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Synthesis, characterization of new 5-(4-nitrophenyl)-4-((4 phenoxybenzylidene)amino)-4H-1,2,4-triazole-3-thiol metal complexes and study of the antibacterial activity

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Abstract

A new Schiff base ligand (HL) was synthesized by condensation of 4-amino-5-(4-nitrophenyl)-4H-1,2,4-triazole-3-thiol with 4-phenoxybenzaldehyde. A new three metal complexes Zn (II), Cd (II) and Hg (II) with Schiff ligand (HL) were synthesized by molar ratio of ligand :metal as 2:1. The ligand and metal complexes were characterized by ¹H-NMR, FT-IR, Atomic absorption, CHNS analysis, molar conductivity, magnetic susceptibility and melting point. There are study thermal analysis TGA-DTG for the ligand and metal complexes. All complexes were found to be non-electrolyte. The biological activity (antibacterial) in-vitro are investigated for the complexes at prepared concentration (1*10⁻³ M) and showed inhibition ability against growth of the four types of pathogenic bacteria: [*Staphylococcus aureus*. and *Streptococcus sp.*] as gram positive and [*Escherichia coli* and *Pseudomonas aeruginosa*] as gram negative. The most of these complexes are effective against both types of bacteria in varying degree, with high activity for Hg (II) complexes.

Key word : 1,2,4-triazole, Schiff base, antibacterial, Zn(II), Cd(II) and Hg(II) metal ions

Introduction:

Heterocyclic compounds having difference heteroatoms such as O, N, or S have a tendency of forming coordination compounds/metal chelates used as active antimicrobial agents[1]. The 1,2,4-triazole Schiff base derivatives had many significant application in industry, agriculture,



and medicine.[2] The 1,2,4-triazole derivative have attracted widespread attention due to their diverse biological activities, especially as antimicrobial agents.[3] Schiff's bases are the compounds containing azimethine group (HC=N). They are condensation products of ketones or aldehydes with primary amines and were first reported by Hugo Schiff in 1864[4]. Schiff's bases of aliphatic aldehydes are relatively unstable and are readily polymerized while those of aromatic aldehydes, having an effective conjugation system, are more stable. Schiff's bases derived from triazole were reported to possess antimicrobial, anti anxiety, anti depressant, plant growth regulatory activity [5]. As ligands, Schiff's bases have been extensively studied. The azomethine group (HC=N), supported by other electron donor groups form stable chelates with many metal ions. Schiff's bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [6].

Experiment:

Material:

All the chemicals were used of Anala R grade and received from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and without purification .

Synthesis of 4-amino-5-(4-nitrophenyl)-4H-1,2,4-triazole-3-thiol.

This compound was prepared as lecture review [7]

Synthesis of Schiff base HL (5-(4-nitrophenyl)-4-((4-phenoxybenzylidene)amino)-4H-1,2,4-triazole-3-thiol) :

Equimolar of 4-amino-5-(4-nitrophenyl)-4H-1,2,4-triazole-3-thiol (0.237g, 1 mmol) in 20 mL ethanol was mixed with alcoholic 4-phenoxybenzaldehyde (0.198g, 1 mmol) in presence (3 drops) of glacial acetic acid (AcOH) and the reaction mixture was left under reflux for 4 h. The formed solid products were separated by filtration, purified by crystallization from ethanol, dried in a vacuum over anhydrous calcium chloride. The yellow color Schiff base product is produced in 75% yield .[8]

Eq.(1): synthesis of Schiff base HL

Synthesis of metal complexes (C1-C3):

Ethanoic solution of the metal salt chloride [Zinc chloride , Cadmium (II) chloride and mercury

chloride a hot solution of Schiff base ligand (HL) were mixed in 2:1 (ligand : metal) molar ratios under reflux for 2h whereupon the colure complexes precipitated.. The complexes were filtered and washed with hot alcohol. The products were dried at room temperature.

