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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF TWO PHENOL- SCHIFF BASES AND FORMALDEHYDE RESIN COBALT (II) - COMPLEXES.

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ABSTRACT: *Transition metal, cobalt (II) acetate, complexes of salicylaldehyde derived Schiff bases: 2-{[(2- hydroxophenyl) imino] methyl} phenol (OHMP), 2-{[(2- carboxy- phenyl) imino] methyl} phenol (COOHMP), and anthranilic acid- formaldehyde resin (R-COOHMP) were synthesized and characterized by various analytical and spectroscopic studies (FT-IR, UV-Visible and ^{1}H NMR). The Schiff base ligands, formaldehyde chelating resin and their Co(II) complexes were also screened for their urease, α – chymotrypsin, acetylcholinesterse and butylrylcholinesterase inhibition activities.The ligands were found active against two bacterial species: Staphylococcus aureus and Escherichia coli, all theligands and complexes were evaluated for their thermal degradation studies using TG- DTA analytical methods in static air.*

KEYWORDS: biological activity, formaldehyde resin, Cobalt (II)-complexes.

INTRODUCTION

Chelating properties of Schiff bases or Schiff bases resins towards different metal ions have been published investigating a variety of biological, clinical, analytical and industrial applications (1-4).The coordination compound are of considerable interest because metal ions are found in the active sites of a large number of metalloproteins such as hemocyanin, and also in metalloenzymes like in ureases, tyrosinase, lactase and ascorbate oxidase (5-7).These proteins are involved in various biological process such as biological electron-transfer reaction, oxygen atom insertion into substrates, dioxygen reduction to hydrogen peroxide or water and hydrolytic reactions.

Schiff bases have been known since 1864 when Hugo Schiff reported the condensation of primary amines with carbonyl compounds (8).Nowaday, the research field dealing with Schiff base coordination chemistry has expanded enormously. The important of Schiff base complexes for bioinorganic chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed(9).

Schiff bases resulted from aromatic aldehydesortho- substituted with a hydroxyl group have initially arouse the researchers' interest because of their ability to act as bidentate ligands for transitional metal ions (10-14). Schiff bases of salicyladehydes have also been reported as plant growth regulators (15) and antimicrobian (16) or antimycotic (17) activity.O-phenylenediamine Schiff bases show clinical properties (18). Istin Schiff bases were reported to possess antiviral, anti- HIV, antiprotozoal and anthelmintic activities (19). Certain cobalt Schiff base complexes are potent antiviral agent (20).

The thermal and anti-microbial properties of oligophenols with a Schiff base substitute and their polymer- metal complex compounds were investigated by Kaya etal.(21). In this article, we report the synthesis, characterization spectroscopy studies, thermal decomposition behavior and biological activity of two phenol- Schiff bases and formaldehyde resin cobalt (II) complexes.

Experimental:

General experimental

All the chemicals and solvents were of analytical reagent grade supplied by BHD and Merck, and used without further purification. The elemental analysis carried out by using CE-440 Elemental ANALYZER EAI EXETER ANALTICAL, INC. FT-IR spectra by KBr pellets were recorded with a FT-IR 8400S spectrophotometer model 2000 from SHIMADZU Japan. The absorption spectra in the UV- Visible range (200-800) nm were studied with a UV- 9200 BIOTECH ENGINEERING MANAGEMENT Co. LTD (UK.) UV. Spectrophotometer. The^{1}HNMR spectra was measured at room temperature by using a NMR spectrometer (Bruker, 300 MHZ). Thermogravimetric measurements were carried out under nitrogen atmosphere using a TGA $Q_{50}V_{20}$, 13 Build 39.

Synthesis of the two phenol – Schiff bases (OHMP), (COOHMP) and formaldehyde resin (R-COOHMP) by method similar to those reported in the literature (22-24).

