



## Synthesis and structural study of some new metal complexes of Schiff base from 2-thenoyltrifluoroacetone with alkyl amine and its thione derivative by NMR, IR and TGA analysis methods

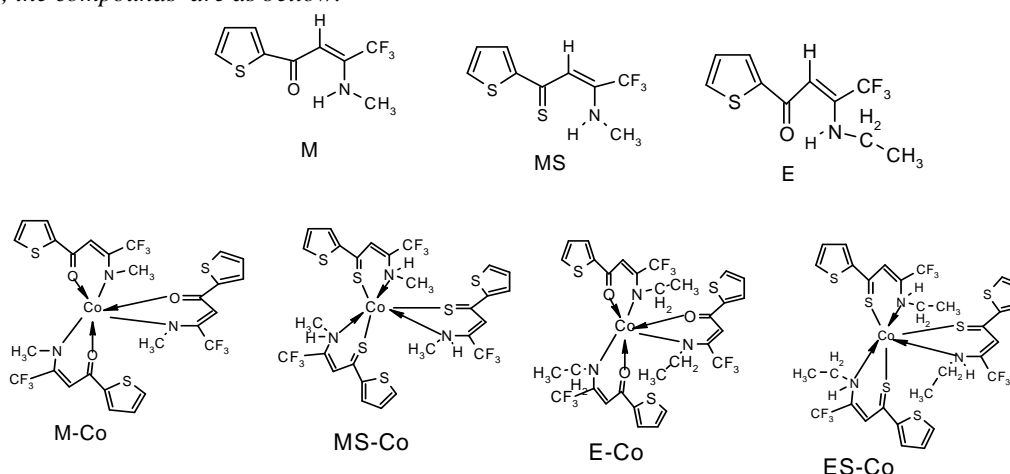
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### ABSTRACT

Synthesis of new Schiff bases and its thione derivatives from 2-thenoyltrifluoroacetone has been carried out. The metal complexes of these reagents were prepared. In addition new metal complexes of the 2-thenoyltrifluoroacetone reagent are also prepared. The prepared compounds have been characterized by melting points, CHN analysis, I.R, NMR and TGA techniques. A full analysis of CHN, I.R, NMR spectra and TGA curves of the studied compounds gave the molecular structures of the compounds., the study has involved preparations of two Schiff bases derived from 2-thenoyl-trifluoroacetone with methyl amine and ethyl amine and their thiones derivatives and proved their structures, the compounds are as bellow:



**Key words:** Schiff bases, 2-thenoyltrifluoroacetone, metal complexes

### INTRODUCTION

The most common  $\alpha,\beta$ -unsaturated carbonyl compounds are  $\alpha,\beta$ -unsaturated ketones, aldehydes, esters, and carboxylic acids. Schiff bases of and their metal complexes have been used as precursors in metal-organic chemical vapor depositions<sup>[1,2]</sup>, anticancer and antimicrobial agents<sup>[3,4]</sup>, catalysts<sup>[5,6]</sup>, in optics and material science<sup>[7,8]</sup>, as MRI contrast agents and biological markers<sup>[9-12]</sup>. Recently, chloro, methyl and methoxy derivatives of pyrimidinyl Schiff bases are used. Literature review showed that little information is available on the Schiff bases derived from p-nitro aniline and 2-thenoyltrifluoroacetone / benzoyltrifluoroacetone and their metal(II) complexes (M=Mn, Co, Ni, Cu, Zn and Pd). A. A. Osowole and A. C. Ekennia<sup>[13]</sup>, synthesized and characterized of these two Schiff bases and their

metal complexes with the aims of investigating their structure related antibacterial activities against human pathogens in-vitro, and the effect of the various substituent's on their electronic properties and geometries

## MATERIALS AND METHODS

### 1. Instruments and Measurements

$^1\text{H}$ ,  $^{13}\text{C}$ , HMBC and HSQC-NMR were measured in a Bruker 500 MHz, at 25 °C using different solvents: MeOD,  $\text{CDCl}_3$  and  $\text{MD}_3\text{SOMD}_3$ . Infrared spectra were recorded in two ways solid and liquid states in the range of 4000-400  $\text{cm}^{-1}$  using a FT-IR spectrophotometer. Perkin Elmer, Micro-elemental analysis for Carbon, Hydrogen and Nitrogen for the prepared compounds was carried out. All measurements were performed at the department of Chemistry, University of Surrey, UK.