Result and discussion :

Physical properties and elemental analysis :

The data of atomic absorption ,CHNS and chloride analysis as well as the physical properties of the ligands and their metal complexes are show in Table (1). The molecular formulae of studied compounds were suggested depending on CHNS, chloride content, atomic absorption analysis , spectral data and conductivity measurements. The analytical data of the metal complexes are given in (Table 1). The data reveal the formation of complexes having 2:1 (ligand :metal ion)ratio . The data clearly indicate that, the ligand used act as neutral bidentate. The complexes are insoluble in common organic solvents but all complexes completely soluble in DMF and DMSO

FT-IR of Schiff base (ligand)(HL) and their complexes :

. The properties bands in the FT-IR spectra of Schiff base ligand and their complexes (C1-C3) were list data in Table (2) . These results establish that the ligand chelates with metal ions through the deprotonated sulphur of the (thiol) group and the nitrogen of the Azomethine group as bidentate ligand,[9, 10] Fig. 2.

Table (2):FT- IR-spectral data of Schiff base (ligand) and their complex

^1H -NMR of Schiff base (ligand)(HL):

The ^1H -NMR spectrum of Schiff base (ligand)(HL): in DMSO-d₆ is shown in (Fig.2) Signal assignments .Chemical shifts of N=CH Proton of azomethine exhibited a peak at δ = (8.40) ppm[11]. Chemical shifts of aromatic and triazole ring protons appeared at δ =(6.5 -7.8) ppm[12] , and δ =(8.70) ppm[24] respectively .The spectrum exhibited sharp peak at low field at δ =(12.00) ppm which signed to S-H proton of thiole and thion[9, 10] .

Fig.(2): ^1H -NMR spectra of Schiff Base Ligand

(HL) Molar conductance :

The molar conductance values of the synthetic complexes obtained in DMSO as a solvent at room temperature were listed in Table (3). The results which are given in this table showed

that all complexes have non-electrolytic nature[13].

Magnetic susceptibility:

The magnetic susceptibility measurements were contributed in the determination of complexes structure. These measurements provide information about the type of bonding and strength of the ligand field of complexes and also give information about the number of unpaired electrons. The effective magnetic spin of the complexes were measured by using only a spin magnetic moment ($\mu_{S.O}$) according to the following equation[14]

$$\mu_{S.O} = 2 \sqrt{S} \text{ (B.M) where } S = n/2 \text{ (n = number of unpaired electrons).}$$

The results obtained from this equation were compared with the actual values obtained through the magnetic measurements as in Table (3). These values were corrected for diamagnetic effects using the following relationship[15]

Thermal analysis :

The Thermal decomposition of Schiff base (ligand)and their metal complex (C1-C3) follows Thermogravimetric and Differtial thermal analyses under nitrogen inert gas with heating range (50-1000) °C and heating rate 10 °C/min. The following results were obtained and explained according to analytical suggestions mentioned in the literature [16]. As a common behavior, at low temperatures some TG and DTG curves of the synthesized complexes mentioned above are shown the stage of mass-loss of water hydration molecules as show in Figures (3-6).

Biological activity :

The are many factors influence on the biological activities of ligands and metal complexes such as type of ligand, type of metal ion ,electron configuration of metal ion , the transition series and geometry of complexes[17] . In vitro Antibacterial Activity The antibacterial screening of all synthesis compounds were tested against (Escherichia Coli ,Klebsiella Pneumonia) as gram negative bacteria and (Staphylococcus aureus,streptococcus sp.) as gram positive bacteria with agar diffusion method , using (10⁻³ M) of studied compounds in DMSO.The antibacterial activities of studied compounds (L&C1-C3) were compared with antibiotics Amicillin [18].The antibacterial data were listed in Table.4

