the range 1000–625 cm-1.

The number of nearby hydrogen atoms can be used to describe the band position.

The out-of-plane C-H deformation of two nearby hydrogen atoms is ascribed to the weak to medium bands at 848 – 835 cm $^{-1}$. The strong band at 729 cm -1 in the spectra of compound (I) is caused by the deformation vibration of three neighboring hydrogen atoms.

New bands at (580-592)cm-1 which are not present in the free ligand are attributed to **υ**(M-O) and (M-N) vibration. The appearance of weak intensity bands in spectra of metal complexes[30]

Symb. Of Comp.	νN-H	νO-H	νC=O	νC=CAr	ν N=N	ν C-N	υ(M-O)	υ(M-N)
T1	3480	3500	1697	1558	1558	1606		
T1Cu	3419.79	3442	1703	1598	1529	1465	520	422
T1Co	3419.79	3454	1633	1598	1533	1421	551	451
T2	3442	3342	1701	1606	1548	1195		
T2Cu	3444	3338	1691	1612	1527	1170	758	524
T2Co	3462	3365	1741	1633	1508	1172	759	551

3.2 The 1-HNMR spectra of T1 and T2

Figure 1-2 shows a variety of signals between (δ =6.688-8.3) ppm that correspond to aromatic protons in the 1HNMR spectrum of the ligand.Spectra revealed a sharp peak at 3.4 ppm owing to dissolved water in DMSO, and a peak at 2.5 ppm attributed to the DMSO solvent.In DMSO as a solvent, the 1H-NMR spectra of the azodyes (Figs. 1 and 2) were determined.In the spectrum data of theazodyes, the phenyl ring displays peaks at (6.82-8.12 ppm).A single peak (δ 15.46 ppm) is produced by the OH groups in azodyes.

The signal peaks at 1.05-1.1 ppm due to s,2H,NH2 The result is shown in Table (3) [33].