## 2. SYNTHESIS METHODS

### 2.1 Ligand Preparation

#### 2.1.1 The Synthesis of 1,1,1-trifluoro-4-methylamino or ethylamine-4-(2-thienyl)-3-yl-2-butanone (M,E respectively)

The compounds were synthesized according to the literature<sup>[13,14]</sup> with some modifications. A solution of 2-thenyltrifluoroacetone (2.2218 g, 10 mmol) in 22 ml ethanol absolute, 2.5 ml acetic acid and 5 drops HCl was added to methylamine (10 ml, 10 mmol). The mixture was refluxed for 24 hrs. Until the reaction was completed (GC-MS). The resulting solution was left over night, the solvent was removed to give a residue, which was chromatographed on a silica gel (1.5 × 15 cm) with a 1:9 mixture of EtOAc and *n*-hexane as the eluent to give 38% yield, Schiff base resulted from methylamine was low melting point but another result was oily. Table 1 some physical properties and spectral data of the product Schiff bases.

Table 1 some physical properties and spectral data of the product Schiff bases and the product thione

Compound symbol	M.P. °C	color	FW	IR $\nu$ $\text{cm}^{-1}$	NMR $\delta$	GS-MS
M	38-39	yellow	235.28	2922.4, 1617.4	3.09, 6.10, 7.14, 7.75	111.0, 202.1, 235.1
MS	oily	black	251.28	3100.0, 1015.5	3.17, 6.54, 7.57, 13.34	127.0, 218.0, 251
E	oily	yellow	249.3	3102.3, 2880.5, 1623.2	1.26, 3.44, 6.10, 7.12, 7.70	111.0, 216.1, 249.1
ES	oily	black	265.3	3104, 2860.2, 1053.1	1.31, 3.44, 6.04, 10.34	81.0, 264.1

#### 2.1.2 The synthesis of 1,1,1-trifluoro-4-methylimino-4-(2-thienyl)-2-thio-3-butene (MS)

To a stirred solution (0.857 g, 3.6 mmol) of 1,1,1-trifluoro-4-methylimino-4-(2-thienyl)-2-thio-3-butene (MS) in dry toluene (90 ml), Lawesson's reagent (0.88 g, 2.2 mmol) was added. Then, the reaction mixture was stirred at a temperature of 80 °C, for 3 hrs until the reaction was completed (GC-MS). After cooling the mixture was filtered, the product was purified by column chromatography, the result was liquid and the color was black. The IR, NMR and GC-MS spectrometry proved suggest that the product has the following molecular formula,  $(\text{C}_9\text{H}_8\text{F}_3\text{NS}_2)$ .

#### 2.1.3 The synthesis of 1,1,1-trifluoro-4-ethylimine-4-(2-thienyl)-2-thio-3-butene (ES)

To a stirred solution (0.196 g, 0.786 mmol) of 1,1,1-trifluoro-4-ethylimine-4-(2-thienyl)-2-thio-3-butene (ES) in dry toluene (20 ml), Lawesson's reagent (0.19 g, 0.47 mmol) was added. The reaction mixture was stirred at a temperature of 80 °C, for 3 hrs until the reaction was completed, followed by (GC-MS). After cooling the mixture was filtered. The product was purified by column chromatography, the result was black liquid, NMR, IR and GC-MS spectrometry proved suggest that the product has the following molecular formula,  $(\text{C}_{10}\text{H}_{10}\text{F}_3\text{NS}_2)$ .

## 2.2 Complex Preparation

### 2.2.1 The synthesis of complex of MS or ES with Cobalt

The compound was synthesized according to the literature<sup>[13-15]</sup> with some modifications.  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (0.18 g, 0.726 mmol) in 3.5 ml of 70% ethanol was added to the 1,1,1-trifluoro-4-methyl or ethylimine-4-(2-thienyl)-2-thio-3-butene (MS or ES respectively) (0.683 g, 2.18 mmol) in 3.6 ml of ethanol, while stirring at 70 °C. There was immediate precipitation and the mixture was stirred for 3 hr then, the precipitate was filtered and washed by 50% aqueous ethanol and dried in vacuum, the product was black solid of melting point 138-140 °C. The molecular formula of the product was confirmed by CHN, IR and NMR spectrophotometers Table 2, suggest that the product has the following molecular formula,  $[\text{Co}(\text{C}_{14}\text{H}_{10}\text{F}_3\text{NS}_2)_3]$ . Table 2 shows physical properties and some spectral data of the product metal complexes thione.

## RESULTS AND DISCUSSION

The microanalysis data of compounds of the complexes are tabulated in Table 2, and are consistent with the formulas (Table 1.) the GC-MS data shown are molecular weight nearly to calculate of all Schiff bases and thiones compounds and shown one fragment at 111.0 of Schiff bases clearly is attributed to C<sub>5</sub>H<sub>3</sub>SO moiety.