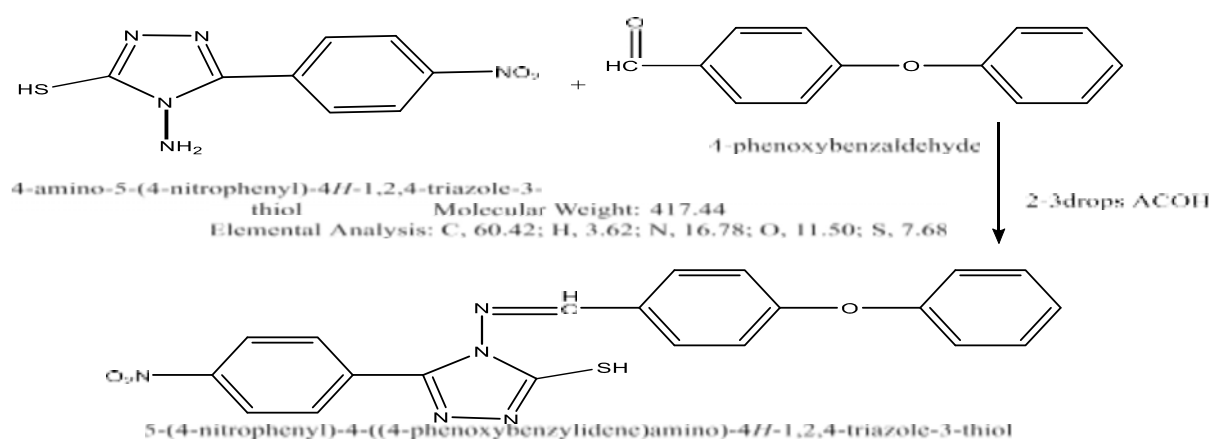
Conclusion :

The Schiff bases ligand (HL) were synthesized from 4-phenoxybenzaldehyde with 2-amino triazole derivative using reflux as reported in literature, three complexes have been synthesized with new ligand. These complexes of the type (1:2) where the order is metal: ligand, were identified and their structures were confirmed by elemental analysis (CHNS), atomic absorption, thermal analysis (TG, DTG), FTIR, ¹H-NMR, molar conductance and magnetic properties. In this study the synthesized ligand represents a group of bidentate ligands of Schiff-bases type exhibiting good complexing properties. In all complexes the coordination of Schiff-bases with metal ions took place through the azomethine nitrogen and thion groups. All the synthesized complexes were tested in-vitro against some gram positive and gram negative bacteria and their results were compared to the broad spectrum antibiotic (Ampicillin). Mercury of the complexes showed very good results activity against the tested bacteria results and some of the synthesized complexes were even better than the antibiotic itself.

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Eq.(1): synthesis of Schiff base HL

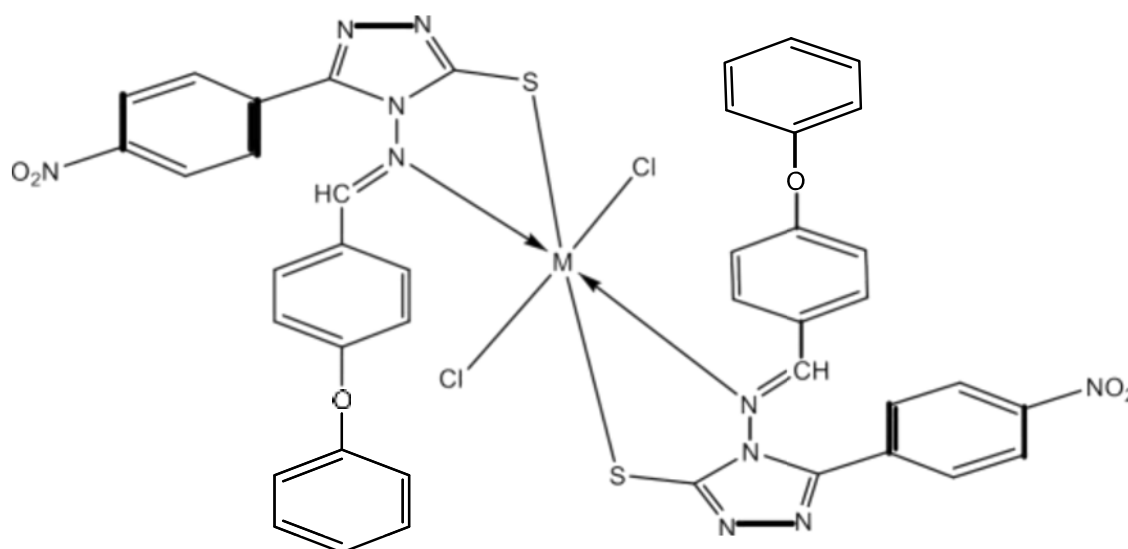
Table (1) : Physical properties and analytical data for Schiff Base ligand and their complexes

