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PREPARATION, CHARACTERIZATION, THERMAL STUDIES, PHOTOCHEMICAL BEHAVIOURS AND ANTIMICROBIAL ACTIVITY OF COMPLEXES DERIVED FROM 5-METHYL-3-FURALDEHYDE THIOSEMICARBAZONE AND HG(II) SALTS OF HALLO ACIDS

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تم تحصير ثلاثة متراكبات مختلطة المخالب لأملاح الزئبق الثنائي المشتقة من الأحماض الغير العضوية (حمض الهيدروكلوريك) والعضوية (ثنائي كلورو حمض الخليك أو ثلاثي فلورو حمض الخليك). درست المتراكبات بإستخدام أطياف المنطقة المرئية والفوق بنفسجية والمنطقة دون الحمراء. كما درس السلوك الحراري لهذه المتراكبات و أظهرت منحنيات التحلل الوزني الحراري عددا من مراحل التفكك يدل على أن التحلل الحراري للمركبات السابقة ليس بسيطا. وتم حساب الثوابت الحركية لخطوات التحلل المختلفة. كما تم دراسة النشاط الضوئي لهذه المركبات في وجود فوق أوكسيد الهيدروجين، وقد أظهرت النتائج أن النشاط الضوئي لهذه المركبات يتسارع بشدة مقارنة بعدم وجود فوق أوكسيد الهيدروجين وقد أعزيت هذه النتيجة الى تكون الشق الحر (OH). وتم دراسة الفاعلية البيولوجية لهذه المركبات على عدد من الفطريات وعدد من البكتيريا موجبة الجرام وسالبة الجرام فى الأنبوب ، حيث أوضحت الدراسة أن المتراكبات المختلطة أكثر تأثيرا على تثبيط نمو الفطريات والبكتيريا مقارنة بالليجند ومتراكباتها الثنائية.

Complexes from of 5-methyl-3-furaldehydethiosemicarbazone (5M3HFTSC) and Hg(II) salts derived from inorganic (HCl) and organic hallo acids ($CHCl_2COOH$ or CF_3COOH) have been prepared. There chemical structures were characterized using elemental analyses, conductivity spectral measurements, thermogravimetric methods and photochemical behaviours. The thermal studies of such complexes using thermogravimetric analysis (TGA), derivatives thermogravimetry (DrTG) from ambient temperature to 750°C showed three decomposition steps. These studies indicated that the thermal decompositions are not simples. The photolysis of the studied compounds has been carried out in the presence of H_2O_2. It was found that, the photolysis was enhanced in the presence of H_2O_2 due to the generation of $^{\cdot}OH$ radicals which are very strong oxidizing agent. Biological activity of theses compounds was tested and screened for their in-vitro antibacterial and antifungal activity. The mixed ligand complexes generally are more active than the binary and free thiosemicarbazne ligand.

INTRODUCTION

Thiosemicarbazones are of significant interest not only for their chemotherapeutic activity against bacteria, viruses, fungi and cancer[1&2], but also for their capacity for chemical recognition of anions and metals of biochemical medical and environmental importance[3-5]. They usually act as chelating ligands with metal ions, by bonding through semicarbazone sulfur and azomethine nitrogen atoms. When such ligands are complexed with metal ions their biological activities were enhanced[6]. Accordingly, the present work involves preparation of complexes from 5-methyl-3-furaldehydethiosemicarbazone (a) with Hg(II) salts of inorganic acid (HCl) and organic hallo acids (dichloroacetic acid (b) or trifloroacetic acid (c)) (Fig. 1). Spectroscopic characterization of such complexes using different techniques were performed. Biological studies of these compounds have been carried out *in-vitro* on some human pathogenic bacteria and fungi.

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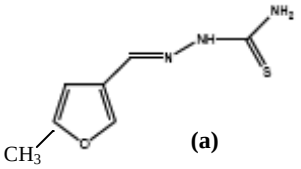

(a) $CHCl_2COOH$ (b) CF_3-COOH (c)

Fig. 1: The structures of 5-methyl-3-furaldehyde-thiosemicarbazones (5M3HFTSC) and hallo acids ligand.

EXPERIMENTAL

Solvents and reagents were of Analar grade and were obtained from commercial sources and used as such without further purification. Spectrograde solvents were used for spectral and conductance measurements**.**

Preparation of ligand and complexes

Salts of Hg(II) 1,1-dichloroacetate and 1,1,1-trifluroroacetate were obtained from the reaction of hall acids ($CHCl_2COOH$ or CF_3COOH, respectively) and $HgCl_2$ in ethanolic solution[7]. The 5-methyl-3-furaldehyde thiosemicarbazone ligand was prepared by the methods reported earlier[8-10]. The Hg(II) binary complex of 5MHFTSC was prepared by mixing an ethanolic solution (20 ml) of 5M3HFTSC (2 mmol) with an ethanolic solution (20 ml) of $HgCl_2$ (1 mmol). The mixed was refluxed on a boiling water bath for 1 h to afford coloured solution. This solution was concentrated to half of them volume. After cooling to room temperature, crystalline solid was isolated, which was washed with ethanol and dried in vacuum. The mixed ligand complexes derived from 5M3HFTSC with Hg(II) salts of acids were prepared by adding an ethanolic solution (10 ml) of 5M3HFTSC (2 mmol) to a 10 ml ethanolic solution (1 mmol) of the respective Hg(II) salts. Reaction mixture was heated under reflux for 1 h on a boiling water bath. On cooling, the solid complexes were separated out, filtered, washed repeatedly with ethyl alcohol, recrystallized from absolute ethanol and dried in vacuum.

