Thermal Studies for Co(II), Cu(II), Zn(II) and Sn(II) complexes of thiosemicarbazide (HTS)

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Abstract: *There has been considerable interest in the chemistry of transition metal complexes of thiosemicarbazide, primarily because of their bioinorganic relevance[1, 2]. Thiosemicarbazide usually bind to a metal ion as bidentate N,S-donor via dissociation of the hydrazinic proton, forming five-membered chelate rings [3]. This class of complexes is of particular importance because of their potentially beneficial biological (viz, antibacterial, antimalarial, antiviral and antitumor) [2-7]. Because of their simple preparation and excellent complexation not only of transition but also non-transition p-block elements, interesting structural characteristics of their complexes, along with the possibility of their analytical application, thiosemicarbazide have become a subject of intense research interest. This has resulted in a large number of papers and several reviews[8-17].*

1. INTRODUCTION

Herein we report the preparation, thermal, spectral and biological evaluations of Co(II), Cu(II) , Zn(II) and Sn(II) complexes formed from the electrochemical reactions between thiosemicarbazide and metals. Complexes of Co(II), Cu(II) , Zn(II) and Sn(II) with a general formulas [Co(TS)$_2$(ac)$_2$]ac, [Cu(TS)$_2$(ac)$_2$]C$_2$H$_5$OH, [Zn(TS)$_2$(ac)$_2$]C$_2$H$_5$OH and [Sn(TS)$_2$(ac)$_2$]2ac.2H$_2$O where L = thiosemicarbazide and (ac) = acetone, have been synthesized and interpreted using CHN elemental analysis, magnetic susceptibility measurements, molar conductance, thermal analysis and spectroscopic techniques (infrared, electronic UV/vis, ^{1}H-NMR and mass spectra).

The elemental analysis and some physical data of the compounds are given in Table (1.1). The complexes are air-stable, with higher melting points, insoluble in water and most of organic solvents, but soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF).

1.1 Molar conductivity

Conductivity measurements provide a method of testing the degree of ionization of the complexes, the molecular ions that a complex liberates in solution (in case of presence anions outside the coordination sphere), the higher will be its molar conductivity and vice versa[18-23]. The molar conductivity values of the thiosemicarbazide complexes in DMSO solvent (1.0 x 10^{-3} mol L^{-1}) were 30 μs for [Co(TS)$_2$(as)$_2$].ac, 32 μs for [Cu(TS)$_2$(ac)$_2$].C$_2$H$_5$OH, 40 μs for [Zn(TS)$_2$(ac)$_2$].C$_2$H$_5$OH and 35 μs for [Sn(TS)$_2$(ac)$_2$]2ac.2H$_2$O. The molar conductivity located in the range of non-electrolytes (Table 1.1).

1.2 Infrared spectra

The relevant infrared data are presented in Table (1.2) The assignments of the infrared bands were performed by comparing the spectra of the complexes with the free ligand. Based on the thiosemicarbazide, the infrared bands of the -NH$_2$ and NH groups exist at 3366 and 3163 cm^{-1}, respectively. The bands due to ν(C=S) and ν(C=N) appeared at 802 and 1533 cm^{-1}. On complexation these bands were shifted toward higher wavenumbers and strong peak of ν(C=S) may be disappeared or decreasing in its intensity. This suggests that the ligand acts as a bidentate chelating agent[26-28]. Broad bands located above 3300 cm^{-1} for all the synthesized complexes were assigned to ν(O-H) of the uncoordinated water molecules for Sn complex and ethanol for Cu and Zn complexes . In metal complexes, it is difficult to distinguish the bands of -NH$_2$ and NH because of the presence of bands of ethanol. The coordination *via* nitrogen and sulfur atoms is confirmed by bands at 569-582cm^{-1} and 490-500 due to ν(M-N) and ν(M-O) respectively. IR spectra of ligand and its metal complexes are shown in the Figure (1.2).

1.3 Electronic spectra

The electronic spectra of thiosemicarbazide and its complexes are listed in Table (1.3). There are two main absorption bands in the first at the 234-266 nm assigned to π-π*[29], and the second at 305-354 nm due to n-π* intraligand transitions[28,29]. These absorptions also present in the spectra of the Co(II), Cu(II) , Zn(II) and Sn(II) complexes, but shifted. The hyperchromic shift (increasing in the absorbance) in the spectra of all complexes attributed to the complexation behavior of the ligand towards metal ions which was supported the coordination of the Iigand-to-metallic ions.

1.4 Magnetic properties

The cobalt(II) and copper(II) complexes have 1.00

and 1.66 BM, respectively hence, these complexes have an octahedral configuration with d^2sp^3 hybrid orbital.

1.5 ^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the $[Zn(TS)_2(ac)_2].C_2H_5OH$ on comparing with those of spectrum of the free thiosemicarbazide indicate that, the presence of the protons of NH and NH_2 groups and absence of NH atom as shown in Figure (1.4).