symbol	color	m.p °C	Yield %	M.Wt	Micro Elemental Analysis Found (calc.)				Metal content % Found (calc.)	Chloride content % Found (calc.)
					C%	H%	N%	S%		
L	Yellow	270-272	75	417.44	(60.42) 59.90	(3.62) 3.44	(16.78) 16.10	(7.68) 7.20	-----	-----
C1	Brown	>300	60	996.15	(52.05) 51.90	(2.91) 2.60	(14.45) 13.95	(6.62) 6.02	(6.75) 6.12	(7.32) 6.96
C2	Green	>300	65	1053	(44.87) 44.66	(3.59) 3.11	(12.46) 12.00	(5.70) 5.20	(7.50) 7.80	(6.31) 5.97
C3	yellow	>300	55	1106	(45.68) 45.01	(2.56) 2.12	(12.68) 12.42	5.81 (5.44)	(18.16) 18.20	(6.42) (7.81)

Table (2) :FT- IR-spectral data of Schiff base (ligand) and their complex

Group	Assignment (cm ⁻¹)			
	L	C1	C2	C3
$\nu(\text{N-H})$ stretch (asym, sym)	3272-3373	3369-3425	3232-3323	3217-3369
$\nu(\text{C=N})$ imine	1568	1569	1571	1564

$\nu(\text{C}=\text{S})$	1166	1166	1168	1168
$\nu(\text{C}=\text{N})$ trz	1604	1602	1602	1600
$(\text{C}-\text{H})$ Ar	3033	3029	3035	3035
M-N		520	530	450
M-S		545	532	430
M-Cl		330	340	350



M(II)= Zn (II),Cd(II) and Hg(II)