Physical measurements

Electrical conductivity of 10^{-3} M solution of the complexes were measured at room temperature by a Jenway 4330 conductivity meter. IR spectra were recorded on a 470 shimadzu infrared Spectrophotometer (4000-400 cm^{-1}) using KBr disks. The electronic adsorption spectral measurements in the ultraviolet and visible regions were carried out in DMF on a UV-2102 PC Shimadzu Spectrophotometer using 1 cm matched quartz cell in the wavelength range 200-900 nm. Elemental analyses of CHNS were determined by Gmbh Vario El analyzer. The thermogravimetric (TG) and differential thermal analysis (DTA) of the solid complexes were preformed using a DTG-60H thermo-gravimetric analyser (Shimadzu) from ambient temperature to 750°C with a 10°C min^{-1} heating rate in dynamic air atmosphere. The photolyses were achieved using an Osram HBO 200 w/2 Lamp as a light source. Cut-one filter of 299 nm was used. Irradiations were carried out in DMF in 1-cm Spectrophotometer cells at room temperature. The photolysis progress was monitored by the above mentioned spectro-photometer.

Biological data

1. Materials and methods

The 5M3HFTS ligand and its complexes were stored dry at room temperature and dissolved in dimethyl sulfoxide (DMSO) just before their use.

2. Antibacterial and antifungal tests

The antibacterial and antifungal properties of 5M3HFTSC and its complexes were determined by the standard "disc diffusion" method[11]. Here the bacteria and fungi were grown in nutrient and Sabouraud dextrose agar slants and the viable bacterial cells and fungal spore harvested into phosphate buffered saline and swabbed in to nutrient agar and Sabouraud dextrose agar plates, respectively. The compounds to be tested were dissolved in DMSO to a final concentration of 0.1% and soaked in filter paper discs of 5 mm diameter and 1 mm thickness. These filter papers were found to hold a quantity 0.01 cm^3 solution. These discs were placed on already seeded plates and incubated at 28 ± 0.4°C for 48 to 72 h. A clearing zone around the disc indicated the inhibitory activity of the compound on the organism.

RESULTS AND DISCUSSION

Characterization of Hg(II) complexes

The reported Hg(II) complexes provided satisfactory C, H, N, and S analyses (Table 1)

Table 1: Physical properties and elemental analysis of the 5-methyl-3-feuraldehydethiosemi carbazone and Hg (II) complexes.

5M3HFTSC and complex	M. F (M. Wt)	Colour	m.p/ °C (Decomp)	Found / (Calc.)			
				C%	H%	N%	S%
5M3HFTSC	$C_7H_{10}N_3OS$ (183.04)	Dark brown	179	45.31 (45.91)	5.46 (5.32)	23.41 (23.74)	17.48 (17.62)
$[Hg(5M3HFTSC)_2Cl_2]$	$C_{14}H_{20}Cl_2HgN_6O_2S_2$ (637.662)	Yellowish brown	293	26.67 (26.35)	3.24 (3.14)	13.61 (13.17)	10.387 (10.03)
$[Hg(5M3HFTSC)_2(CF_3COO)_2]$	$C_{18}H_{20}F_6HgN_6O_6S_2$ (792.66)	Light Yellow	319	27.19 (27.26)	2.43 (2.52)	10.51 (10.60)	7.93 (8.07)
$[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$	$C_{18}H_{22}Cl_4HgN_6O_6S_2$ (822.722)	Light brown	314	26.83 (26.26)	2.92 (2.67)	10.42 (10.21)	7.89 (7.78)

which confirmed the general composition $[Hg(5M3HFTSC)_2X_2]$ (where X=Cl , $CHCl_2COO$ and/or CF_3COO). The formation of the complexes may be represented by the following equations.

$$HgCl_2 + 2(5M3HFTSC) \longrightarrow [Hg(5M3HFTSC)_2Cl_2] \quad (1)$$

$$Hg(CHCl_2COO)_2 + 2(5M3HFTSC) \longrightarrow [Hg(5M3HFTSC)_2(CHCl_2COO)_2] \quad (2)$$

$$Hg(CF_3COO)_2 + 2(5M3HFTSC) \longrightarrow [Hg(5M3HFTSC)_2(CF_3COO)_2] \quad (3)$$

Conductivity measurements

The molar conductance values of the complexes measured in DMF at the concentration 10^{-3} M are 30, 52 and 46 Ohm^{-1} cm^2 mol^{-1} for the $[Hg(5M3HFTSC)_2Cl_2]$, $[Hg(5M3HFTSC)_2(CF_3COO)_2]$ and $[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$, respectively. These values indicate the electrolytic nature of the complexes[12].