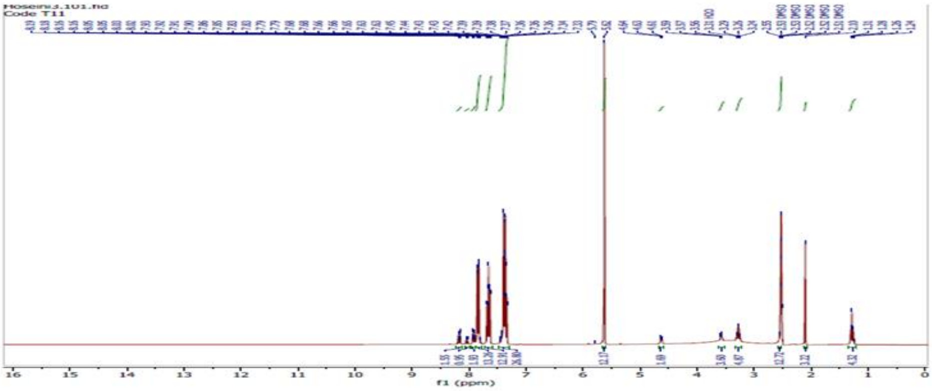


Fig1. NMR spectra of T1

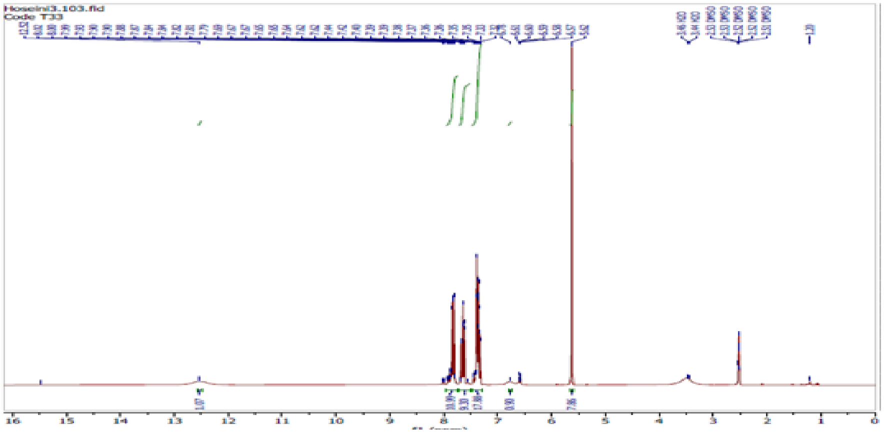


Fig2. 1H NMR spectra of T2

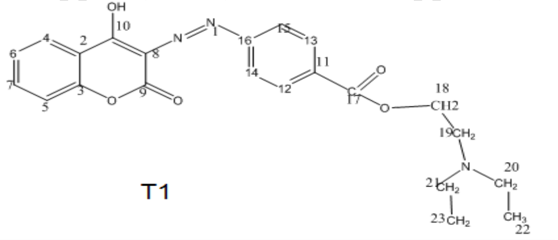
TABLE 2 .^{1}H-NMR- Spectra of T1 and T2 compounds.

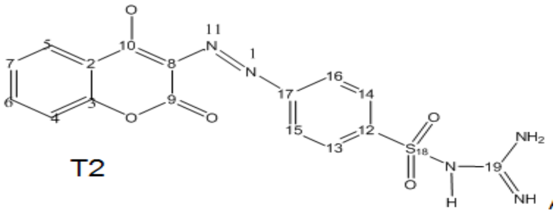
Legand	Chemical shif (δ (ppm))
T1	2.2(2H, CH_2) , 2.5 (2H , CH_2) , 5.6 (5H , C_2H_5) 8.2 (1 H , OH) , 8.5 (8 H , Ar- H)
T2	6. 71 (1H ,NH) , 3.5 (2H , NH) , 12.5 (1 H , NH) 5.55 (1H , OH) ,6.5 (8 H,Ar –H)

3.3The 13-C NMR spectra of T1 and T2

Using DMSO as a solvent, the 13C-NMR spectrum of azo ligands T1 and T2 was measured.

T1 azo dye ligand has a 13C-NMR spectrum of δ =40 ppm (C20), δ =67 ppm (C17), δ =165 ppm (C9), and δ =162 ppm (C16)fig 3.ligand T2 (Figure 4) δ =154 ppm (C17), δ =177 ppm (C10), δ =163 ppm (C9), δ =110-150 ppm (C-Ar), and δ =90 ppm (C-Ar) (C19) (33)