Fig.(1) :structure proposal of metal ion complexes

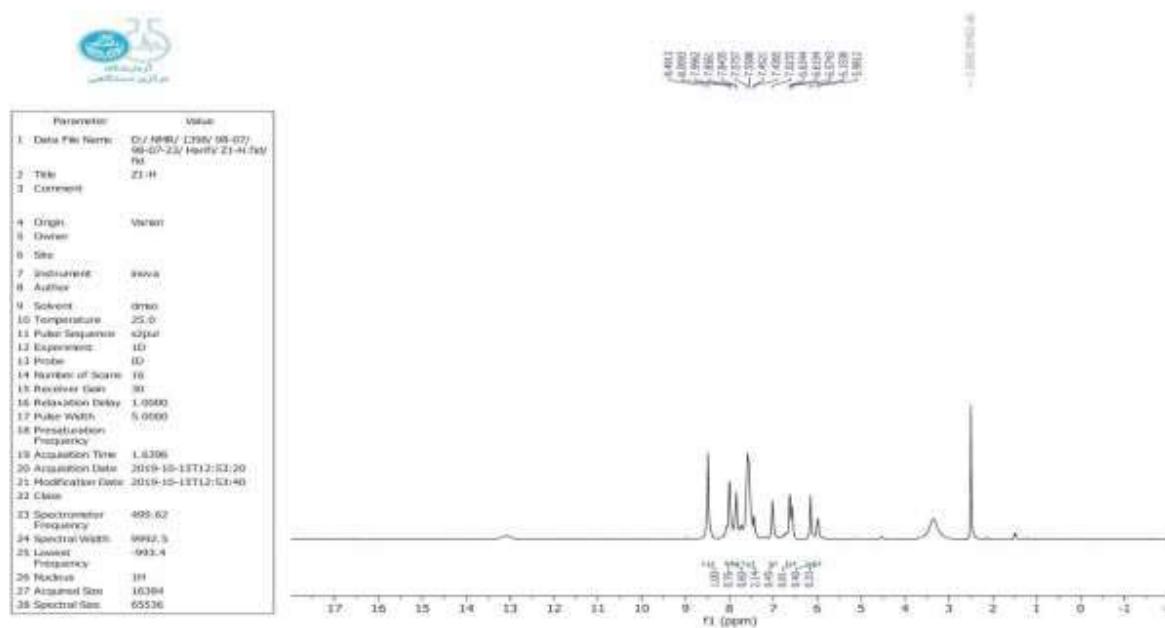


Table (3): Thermal decomposition data of the ligand and its metal ions complexes

Co mp.	Molecular formula M.Wt	Step	Temp. rang of the Decomposition C°	Suggested Formula of loss	Mass loss%	
					Cal.	Found
L	C₂₁H₁₅O₃N₅S (417)	1	0-175	CH	3.11	2.469
		2	175-	C ₁₂ H ₉ O	7	40.63
		3	340	C ₄ H ₂ N ₄ S	40.5	33.59
		4	340-	C ₄ H ₃	27	12.55
		5	560	Residue NO ₂	33.0	10.761
			560 - 1000 > 1000		93 12.2 30 11.0 33	
C₁	[Zn(L)₂Cl₂] (970)	1	0-170	CNO ₂	5.97	5.324
		2	170-	C ₉ H ₆ N ₄ SCl ₂	9	27.31
		3	320	C ₁₁ H ₉ NO ₃	28.0	20.89
		4	320-	C ₁₀ H ₆ N ₄ S	4	22.47
		5	470	Residue C ₁₁ H ₉ OZn	20.9	24.00
			470 - 1000 > 1000		27 22.0 61 22.9 93	
C₂	[Cd(L)₂Cl₂].6H₂O (1053)	1	0-150	2H ₂ O	3.41	2.387
		2	150-	C ₇ H ₄ N ₃ O ₂ Cl	8	22.47
		3	300	² C ₁₆ H ₁₂ N ₃ O ₃ S	22.6	30.20
		4	300-	C ₁₂ H ₉ N ₄ S	9	22.23
		5	510	Residue C ₇ H ₅ OCd	30.9	22.713
			510- 1000 > 1000		59 22.8 8 20.0 53	
C₃	[Hg(L)₂Cl₂] (1106)	1	0-185	Cl	3.20	3.77
		2	185-	C ₁₁ H ₇ N ₄ O ₂ S	9	27.69
		3	310	Cl	27.8	20.80
		4	310-	C ₇ H ₄ N ₄ S	93	15.37
		5	400	C ₁₁ H ₉ O	20.6	14.84
		6	400- 560	Residue Hg	14 15.9	17.89

			560- 1000 > 1000		13 14.1 9 18.1 8	
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Table (4): Magnetic susceptibility and Molar conductance for metal complexes(C₁-C₃)

compound	Molar conductivity Ohm ⁻¹ ,cm ² ,mole ⁻¹	Magnetic susceptibility(B.M)	
		Cal.	found
C ₁	40.21	diamagnetic	
C ₂	55.21		
C ₃	24.50		

Sample: L
Size: 4.5020 mg
Method: Dual Ramp
Comment: 25-1000@20-Ar

File: C:\099-02-16 98122603\VL.001
Operator: Beam Gostar Taban
Run Date: 07-May-2020 06:53
Instrument: SDT Q600 V20.9 Build 20