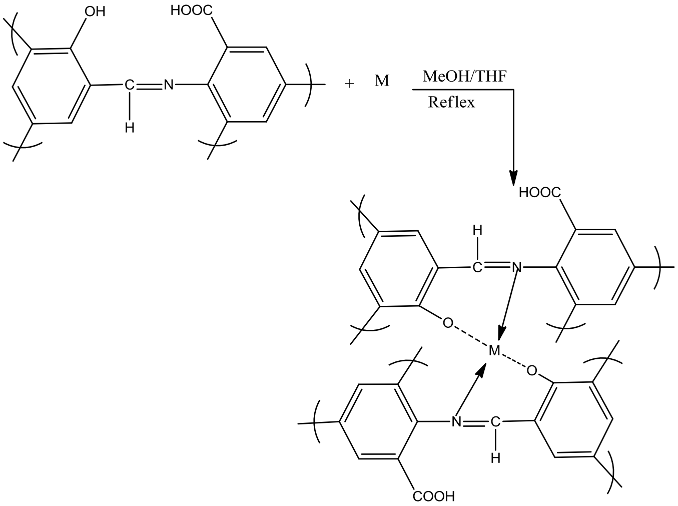
Synthesis of Co (II) - complexes:

[Co(OHMP)], [Co(COOHMP)] complexes

1 mmol of Co $(Ac)_2$. $4H_2O$, was dissolved in about 5-10 ml. of ethanol, was slowly added to a hot ethanolic solution of 1mmol of ligand. The mixture was then refluxed on water bath for 2 hours. The product was cooled to room temperature, upon cooling, coloured precipitates were formed. Which were filtered and washed with ethanol and then diethyl ether followed by drying at $50\overset{o}{C}$. overnight (25).

Synthesis of Co (II)- complex with formaldehyde resin :

A solution of $CoCl_2.6H_2O$ (1 mmol.) in MeOH (10ml.) were added to a solution of anthranilic acid- formaldehyde resin (R-COOHMP) (2mmol/ unit) in THF (20ml.). The mixture was stirred and heated at $70\overset{o}{C}$. for 5 hours (scheme 1). The precipitated complex was filtered, washed with cold methanol / THF(1:1) and dried in a vacuum oven at $110\overset{o}{C}$. (26).



Scheme 1. synthesis of Co(II)- Complex with formaldehyde resin (R-COOHMP-Co)

Antibacterial Activity:

Test-bacteria

The antibacterial activity of the complexes was assessed against some bacterial species: Staphylococcus aureus ,Escherichia coli. Overnight cultures were used. After 24h of incubation, bacterial suspension (inoculums) was diluted with sterile physiological solution, for the diffusion test, to 10^8 CFU/ml. (turbidity = McFarland barium sulfate standard 0.5).

Agar diffusion well-variant

The bacterial inoculums was uniformly spread using sterile cotton swab on a sterile Petri dish MH agar. 50 µl of each concentration of the complexes were added to each well (7 mm diameter holes cut in the agar gel, 20 mm apart from one another). The plates were incubated for 24 h at 36ºC ± 1ºC, under aerobic conditions. After incubation, confluent bacterial growth was observed. Inhibition of the bacterial growth was measured in mm. (27).

RESULTS AND DISCUSSION

The phenol Schiff-basesOHMP and COOHMP were prepared through condensation of one mole salicylaldehyde with1:1 molar equivalent of 2- aminophenol and 2-carboxy-aniline respectively. The formaldehyde resin R-COOHMP were prepared by condensing the Schiff base COOHMP with formaldehyde in alkaline medium. The cobalt (II) complexes of the two Schiff and the formaldehyde resin were prepared. Table (1) shows the physical properties of these compounds, formula, color, CHN analysis and characteristic UV- visible absorption bands.

Table (1): Characterization data of ligand and its Cobalt (II) complexes.

Compound	Formula Color	Found (Calc.) % C H N	UV-Visible(λmax) Π-Π* n-Π* Arom. Azo
Ligand (OHMP)	$C_{13}H_{11}O_2N$ Reddish brown	72.15 5.27 6.77 (73.23) (5.17) (6.57)	250 325 420
Ligand (COOHMP)	$C_{14}H_{11}O_3N$ Orange	69.63 4.72 5.88 (69.70) (4.56) (5.81)	255 330 435
Formaldehyde R-COOHMP	$C_{16}H_{13}O_3N$ Pale orange	71.18 4.82 5.57 (71.91) (4.86) (5.24)	220 275 335
R-COOHMP-Co complex	$C_{30}H_{24}O_6N_2Co$ Olive green	63.51 4.26 4.93 (63.49) (4.23) (4.93)	244 270 422
OHMP-Co complex	$C_{15}H_{12}NO_2Co$ Brown	54.57 3.31 4.69 (57.71) (3.95) (4.26)	268 330 440
COOHMP-Co complex	$C_{14}H_{18}O_7NCo$ Ecru	45.37 4.48 ------ (45.41) (4.86) (3.78)	270 332 ------