T1


T2

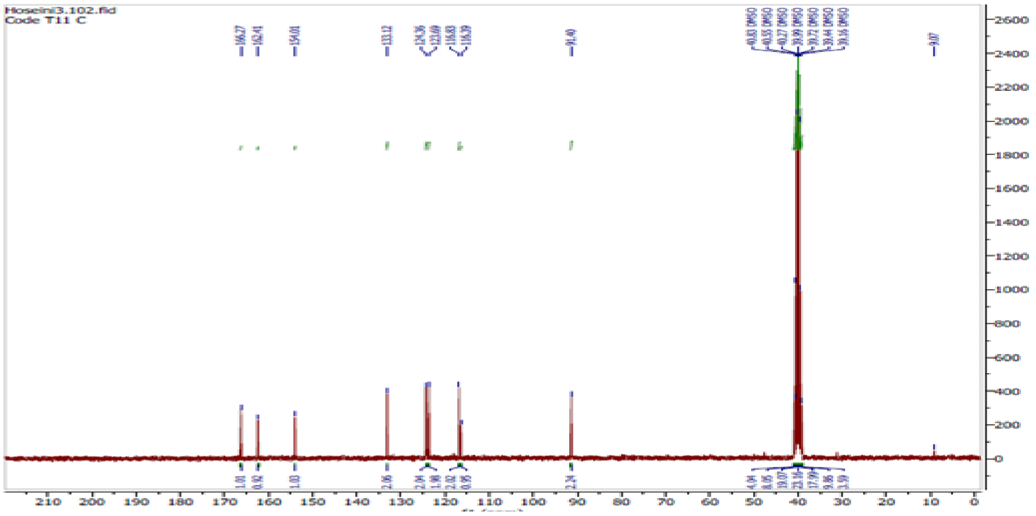


Fig 3 -13C-NMR OF T1

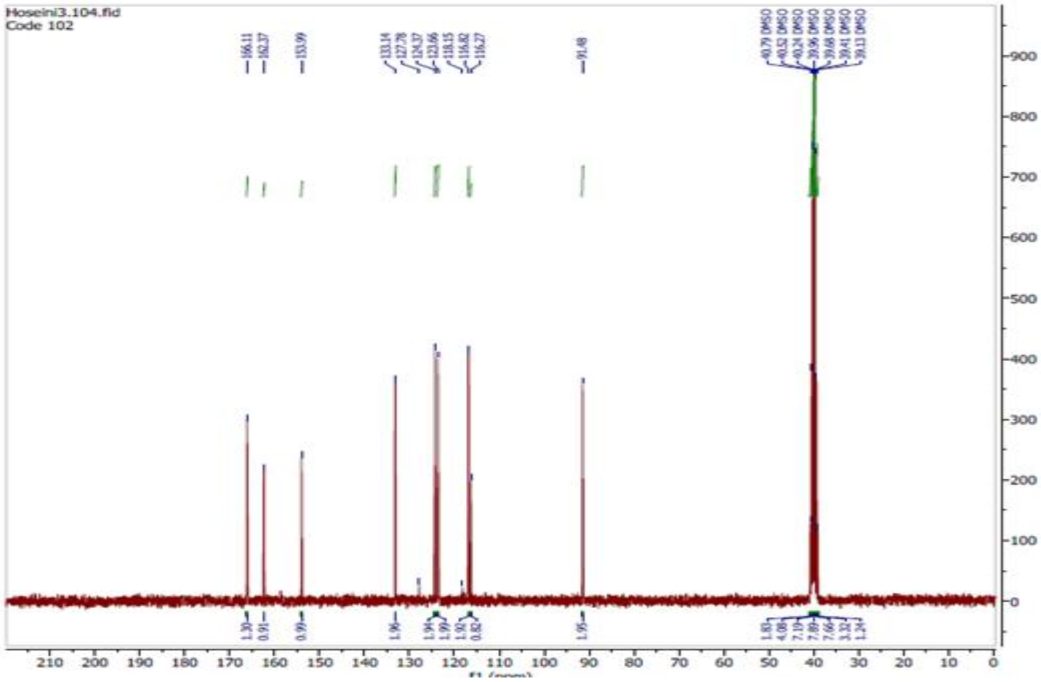


Fig 3 -13C-NMR OF T2

3.4- Mass spectra

The structure of transition metal(II) complexes can be elucidated using mass spectra of synthesized compounds. The stoichiometry of complexes was compared using mass spectra obtained at room temperature (Table 3). (figure 4and 5).Each synthesized complex matched the molecular ion fragment and supported the complexes' proposed structure. [34]

Table-4 Mass spectra of prepared complexes

Compound c	Obtained mass M/Z	Peak assigned
T1Cu	$C_{38}H_{30}O_{10}N_5Cu$	814
	$C_{38}H_{30}O_{10}N_3Cu$	786
T1Co	$C_{29}H_{36}O_7N_4Co$	610
	$C_{29}H_{32}O_7N_4Co$	583
T2Cu	$C_{35}H_{24}O_{10}N_7S_2Cu$	818
	$C_{29}H_{19}O_{10}N_7S_2Cu$	719
T2Co	$C_4H_{11}O_2N_3$	123
	C_4H_5SCo	95