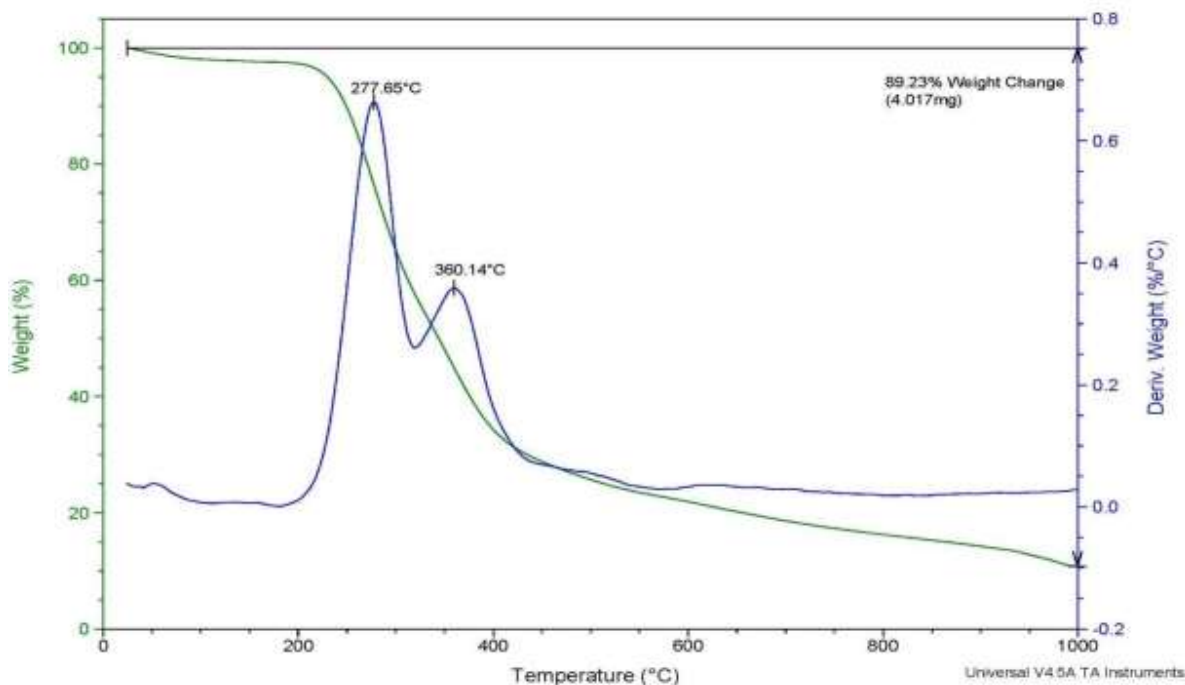


Fig.(3) Thermograph of Schiff base (ligand)