Spectral analysis

The structure of the two phenol Schiff- bases OHMP and COOHMP and formaldehyde resin (R-COOHMP) and their cobalt (II) complexes were established with help of FT-IR, UV-Visible and ^{1}HNMR spectra and previous analytical data available in the literatures (22,28,29and30). The FT-IR spectra of the prepared compounds showed sharp and characteristic absorption bands, listed inTable(2). They were recorded in the wave number range 4000-400cm^{-1} by FT-IR 4800. All ligandsshow a high intensity band observed at (1631, 1620 and 1618) cm^{-1} respectively is assigned to υ(C=N) vibration suggesting the formation of Schiff bases. Weak broad band around (3600- 2300) cm-^{1} due to interamolecular hydrogen bonding between Phenolic –OH and the imines group in the ligands, which disappear for all the cobalt (II) complexes (OHMP-Co, COOHMP-Co and R-COOHMP-Co), but instead a new band appear in the spectra of complexes at (1386, 1408 and 1371) cm^{-1} respectively for υ(C-O)indicating deprotonation and coordination of hydroxyl oxygen with metal ion (31).

A broad band at (3600- 2300) cm^{-1} and a strong sharp band at (746; 754 and 757) cm^{-1} in the spectra of the complexes, indicating the presence of coordinated water molecules (32). Furthermore the presence of coordinated and noncoordinated water molecules is confirmed by the TGA studies. In complex OHMP-Co medium to sharp bands in the region 1599- 1523 and 1411-1323 cm^{-1} has been assigned to asymmetric and symmetric vibration of the coordinated acetate groups. The small difference between υasym OCO and υsym OCO of ~ 200cm^{-1} or more is indicative of a mono- -dentate coordination through the carboxylate groups (33 and 34).

All the complexes showed downshift in the characteristic absorption frequency of the azomethine group Table(2), which indicating that the nitrogen atom of azomethine group was coordinated to the metal (35). So that the bands observed in spectra of ligands at (1631, 1620 and 1618) cm $^{-1}$ are appeared in spectra of complexes (OHMP- Co; COOHMP-Co and R-COOHMP-Co) at lower frequencies(1606; 1614 and 1610) cm^{-1} respectively.

Table (2): FT-IR spectra data (cm^{-1})

Compound	**Ar-C-H**	**CH=N**	**C-O**	**C=C**
OHMP	3047	1631	1274	1591 1531
COOHMP	3070	1620	1245	1566
R-COOHMP	3041	1618	1242	1577
OHMP-Co	3057	1606	1292	1543
COOHMP-Co	3138	1614	1300	1591 1537
R-COOHMP-Co	3139	1610	1284	1537

In ^1H NMR spectra of cobalt (II) complexes we observed a shift of electron density from the ligands to the metal, ^1H NMR spectra of the two Phenolic-Schiff bases, formaldehyde resin and it's cobalt (II) complex, show all the expected signals Table(2) and (fig 1-2).

The resonance of protons has been assigned on the basis of their integration and multiplicity, pattern. The ^1H NMR spectra of the two Schiff- bases OHMP, COOHMP and formaldehyde resin R-COOHMP in DMSO exhibits signals at 10.25, 8.964 and 10.30 ppm. attributed to azomethine protons, respectively (36).The multisignals around 6.5-7.8 ppm. are assigned to the aromatic protons of both rings, were not affected by chelation (37). The signals observed at 10.7, 13.77 and >13.00 ppm. are due to Phenolic –OH of COOHMP and R-COOHMP ligands respectively (38).It should be noted that the Phenolic protons have always a given singlet in off-set at high δ values, thus confirming its involvement in an interamolecular hydrogen bond with the neighboring nitrogen atom(39). The free NH_2 group usually show a broad singlet peak in a region at 4-6 ppm (40). This signal is absent in the observed spectra of Schiff- bases which indicates the formation of the Schiff bases. The number of peaks and proton resonances of the free Schiff base completely differ upon complxation (41), Phenolic –OH is absent and the proton resonance of iminophenol are upfield shifted upon complexation with cobalt(II). A comparison of the proton resonance of free ligand with cobalt (II) complex suggests a binding of iminophenolate with cobalt (II) as evident from ^1H NMRspectra (42).