Spectroscopic characterization

1- Infrared spectra

Important IR bands for the ligand and complexes (Fig. 2) with their tantative assignment are presented in table 2. The free 5M3HFTSC ligand showed C=N at 1600 cm^{-1} and C=S at 830 cm^{-1}. On complexation, the position of these bands is shifted to lower frequency by ca. 10-15 cm^{-1} and 10-60 cm^{-1}, respectively as reported[13-18]. This indicates that, coordination takes place through the azomethine nitrogen and sulfur of the C=S group. This is further supported by appearance of new bands in the regions 435-455 cm^{-1} and 380-395 cm^{-1} for ν(M–N) and ν(M–S), respectively as reported[19-23]. Another medium-intensity band corresponding to ν(NH) is observed at 3110–3440 cm^{-1} indicating the thionic form of the ligands[24-28]. The position of this band did not change in the spectra of the complexes. This indicating that the –NH group does not take part in coordination.

2- Electronic spectral studies

The electronic spectral data of Hg(II) complexes under investigation display strong absorption bands at 33,958، 37,468 ، 32,751 cm^{-1} and 25,778 ، 29,421 ، 25,629 cm^{-1} (Table 3), these bands are assigned as π-π^* transition and an intraligand charge(IL charge) transfer transition[29].

Hg(II), being a d^{10} ion, does not show d-d transitions and, hence, the stereochemistry of its complexes cannot be determined from ultraviolet and visible spectra. However, from comparison between these Hg(II) complexes and complexes of similar environment around Hg(II)[30-36], octahedral geometry is suggested for the prepared complexes.

Thermal studies

1- Thermal behaviour

The thermal behaviour of the Hg(II) complexes under investigation was studied in dynamic air using thermogravimetric analysis (TGA), derivatives thermogravimety (DrTG) and differential thermal analysis (DTA). The thermal decomposition of the complexes was recorded from ambient temperature to 750°C (Table 4). The results showed that the complexes generally decomposed in several thermal events, i.e., two or three decomposition steps. The first step for all complexes correlates well with the theoretical values corresponding to the elimination of the two hallo acid molecules present. The end products of the decomposition were identified from the TG traces to be HgO.

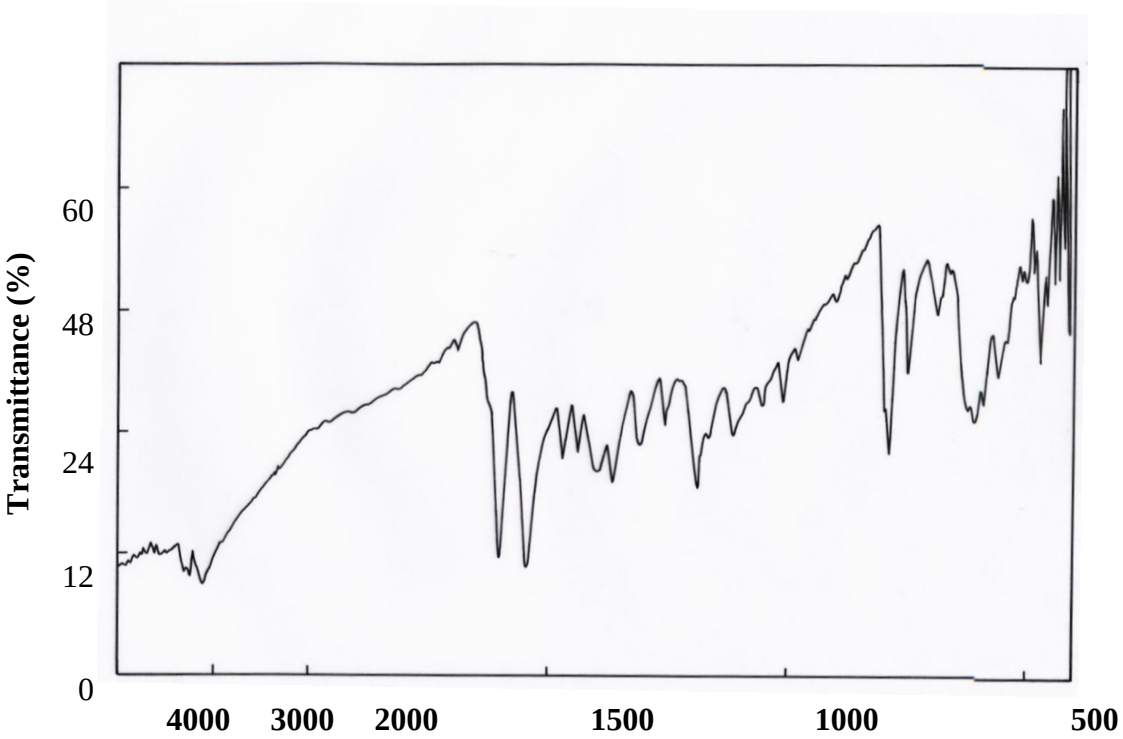

Fig. 2: IR spectrum of $[Hg(5M3HFTSC)_2(CF_3COO)_2]$.

Table 2: IR spectral data (cm^{-1}) of free 5M3HFTSC and Hg(II) complexes.