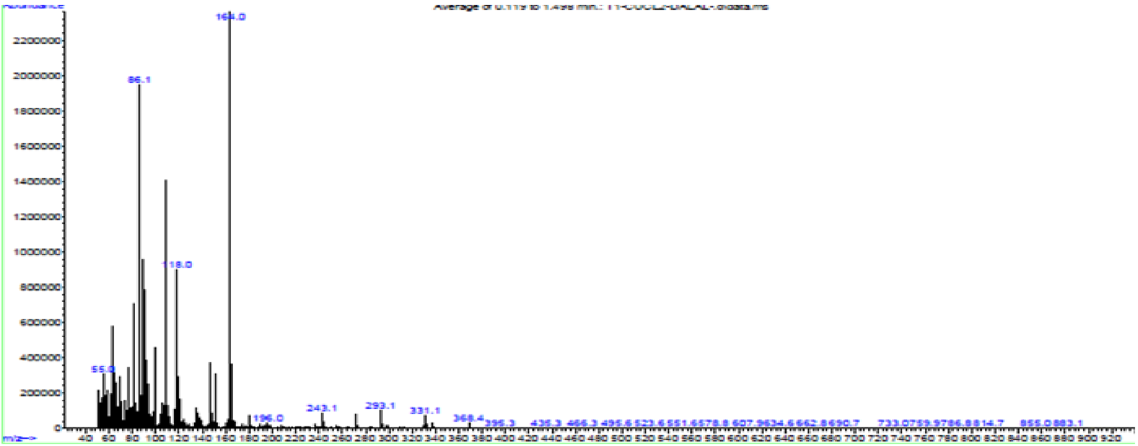


Fig 4-Mass spectra of of T2 l complex

3.5. A study of molar conductivity

The molar conductance of the solid complexes (m) was measured at room temperature in DMSO solvent at a concentration of 10^{-3} M.The findings in Table(1) in the supplemental data demonstrate that the molar conductance of Cu(II) and Ni(II) is comparatively low, indicating that these complexes are non-electrolytic. As a result, the results of the elemental analysis and IR spectral data are confirmed by the molar conductance data (table 1) [35].

3.6.Metal content estimation

The total metal content was estimated using the direct approach of atomic absorption analysis.

Each metal had a number of reference standard solutions developed in various concentration ranges. The absorbances of these solutions were measured using a background adjustment approach at the specified wavelength of each metal[36]. For metals solutions, calibration graphs were plotted. Using the standard values, the concentrations of unknown solutions were determined from their respective absorbances.The findings of the investigation are presented in table 1

3.7.Interpretation of structural

The metal complexes are colorful, air-stable, and water, ethanol, and non-polar solvents insoluble. They showed good solubility in polar solvents such as DMF and DMSO.

The nature of all metal complexes created was non-electrolytes.

The elemental, thermal, and spectral investigations contradict the proposed configuration structures (Fig. 1-3). (Tables 1-3).The structure of all complexes for four ligands can be interpreted with a comparable distribution of like coordinating sites fig(3), which coordinated to Cu(II) and Ni(II) based on the preceding data.) [30].

3.5.Thermal properties

The Cu(II) and Co(II) complexes are stable at room temperature and can be stored for several months without any changes. The obtained compounds were studied by thermogravimetric analysis(TG) from ambient temperature to 1000 0C under N2 atmospheres.. Typical TG curve is presented in Fig.(5&6).The data from TGA indicate the decomposition of the complexes proceeds in three or four steps. Crystal water molecules were lost between 25 and 160 0C and coordinated water between 160 and 250 0C.The second step los of organic moiety and some organic species table (4) [37].