The optical spectrum of the prepared compounds, the ligands and their cobalt(II) complexes, are summarized in the Table(1).The two Schiff base ligands OHMP, COOHMP and formaldehyde resin R-COOHMP shows Π-Π^* transition at (250,255and220)nm. respectively for the aromatic system. While the absorption band attributed to azomethinic (Π-Π^*) transition were appeared at (325, 330 and 275) nm respectively. These bands are not significally affected by chelating (43), whereas the third absorption band at (420, 435 and 335) nm respectively, were assigned to (n- Π^*) transition (44), which were shifted to a longer wavelength (Red shift) upon complexation. This shift maybe attributed to the charge transfer from the nitrogen atoms of the ligands to the cobalt (II) ion (45).

Thermogravimetric study

TG/DTG of the two Schiff- bases ligands OHMP, COOHMP, formaldehyde resin R-COOHMP and their cobalt (II) complexes (OHMP-Co, COOHMP–Co, and R-COOHMP-Co) respectively, were carried out to evaluate the thermal stability of these compounds as shown in Table (3) and fig (1-3). The onset temperature, 50% and 75% weight loss of OHMP was found to be 202 , 336 and 410 ℃ respectively, while the onset degradation temperature,50% and 75% weight loss of OHMP- Co complex was found to be 250, 520 and 595 C, respectively, and so on the relative thermal degradation data of the other ligands and their cobalt (II) complexes were reported.

TG/DTG shows the loss in weight in three stages for all the ligands and complexes. In the first stage they lost the solvent molecules which adesorped in the lattice (45). Then in the second and third stages, they lost most of their original weight by decomposition and volatilization of the low molecular weight fraction (46). Because of the long conjugated bond system in the formaldehyde resin and because of the complexationwith the cobalt (II), the complexes demonstrated higher resistance against high temperature than the ligands themself.

According to the TG analysis, both the stability and the onset of the complexes are higher than that of the ligands and they are more stable than ligands through to temperature and thermal decomposition, which may be indicate the formation of metal- oxygen valance and metal-nitrogen coordination bond between the ligands and metal ion. The presence of water can be seen in TG and DTG curves of the complexes, showing wt % losses in the (50-200)°C rang, corresponding to the loss of water of crystallization (50-150)°C and coordination water (150-200)°C (47).

Table (3): TG/ DTG characterization parameters of the thermal decomposition of the ligands and their Co (II) complexes.

Compound	**Rate of decomp. mg\ min.**	**Temp. of Decomp.(°C)**					**Temp. of 50% weight loss (°C)**	**Residue wt% at 650 (°C)**
		T_1	**T_2**	**T_3**	**T_4**	**T_5**		
OHMP	2.35	202	336	633	---	--	340	9
OHMP-Co	2.07	250	423	557	575	604	520	13
COOHMP	1.30	211	286	535	---	--	295	14
COOHMP-Co	1.95	160	363	498 -	--	-	390	8
R-COOHMP	1.53	212	298	535 -	--	-	340	30
R-COOHMP-Co	0.98	110	269	648 -	--	-	350	25

Antibacterial activity:

The results for the general screening of the antibacterial activity exhibited by compounds were studied. In the screening, it was clear that most of these compounds possess antibacterial activityagainst studied pathogenic bacteria (table 4).

Table (4): Antibacterial activity of studied compounds.