Complex	ν (NH / NH_2)	ν(C=N)	ν(C=S)	ν (M-N)	ν (M-S)
5M3HFTSC	3220 - 3450 m	1600 s	830 s	-	-
$[Hg(5M3HFTSC)_2Cl_2]$	3110 - 3420 m	1590 s	820 s	455 s	395
$[Hg(5M3HFTSC_{)2}(CF_3$-$COO)_2]$	3220 - 3440 m	1585 s	790 s	435 s	380
$[Hg(5M3HFTSC)_2(CHCl_2$ $COO)_2]$	3250 - 3400 m	1588 m	770 m	440 s	385

s: strong, m: medium

Table 3: Electronic spectral data (cm^{-1}) of Hg(II) complexes**.**

Complex	$\nu_{max}(cm^{-1})$	Assignment
$[Hg(5M3HFTSC)_2Cl_2]$	25,778 33,958	IL-charge transfer π - π * transition
$[Hg(5M3HFTSC_{)2}(CF_3$-$COO)_2]$	29,421 37,468	IL-charge transfer π π * transition
$[Hg(5M3HFTSC)_2(CHCl_2$-$COO)_2]$	25,629 32,751	IL-charge transfer π - π* transition

Table 4: Thermal decomposition data of Hg(II) complexes.

Complex	Step	TG/DTG			Mass loss (%)
		T_i/°C	T_m/°C	T_f/°C	
$[Hg(5M3HFTSC)_2Cl_2]$	1st	191	220	278	11.7
	2nd	279	303	346	5.2
	3rd	347	513	579	49.3
$[Hg(5M3HFTSC)_2(CF_3COO)_2]$	1st	263	287	469	29.2
	2nd	471	588	628	21.2
	3rd	628	713	742	23.3
$[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$	1st	211	282	501	30.8
	2nd	502	597	736	43.3

T_i = Initial temperature T_m = Maximum temperature T_f = Final temperature

For compound $[Hg(5M3HFTSC)_2Cl_2]$ (Fig. 3) the TG curve is characterized by three decomposition steps at 191-278, 279-346 and 347-579°C. The elimination of two HCl molecules (Calcd. 11.5%, Found 11.7%) is observed at the first step. This may suggest the existence of the species $[Hg(5M3FTSC)_2]$ (eq. 4). It is assumed that the coordinated neutral ligand losses a proton and becomes to mononegative bidentate ligand. This step is composed of two DTG peaks at 220 and 242°C and two exotherms at 221 and 240°C in the DTA curve.

$$[Hg(5M3HFTSC)_2Cl_2] \longrightarrow [Hg(5M3FTSC)_2] + 2HCl \quad (4)$$

The second step shows a loss of mass indicating an expulsion of $2NH_2^{\cdot}$ radicals (eq. 5) which dimerize to NH_2-NH_2 (hydrazine eq. 6) (Cald. 5.0%, Found 5.3%) (DTG peak at 302°C), for which an exothermic peak at 316°C is recorded in the DTA trace. The formation of this radical ($^{\cdot}NH_2$) strongly points to a free mechanism starting by the preferential homolysis of N-C bond rather than N-N and C-C bonds, according to their bond dissociation energy values of 42.2, 66.4 and 88.6 kcal mol^{-1}, respectively[37]. The third step displays a major mass loss (49.3%), which is characterized by two DTG peaks at 469 and 513°C and two exothermic effects at 465 and 517°C in the DTA trace. The destruction of the complex seems to follow a complicated course and lead to pure mercury oxide (Calcd. 34.0%, Found 32.8%) (eq. 6). The lower weight is probably due to partial sublimation of HgO.

$$[Hg(5M3FTSC)_2] \xrightarrow{281\text{-}348°C} [Hg(C_7H_7N_2OS)_2] + 2NH_2^{\cdot} \quad (5)$$

$[Hg(C_7H_7N_2OS)_2]$ —(348-880°C)→ HgO+ decomposition products

$2NH_2^{\cdot}$ —(Dimerization)→ NH_2-NH_2 (6)

The thermolysis curve of $[Hg(5M3HFTSC)_2(CF_3COO)_2]$ shows three inflection points indicating that the compound decomposes in three distinct steps in the temperature range 263-471, 473-628 and 628-742°C (Fig. 4). The observed mass loss of the first step is compatible with the loss of two (CF_3COOH) molecules (Calcd. 28.5%, Found 29.2%). The DrTG peak of this step occurs at 287°C. An endothermic peak at 284°C is recorded in the DTA curve. The observed mass loss in the second step is supposed to be related to the detachment of 5-methyl-3-(furan)$^{\cdot}$ radicals which dimerize to 5,5\' dimethyl-3,3\' -bifuran (calc.20.4%, found 21.2%). This step corresponds to a small peaks at 516 and 588°C in the DTG trace and an exothermic effect at 622°C (DTA). The third step represents a mass loss of 23.3%. This step is manifested on the DrTG curve at 713°C and the DTA trace furnishes a small exothermic effect at 716°C. The product remaining with 26.3% weight is calculated for HgO (27.3%).