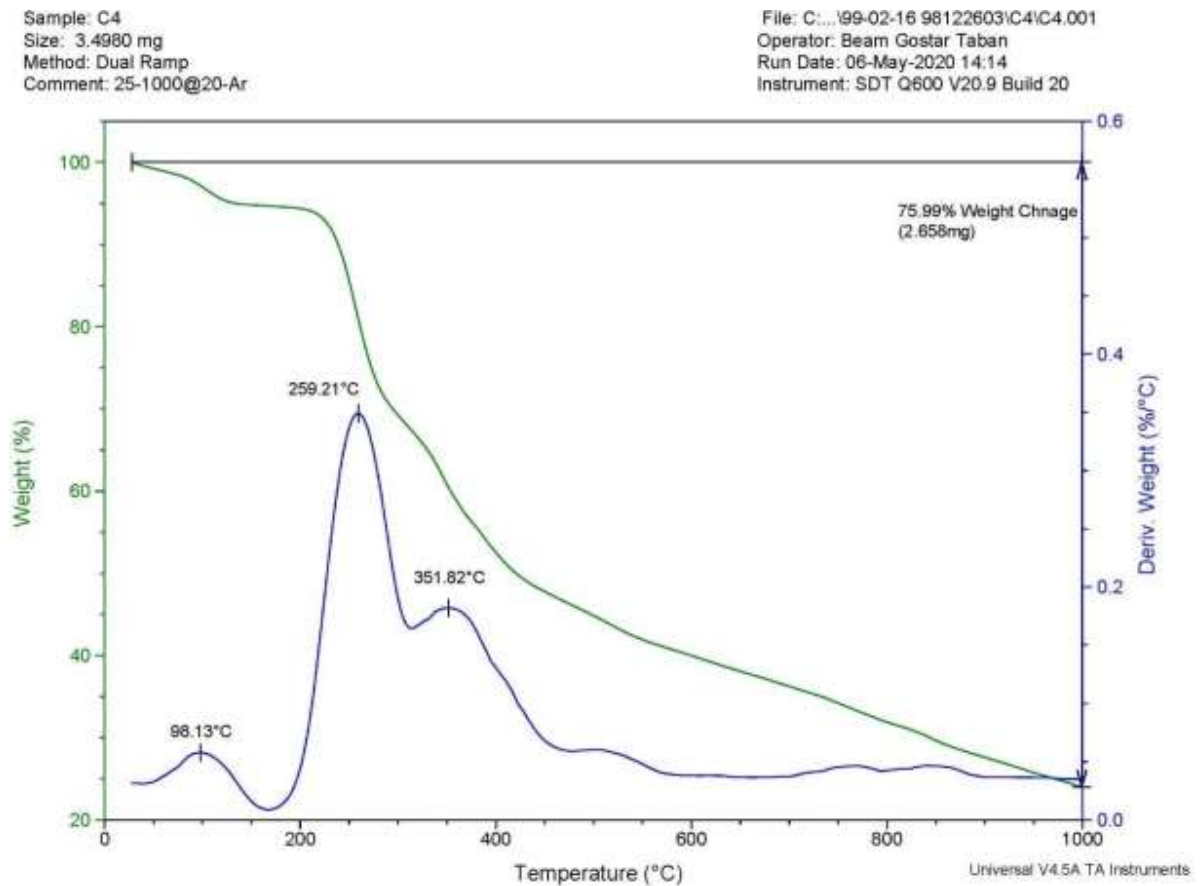


Fig.(4) :Thermograph of C1

Sample: C6
Size: 3.7220 mg
Method: Dual Ramp
Comment: 25-1000@20-Ar

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Operator: Beam Gostar Taban
Run Date: 06-May-2020 17:12
Instrument: SDT Q600 V20.9 Build 20

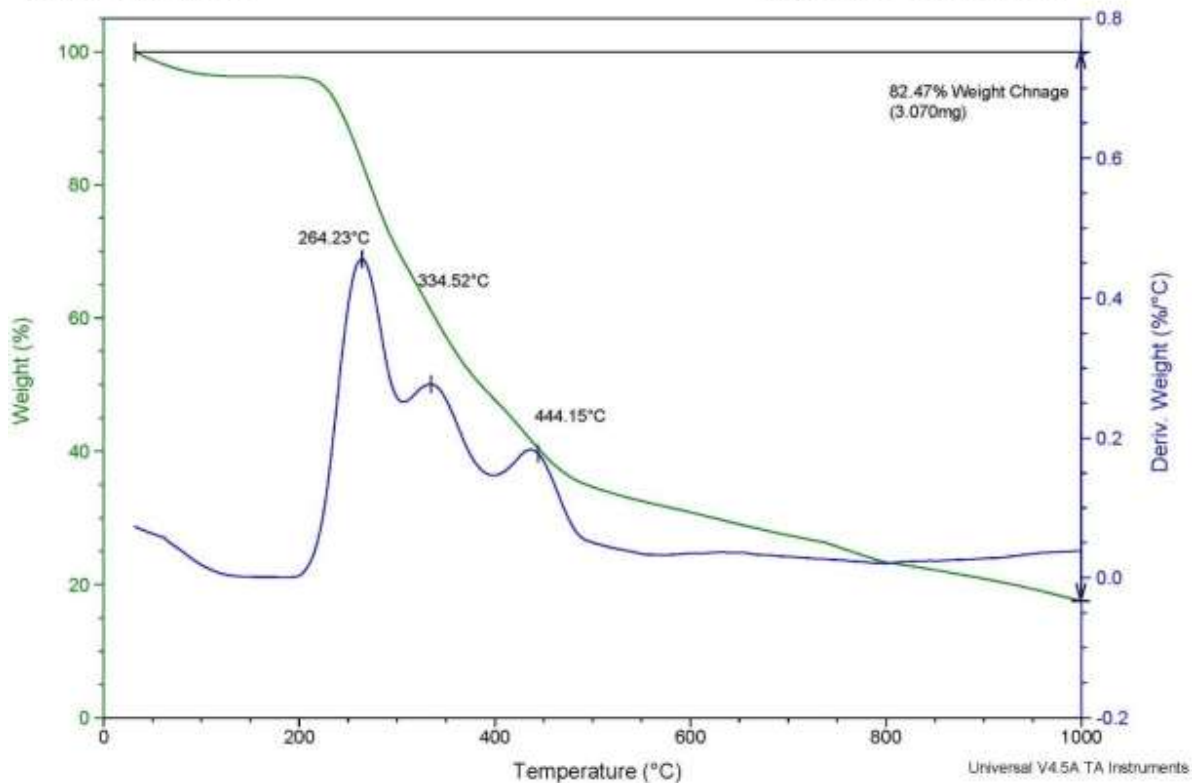


Fig.(5) :Thermograph of C2