Name of compound	**Concentration**	**Inhibition diameters mm**	
		Staphylococcus aureus	*Escherichia coli*
OHMP	25mg/ml	11- 12 mm	14 mm
OHMP-Co	100mg/ml	inhibition	Inhibition
R-COOHMP	25mg/ml	0	14 mm
R-COOHMP-Co	25mg/ml	16mm	16 mm
COOHMP	100mg/ml	0	Inhibition
COOHMP-Co	100mg/ml	inhibition	16 mm

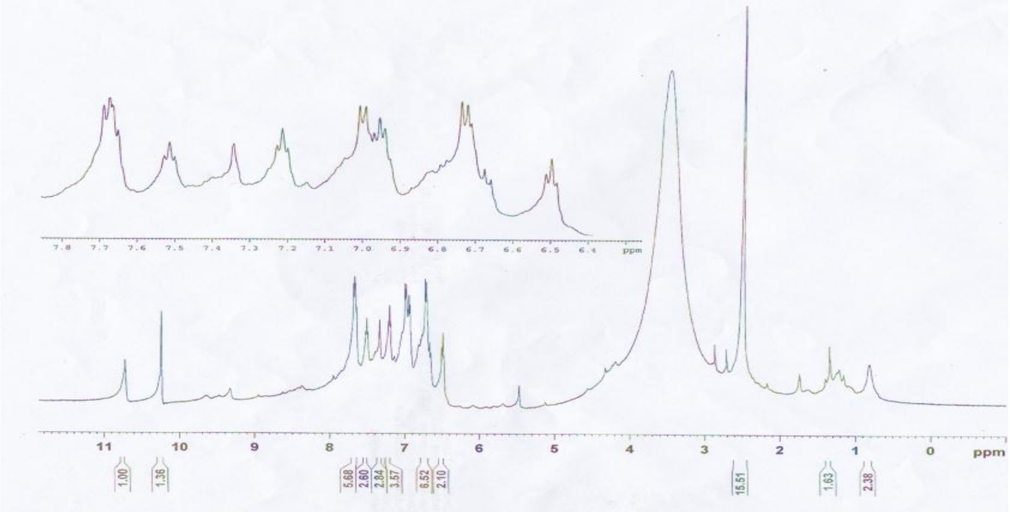


Fig (1): The ^{1}H NMR spectrum of the complex (R-COOHMP-Co)