The stepwise course of the thermogravimetric curve (Fig. 5) of the compound $[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$ is characterized by two decomposition steps in the

temperature range 211-501 and 502-736°C. The first mass loss accounts for the elimination of two $CHCl_2COOH$ molecules, (eq. 7), (Calcd. 31.1%, Found 30.8%) with a DrTG peak at 282°C, and an endothermic peaks at 277°C in the DTA trace. The second step represents the decomposition of the ligand, (eq. 8), (Calcd. 44.5%, Found 43.3%). This step appears to be composed of two broad DrTG peaks at 599 and 703°C, corresponding to three exothermic effects at 594, 649 and 703°C in the DTA trace. The mass loss consideration indicates that the left stable residue is HgO (Calcd. 26.3%, Found 25.9%).

$$[Hg(5M3HFTSC)_2(CHCl_2COO)_2] \xrightarrow{211\text{-}501^\circ C} [Hg(5M3FTSC)_2] + 2CHCl_2COOH \quad (7)$$

$$[Hg(5M3FTSC)_2] \xrightarrow{502\text{-}736^\circ C} HgO + \text{decomposition products} \quad (8)$$

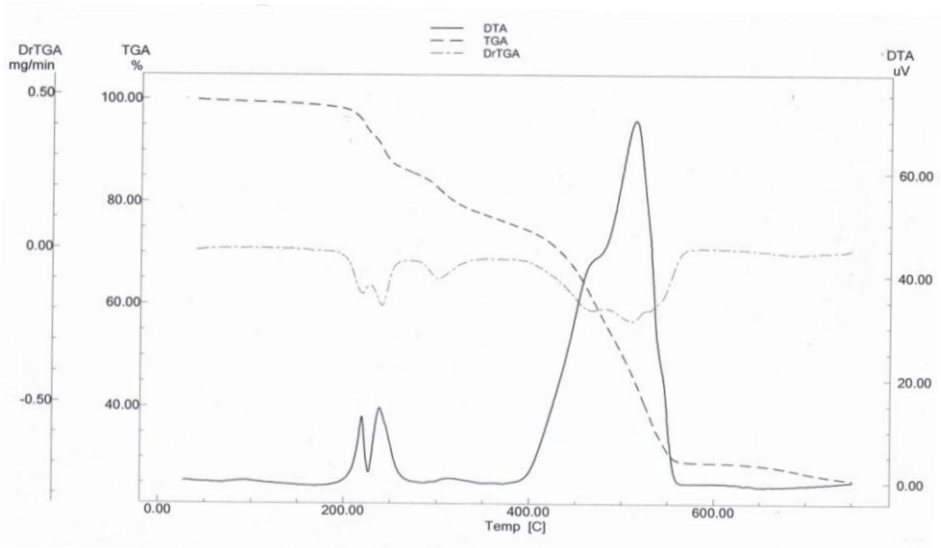

Fig. 3: TGA(---), DrTG(....) and DTA(___) thermograms of $[Hg(5M3HFTSC)_2Cl_2]$.

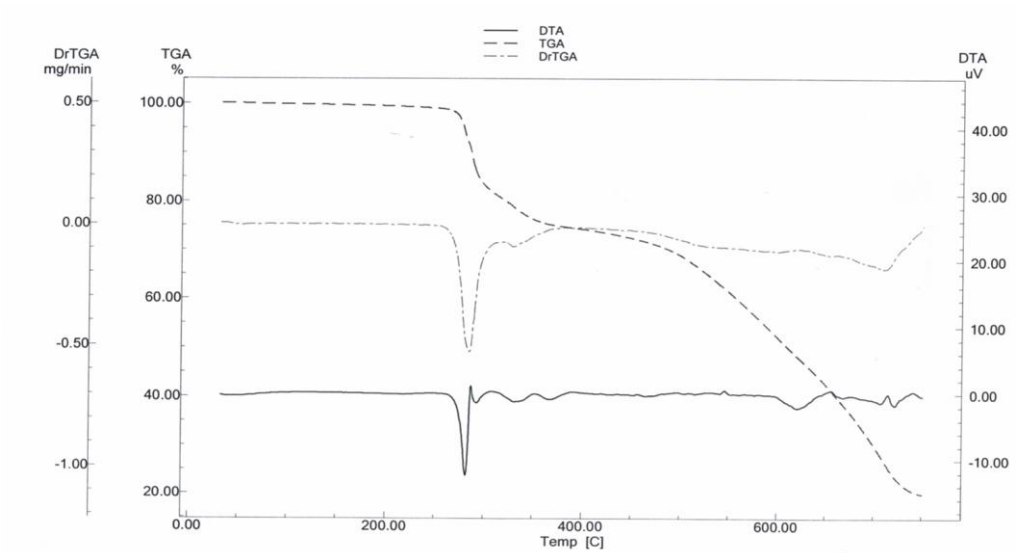

Fig. 4: TGA(---), DrTG(…) and DTA(___) thermograms of $[Hg(5M3HFTSC)_2(CF_3COO)_2]$.