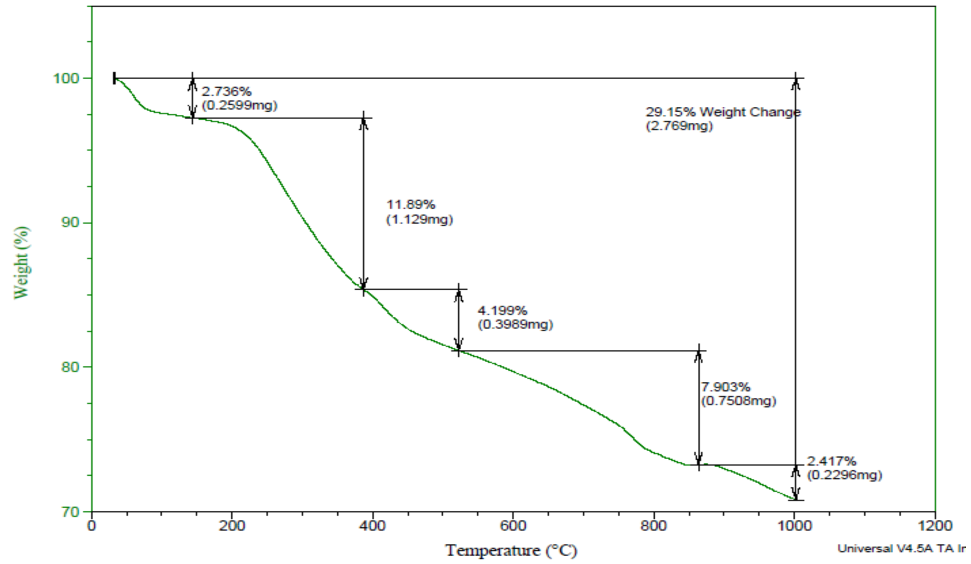


Fig 5-TG curve of T1Cu complex

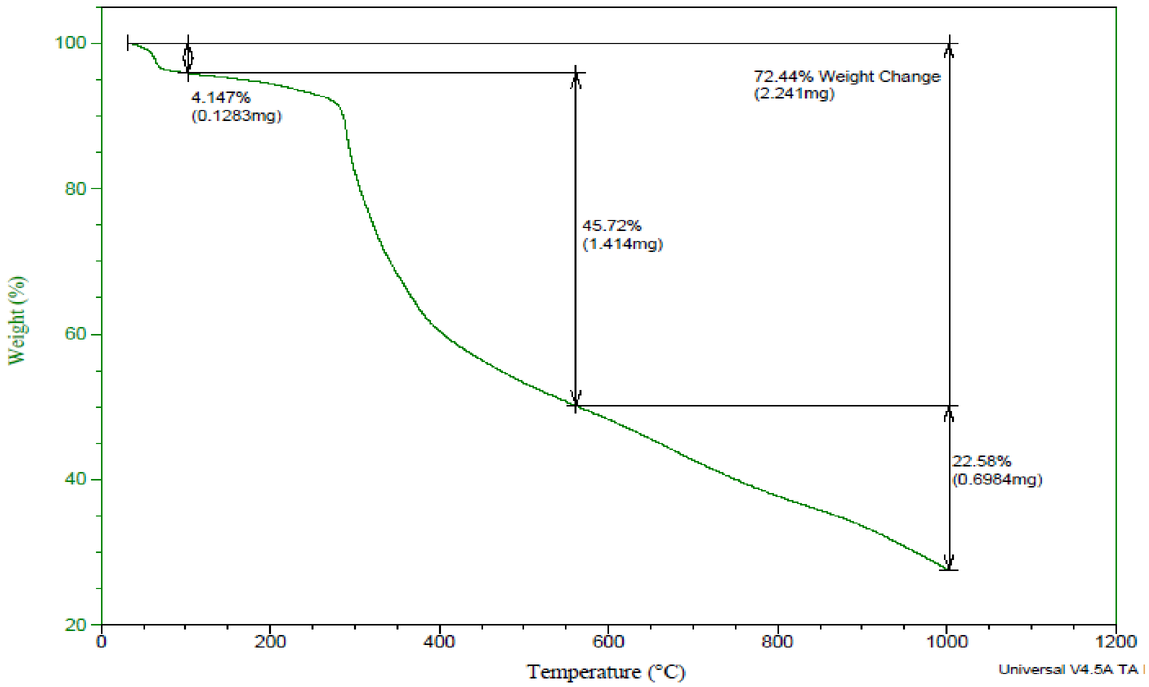


Fig 6-TG curve of T1Cu complex

TABLE 4. Thermoanalytical results for the complexes

Complex	Steps	TG range 0C	Mass loss found %	Mass loss calcd. %	Assignment (Removal of molecule)
T1Cu	1	**(50-150)**	**2.7%**	**2.9%**	**1.5(H2O)**
	2	**(150-400)**	**11.89%**	**11.3%**	$C_6H_{15}N$
	3	**(400-550)**	**4.19%**	**3.8%**	CH_2O
	4	**(550-850)**	**7.90%**	**7.6%**	C_4H_{10}
T1Co	1	**(45-130)**	**4.14%**	**3.95%**	$2H_2O$
	2	**(130-570)**	**45.7%**	**45.6%**	$C_{22}HO_5N_5$
	3	**(570-1000)**	**22.58%**	**21.6%**	$C_6H_{15}N$
T2Cu	1	**(40-150)**	**7.60%**	**7.4**	HSO_2
	2	**(150-440)**	**46.4%**	**46.8%**	$C_{15}H_{13}O_4N_5S$
	3	**(440-1000)**	**22.45%**	**23%**	$C_6H_4N_2$
T2Co	1	(50-150)	**5.77%**	**5.54%**	CH_3N_2
	2	**(150-350)**	**34.23%**	**34.14%**	$C_{13}H_9O_5SN_3$
	3	(350-1000)	**55.88%**	**60.5%**	$C_{15}H_8O_5SN_2$

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