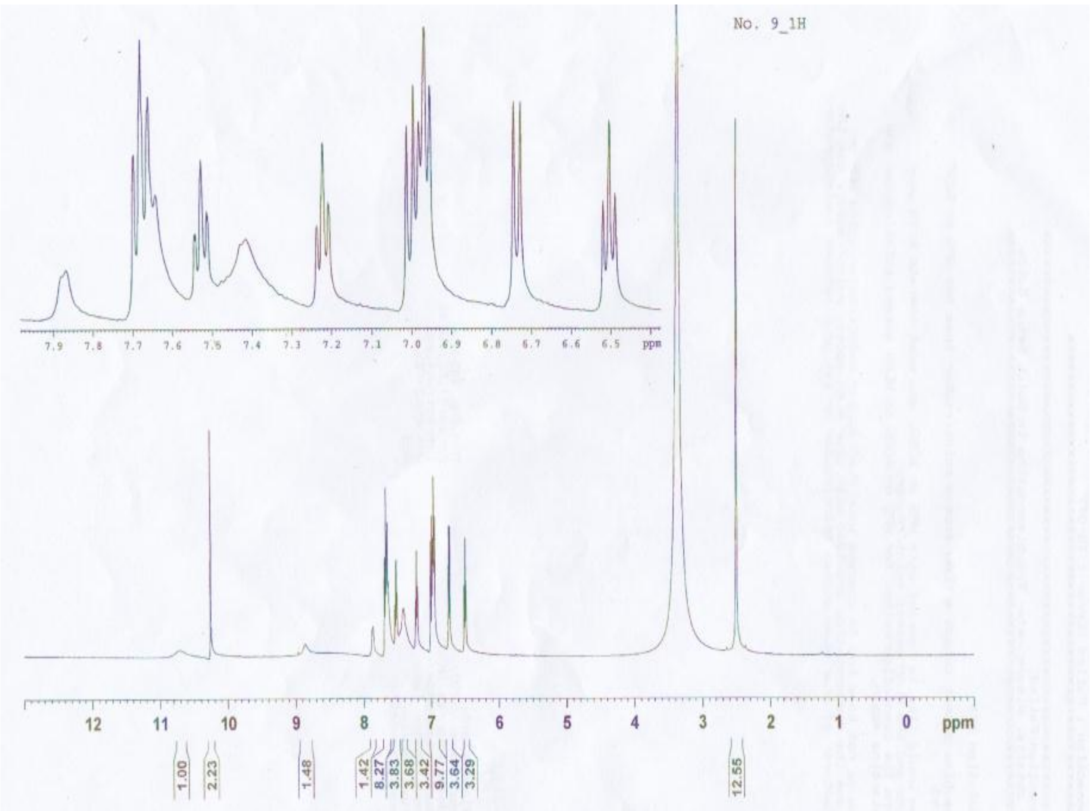


Fig (2): The ^{1}H NMR spectrum of anthranilic acid-formaldehyde resin (R-COOHMP)