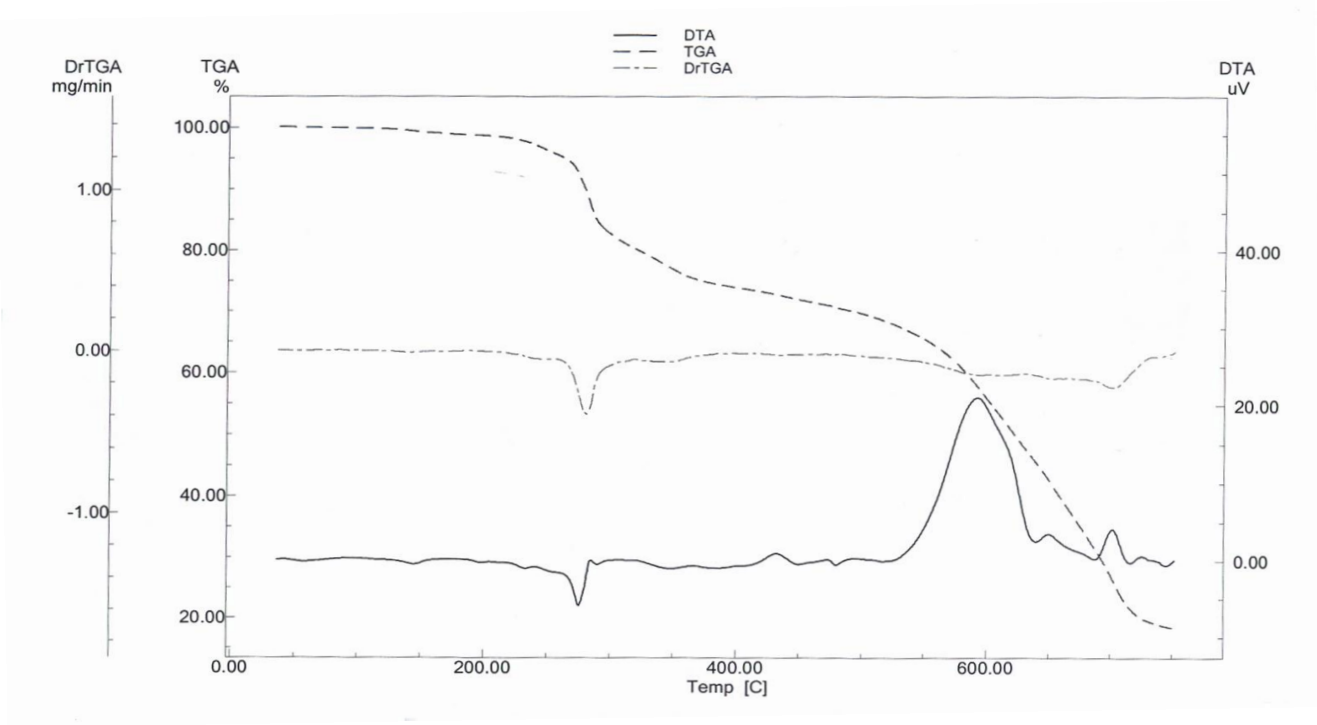

Fig. 5: TGA(---), DrTG(…) and DTA(___) thermograms of $[Hg(5M3HFTSC)_2(CHCl_2COO)_2$.

2- Kinetic analysis

Nonisothermal kinetic analyses for the thermal decomposition of the complexes were carried out by the application of two different, Coats-Redfern[38] and Howowitz-Metzger[39], equations. The kinetic parameters were evaluated only for clear–cut and nonoverlapping stages. The thermal data and kinetic parameters of the thermal decomposition of the complexes are included in table 5. The activation energies, in general, are relatively low indicating the low thermal stability of the complexes.

Photochemical behaviour

1- Photolyses of 5M3HFTSC

Before the investigation of the photochemical behaviour of the prepared complexes, the photolyses of the free 5-methyl-3-furaldehyde thiosemicarbazone was studied.

The spectral changes recorded during photolysis of 5M3HFTSC in DMF solution upon irradiation with cut-on filter of $\lambda_{irr} \geq 299$ nm showed decreased in absorbance at 333 nm (Fig. 6).

2-Photolysis of the Hg(II) complexes

Upon irradiation with light of $\lambda_{irr} \geq 299$ nm, the DMF solution of $[Hg(5M3HFTSC)_2Cl_2]$, $[Hg(5M3HFTSC)_2(CF_3COO)_2]$ and $[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$ complexes under investigation exhibited a light sensitivity, and the absorbance at 333 nm decreased. The behaviour of $[Hg(5M3HFTSC)_2(CF_3COO)_2]$, is depicted in figure 7 as an example.

3-Photolysis in the presence of H_2O_2

The spectral changes of 5M3HFTS and their complexes in DMF solutions in the presence of H_2O_2 upon irradiation with light $\lambda_{irr} \geq 299$ nm at room temperature (25°C) are very fast compared with that in absence of H_2O_2 at the same conditions (Figs 8 & 9).

The UV/H_2O_2 oxidation process is of potential practical important[40]. It is characterized by the generation of a very powerful oxidizing species, namely hydroxyl radicals[41]. The general pattern of the reactions of these radicals with saturated aliphatic products involves abstraction of an H atom (or H^+ ion) in the rate-determing step[42]. On the other hand, when the organic molecule contains a double bond, the abstraction of H atom is competed by an addition of OH radicals on this unsaturated bond[43].

Biological activity

The 5-methyl-3-furaldehyde Hg(II) complexes under investigation were tested against some bacteria and fungi (Table 6). The bacteria and fungi namely: *Bacillus cereus* (Gram positive), *Staphylococcus aureu*s (Gram positive), *Escherichia coli* (Gram negative), *Pseudomonas aeruginosa* (Gram negative), *Aspergillus flavus, Aspergillus niger, Candida albicans, Fusarium oxysporum, Geotrichum candidum, Pencillinum purpurogenum*, Chloramphenicol and Dermatin as antibacterial and antifungal were used as standards, respectively.