Table- 2- Elemental analysis and some physical properties of the metal complexes

Complex symbol	M.P. °C	Phase state	color	C	H	N
				Calc. (Found)	Calc. (Found)	Calc. (Found)
M-Co	50-52	solid	green-yellow	42.42 (44.82)	3.17 (3.24)	5.49 (5.28)
E-Co	48-49	solid	green	-	-	-
MS-Co	146-147	solid	black	39.9 (37.57)	2.97 (2.15)	5.17 (2.40)
ES-Co	-	solid	black	42.18 (38.77)	3.54 (3.05)	4.91 (1.11)

## 1. IR- Spectra of compounds

The synthesized compounds (Table 3) show IR absorption at about 1193 and 1138 cm<sup>-1</sup> which are assigned to CF<sub>3</sub> group. However the IR of compounds M and E show absorption attributed to conjugated C=O group which suggests, the keto-amine structure. However, compounds MS and ES give absorption at about 1050 cm<sup>-1</sup> which may be attributed to C=S bond. Therefore the compounds have thione-amine structure.

Table 3 Infrared frequencies for the compounds (cm<sup>-1</sup>)

Compound symbol	ν(N-H) stret.	ν(C-H) phen. stret.	ν(C-H) thioph. stret.	ν(C-H) alph. stret.	ν(C=O) stret.	ν(CF <sub>3</sub> ) stret.	ν(C-N) stret.	ν(C=S) stret.
M	3157.8	-	3102.9	-	1617.4	1297.0-1230.7	1133.2	-
E	3169.4	-	3102.3	2967.	1623.2	1193.1-1138.8	1133.2	-
MS	-	3100.0	3002.1	2929.	-	1179.6-1144.3	1289.0	1015.5
ES	-	3104.0	3001.0	2929.	-	1179.9-1134.3	1286.7	1053.1

## 2. NMR Spectra

<sup>1</sup>H, <sup>13</sup>C, HMBC, HSQC and dynamic NMR were measured at the department of Chemistry, University of Surrey, UK. Using a Bruker 500 MHz, at 25 °C, using different solvent; MeOD, CDCl<sub>3</sub> and MD<sub>3</sub>SOMD<sub>3</sub>.

2.1. <sup>1</sup>H NMR spectral data of compounds

<sup>1</sup>H NMR spectral data of M and E Schiff bases and MS and ES thione compounds in Table 3 were measured in MeOD and CD<sub>3</sub>Cl at 25 °C using TMS as internal references<sup>[16]</sup>. Table 3 show signal at 3 ppm due to methyl protons of M and MS compounds, signal at 1 ppm due to methyl protons of E, ES and E-Co compounds, and signal at 3.4 ppm due to methylene protons of E, ES and E-Co compounds. The spectrum of E-Co shows all signals not resolved but chemical shifts not change compare with ligand, <sup>1</sup>H NMR of E-Co complex good prove to hybrid of complex and the donate from oxygen atom. Fig -1

Table 3- <sup>1</sup>H NMR (δ) spectral data of the product Schiff bases and complex compound

Compound symbol	Methyl protons	methylene protons	Vinylic proton	Thiophene protons	Proton of N-H group
M	3.09	-	6.14	7.14, 7.70, 7.75	-
E	1.26	3.44	6.10	7.12, 7.69, 7.71	-
MS	3.195	-	6.95	7.08, 7.54, 7.58	13.34
ES	1.315	3.44	6.05	7.115, 7.635, 7.8	10.38
E-Co	1.27	3.43	6.10	7.12, 7.36, 7.71	-