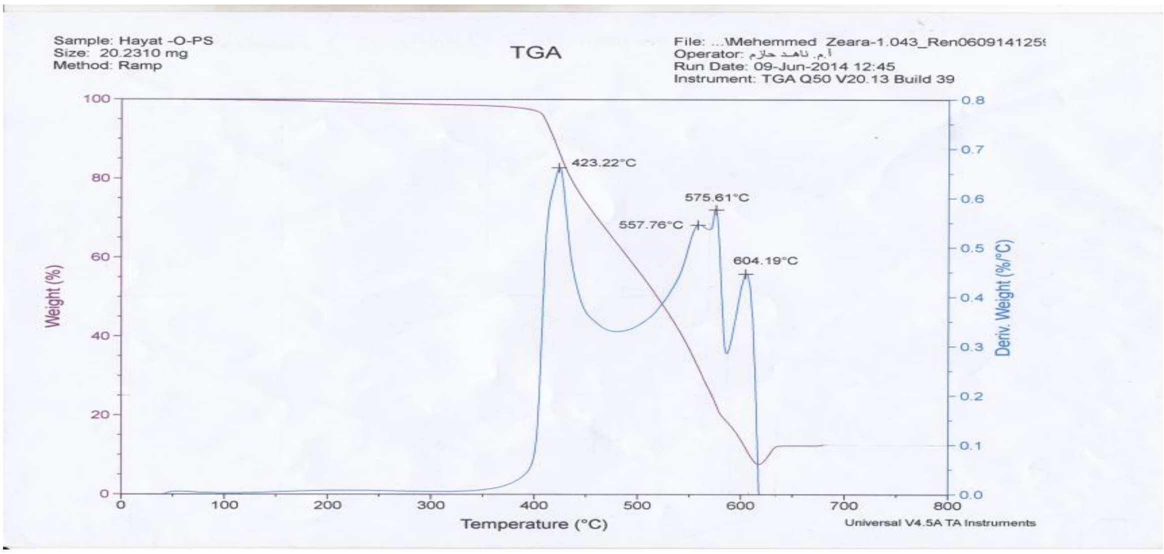


Fig (3): The TG / DTG thermograms of (OHMP-Co) complex

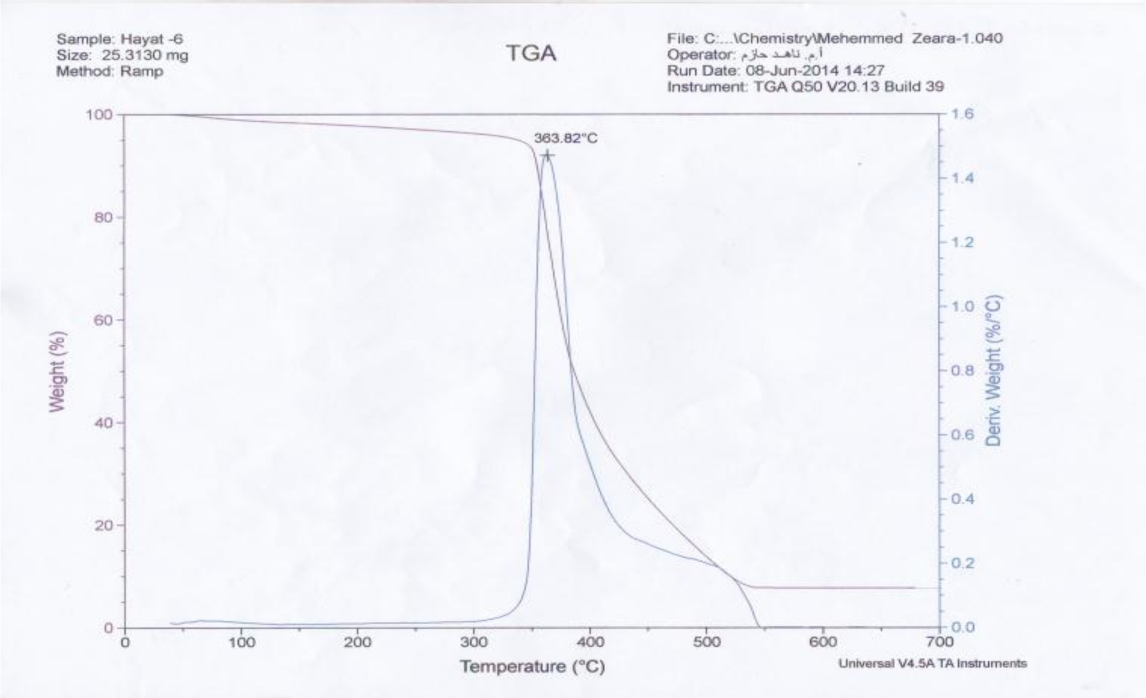


Fig (4): The TG / DTG thermograms of (COOHMP-Co) complex

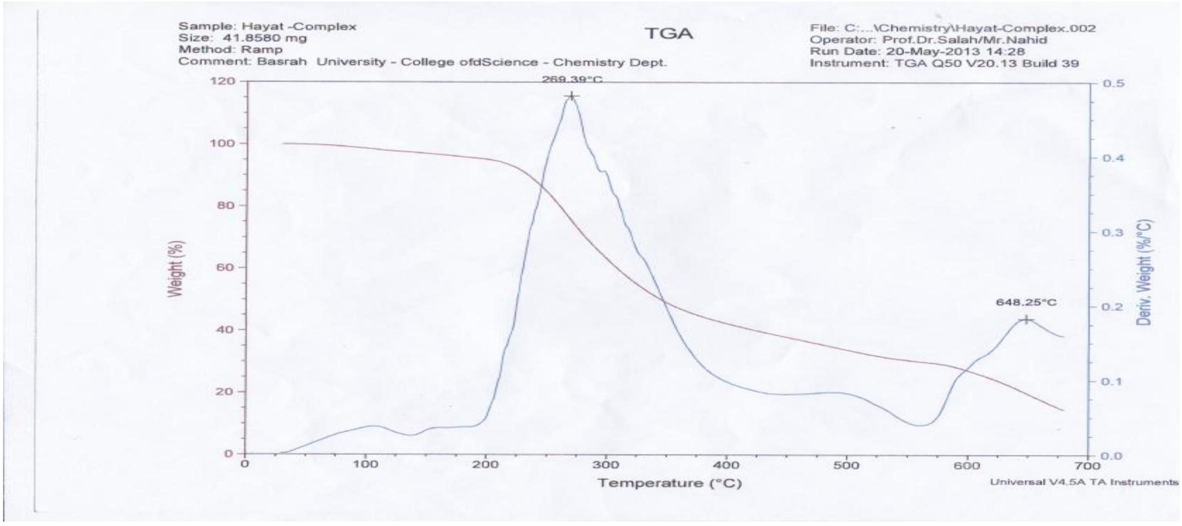


Fig (5): The TG / DTG thermograms of (R-COOHMP-Co) complex

CONCLUSION

Cobalt (II) complexes of two Schiff-bases : 2-{[(2- hydroxophenyl) imino] methyl} phenol (OHMP), 2-{[(2-carboxyphenyl) imino] methyl} phenol and anthranilic acid-formaldehyde resin were synthesized and characterized by analytical and spectraltechniques. The ligand and complexes were screened for their antibacterial activity against Staphylococcus aureus and Escherichia coli .The minimum inhibitory concentration was determined .The ligand and their complexes showed antibacterial activity against studied pathogenic bacteria .The metal chelation significantly affects the antimicrobial behavior of the Schiff -bases .

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