A critical examination of the antimicrobial action of these compound indicates that in general the mixed ligand complexes are better toxic agents against various bacteria and fungi than the $[Hg(5M3HFTSC)_2Cl_2]$ complex and the 5M3HFTSC ligand.

The antimicrobial activity of metal ion complexes were explain several workers[44&45] assuming that the neutral complexes mixes ligand complexes first penetrate the cell and at the site of action undergo dissociation to 1: 1 complexes which will become toxic by blocking the metal binding sites on enzymes. This can proposed for the complexes included in table 6.

Table 5 : Kinetic parameters for the thermal decomposition of Hg(II) complexes using non-mechanistic equations.

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
$[Hg(5M3HFTSC)_2)Cl_2]$	1^{st}	0.00	0.9992	193.2	$4.20X10^5$	0.00	0.9987	188.2	$1.28X10^5$
		0.33	0.9992	101.3	$3.31X10^6$	0.33	0.9991	197.6	$1.51X10^6$
		0.50	0.9992	217.4	$1.34X10^7$	0.50	0.9993	221.4	$2.30X10^8$
		0.66	0.9999	232.8	$2.73X10^7$	0.66	1	238.4	$2.54X10^8$
		1.00	0.9992	246.8	$5.13X10^9$	1.00	0.9989	252.3	$2.25X10^{10}$
		2.00	0.9984	312.4	$3.21X10^{15}$	2.00	0.9979	321.1	$1.11X10^{16}$
$[Hg(5M3HFTSC)_2(CF_3COO)_2]$	1^{st}	0.00	0.9979	69.8	$1.62X10^6$	0.00	0.9986	78.8	$1.41X10^7$
		0.33	0.9999	86.4	$1.12X10^7$	0.33	0.9993	85.4	$4.24X10^8$
		0.50	0.9998	95.5	$1.08X10^8$	0.50	0.9989	98.5	$2.41X10^9$
		0.66	1	108.9	$3.29X10^9$	0.66	1	111.9	$2.21X10^{10}$
		1.00	0.9997	122.1	$4.51X10^{11}$	1.00	0.9999	128.4	$1.22X10^{12}$
		2.00	0.9971	251.5	$2.52X10^{19}$	2.00	0.9979	252.5	$1.23X10^{19}$
$[Hg(5M3HFTSC)_2(CHCl_2COO)_2]$	1^{st}	0.00	0.9994	112.1	$1.05X10^7$	0.00	0.9997	121.2	$2.14 X 10^7$
		0.33	0.9978	142.3	$1.24X10^8$	0.33	0.9989	152.1	$1.60 X 10^7$
		0.50	0.9983	159.5	$1.13X10^9$	0.50	0.9984	169.4	$1.05 X 10^9$
		0.66	1	181.0	$1.03X10^{11}$	0.66	1	188. 5	$3.14 X 10^{10}$
		1.00	1	208.4	$1.13X10^{13}$	1.00	0.9999	202.3	$3.16 X 10^{11}$
		2.00	0.9993	292.7	$1.12X10^{17}$	2.00	0.9991	296.1	$2.14 X 10^{16}$

E in kJ mol^{-1}; Z in s^{-1} underlined *r* in all tables represent the best fit values of n, E and Z

n = order of the decomposition reaction r = correlation coefficient

E = activation energy of decomposition Z = preexponential factor

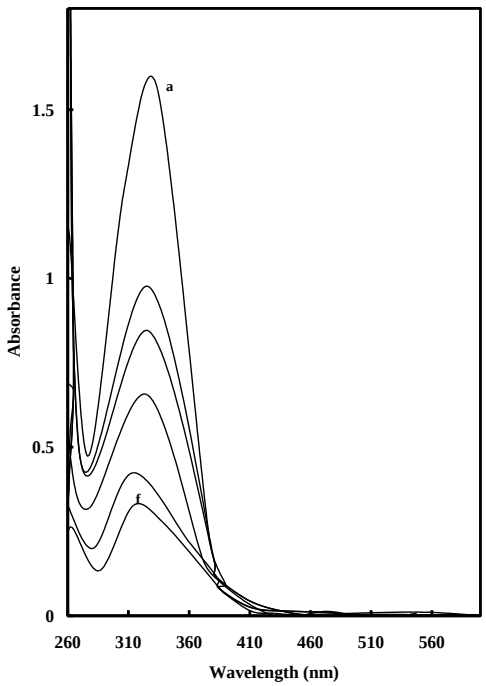

Fig. 6: Spectral changes during the photolysis of 5-methyl-3-feuraldehyde-thiosemicarbazone (5M3HFTSC) in DMF; at irradiation time of a= 0, b=3, c=5, d=7, e= 8 and f = 9 min, $\lambda_{irr} \geq 299$ nm, 1-cm cell.