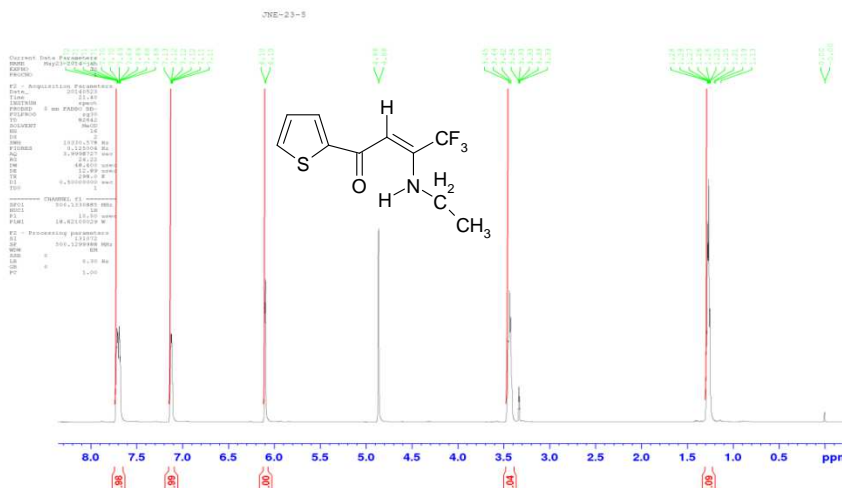


Fig -1- Fig. 2 <sup>1</sup>H NMR of E compound

**3 Thermal Gravimetric Analysis (TGA)**

The instrument model TGA Q500 V6.7 Build 203. The comment ramp 10 °C/min from RT to 900 °C in N<sub>2</sub> were performed at the department of Chemistry, University of Surrey, UK.

**3.1 TGA Spectra of M compound**

Thermal analysis of complex TGA cover shows one step weight loss C<sub>9</sub>H<sub>8</sub>SON. The compound may be volatile Fig.2.

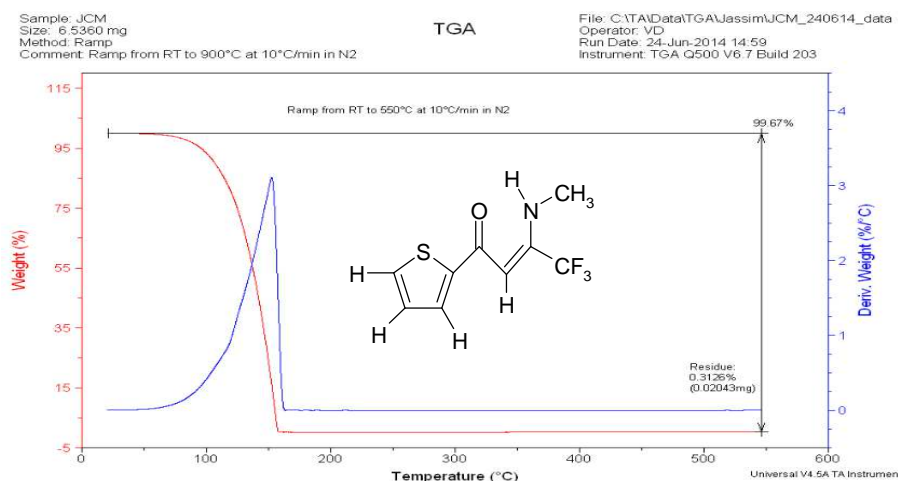


Fig. 2 TGA Spectrum of M Compound

**4.3.5 TGA Spectrum of complex (M-Co)**

Thermal analysis of complex TGA shows two steps of losing 95.4% at 150 °C and the second step loss 3.646% at 200 °C and the residue was 0.56%. Table 4. shows the observed steps are in agreement with the calculated value.

**Table 4. stage of weight losing TGA of complex [M-Co] [Stable]-(exit)**

Step	Temp.-Range	Weight Loss%		Assignment
		Obs.	Cal.	
1	80-160	95.79	96.07	[CO]-(M-Co)
2	170-210	3.646	3.663	[M-Co]-(CO)

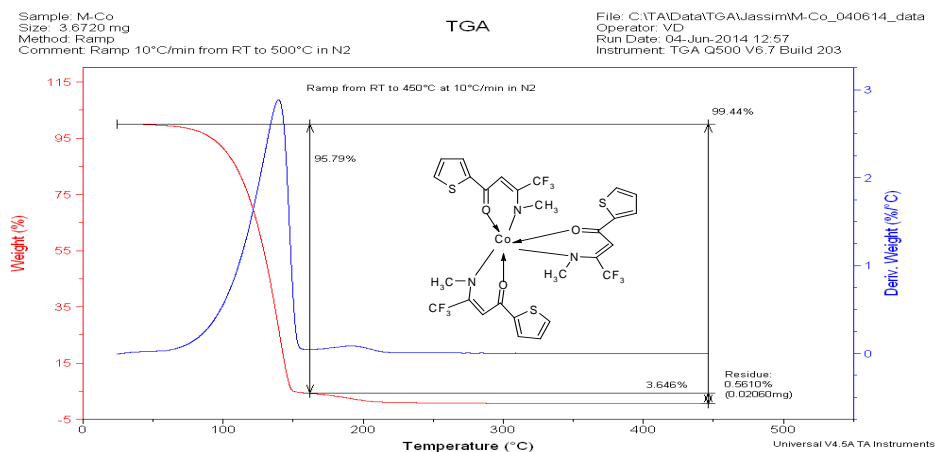


Fig. 3 TGA Spectrum of Complex (M-Co)

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