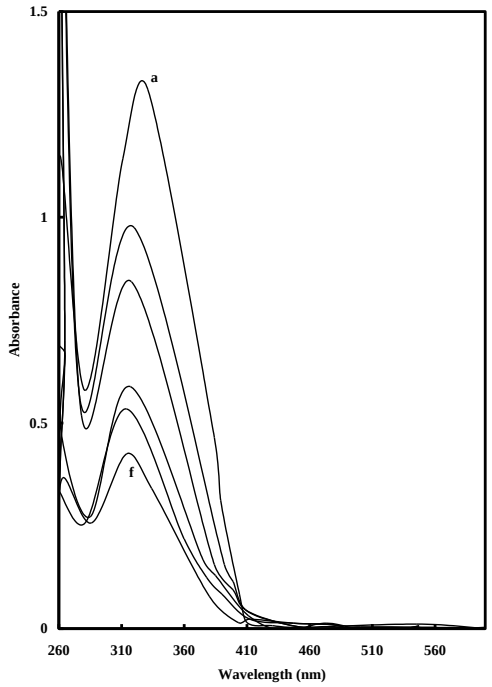

Fig. 7: Spectral changes during the photolysis of [Hg $(5M3HFTSC)_2(CF_3COO)_2$] in DMF; at irradiation time of a= 0, b=3, c=6, d=12, e= 16 and f= 20 min, $\lambda_{irr} \geq 299$ nm,1-cm cell.

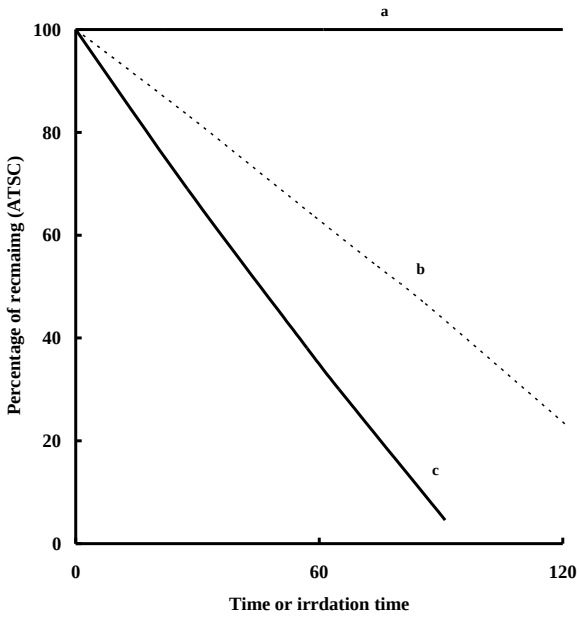

Fig. 8: Percentage of 5M3HFTSC remaining as a function of time or irradiation time; (a) in dark and in presence of H_2O_2, (b) under illumination with light of $\lambda_{irr} \geq 299$ nm a without H_2O_2, (c) under illumination with light of $\lambda_{irr} \geq 299$ nm and in presence of H_2O_2.

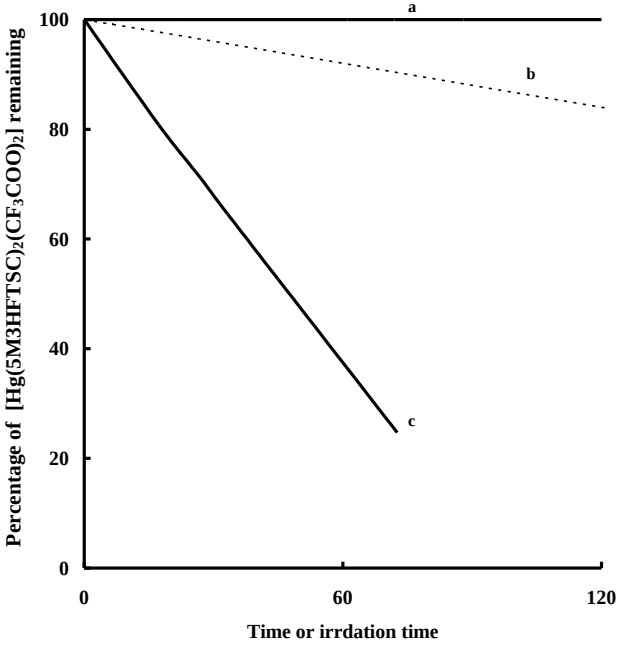

Fig. 9: Percentage of [$Hg(5M3HFTSC)_2(CF_3$-$COO)_2$] remaining as a function of time or irradiation time; (a) in dark and in presence of H_2O_2, (b) under illumination with light of $\lambda_{irr} \geq 299$ nm a without H_2O_2, (c) under illumination with light of $\lambda_{irr} \geq 299$ nm and in presence of H_2O_2.

Table 6: Microbiological screening of 5M3HFTSC and their complexes.

Organism / Complex	*B. cereus* (G+ve)	*S. aureus* (G+ve)	*E. coli* (G-ve)	*P. aeruginosa* (G-ve)	*A. flavus*	*A. niger*	*C. albicans*	*F. oxysporm*	*G. candidum*	*P. purpurogenum*
5M3HFTSC	0	9	8	9	7	0	0	0	0	20
$[Hg(5M3HFTSC)_2 Cl_2]$	11	18	19	10	12	7	14	0	0	13
$[Hg(5M3HFTSC)_2 (CF_3\text{-}COO)_2]$	36	33	29	11	22	33	24	17	26	25
$[Hg(5M3HFTSC)_2 (CHCl_2\text{-}COO)_2]$	39	37	27	13	26	34	28	15	29	23
Standard* (Antibacterial) (Antifungal)	50	30	38	52	40	23	11	20	21	25

*Standard, Antibacterial = Chloramphenicol, antifungal= Dermatin

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