- (HTS) ^{1}H-NMR δ (ppm): 2 (N^1H_2 or N^2H), 8.56 (N^5H_2)

-$[Zn(TS)_2(ac)_2].C_2H_5OH$ ^{1}H-NMR δ (ppm): 1.6(CH_3 of acetone or ethanol), 1.75–1.9 (NH_2 shifted), 2.25 (CH_2 of ethanol), 7.2–7.8 (NH_2), 9.65 (OH of ethanol). The spectrum of thiosemicarbazide and its Zn complex is existed in

1.6 Thermogravimetric analysis

Thermogravimetric analysis curves (TGA and DTG) of the thiosemicarbazide complexes are shown in Fig. (1.5). The thermoanalytical results are summarized in Table (1.4) $[Co(TS)_2(ac)_2].ac$ was thermally decomposed in four decomposition steps within the temperature range 25–800ºC. The first decomposition step (obs. = 29%, calc. = 28.1%) at 25– 205ºC, may be attributed to the liberation of the two acetone molecules. The second decomposition steps at 205– 260ºC (obs. = 26.5%, calc. = 27.6%), due to the removal of acetone and $C_2N_2H_4$. The rest of organic moiety ($H_4N_2S_2$) removed on the third step at 260– 655ºC (obs. = 30%, calc = 30%). The decomposition of the Co(II)/L complex molecule ended with a final cobalt residue (obs. = 14.5%, calc = 14.3%).

The TG curve of $[Cu(TS)_2(as)_2].C_2H_5OH$ indicates that the mass change begins at 25ºC and continuous up to 800ºC. The first mass loss corresponds to the liberation of two acetone, ethanol and ($C_2N_2H_4$) fragments (obs. = 53.9%, calc = 53.7%) at 25– 232ºC. The second decomposition step occurs at 232– 729ºC and corresponds to the loss of 2(NH_2-NH_2), N_2 and S_2 (obs. = 30.6 %, calc = 30.7%). The final is copper metal (obs. = 15.5%, calc = 15.6%).

$[Zn(TS)_2(as)_2].C_2H_5OH$ complex was thermally decomposed in three decomposition steps at 25– 800ºC. The first decomposition step (obs. = 63.6%, calc = 62.3%) within the temperature range 25– 250ºC, is attributed to the liberation of two acetone, ethanol, 2(NH_2-NH_2) and N_2 fragments. The second step at 250– 430ºC (obs. = 15.7%, calc = 16%), is due to the removal of S_2. The third step at 430– 605ºC (obs. = 5.7%, calc = 5.9%), is due to the removal of C_2. The rest Zn contaminated NH_2 (obs. = 14.7%, calc = 16%).

$[Sn(TS)_2(ac)_2]2ac.2H_2O$ is thermally stable up to 50ºC and the first step with mass loss at 242ºC corresponds to the loss of four acetone, two hydrated water 2(CH_2- CH_2) and $2N_2$ fragments (obs. = 62.4%, calc = 63%). Continuous mass loss from 242 to 410ºC corresponds to the loss of (NH_2-NH_2) + S_2 $2N_2$ fragments (obs. = 19%, calc = 17.3%). The final decomposition is Sn metal (obs. = 18.6%, calc = 19.7%).

1.7 Kinetic studies

Several equations[30–37] have been proposed as means of analyzing a TG curve and obtaining values for kinetic parameters. Many authors [30–36] have discussed the advantages of this method over the conventional isothermal method. The rate of a decomposition process can be described as the product of two separate functions of temperature and conversion [37], using

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad \text{........ (1.4)}$$

where a is the fraction decomposed at time t, k(T) is the temperature dependent function and $f(\boldsymbol{\alpha})$ is the conversion function dependent on the mechanism of decomposition. It has been established that the temperature dependent function k(T) is of the Arrhenius type and can be considered as the rate constant k

$$k = A\ e^{-E*/RT} \qquad \text{........ (1.5)}$$

where R is the gas constant in (J mol^{-1} K^{-1}). Substituting Eq. (1.5) into Eq. (1.4), we get $\frac{d\alpha}{dt} = (A/\varphi\ e^{-E*/RT})f(\alpha)$ where φ is the linear heating rate dT/dt. On integration and approximation, this equation can be obtained in the following form.

$$\ln g\ (\alpha) = -[E*/RT] + \ln [AR/\varphi\ E*] \qquad (1.6)$$

where g(α) is a function of a dependent on the mechanism of the reaction. The integral on the right-hand side is known as temperature integral and has no closed for solution. So, several techniques have been used for the evaluation of temperature integral. Most commonly used methods for this purpose are the differential method of Freeman and Carroll integral method of Coat and Redfern, the approximation method of Horowitz and Metzger. In the present investigation, the general thermal behaviors of the prepared complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are shown in Fig. (1.6) and Table (1.5). The kinetic parameters have been evaluated using the following methods and the results obtained by these methods are well agreement with each other. The following two methods are discussed in brief.

In the present investigation, the general thermal behaviors of the HTS complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are discussed in Table (1.5) and Fig. (1.6) The kinetic parameters have been evaluated using the Coats-Redfern equation:

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\varphi}\int_{T_1}^{T_2}\exp(-\frac{E^*}{RT})dt \qquad (1.7)$$

This equation on integration gives;

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \qquad (1.8)$$

A plot of left-hand side (LHS) against 1/T was drawn. E^* is the energy of activation in J mol^{-1} and calculated from the slop and A in (s^{-1}) from the intercept value. The entropy

of activation ΔS^* in $(JK^{-1}mol^{-1})$ was calculated by using the equation:

$$\Delta S^* = R \ln(Ah/k_B T_s)$$

Where k_B is the Boltzmann constant, h is the Plank's constant and T_s is the DTG peak temperature (**Flynn and Wall 1996**).

The Horowitz-Metzger equation is an illustrative of the approximation methods.

$$\log[\{1-(1-\alpha)^{1-n}\}/(1-n)] = E^*\theta/2.303RT_s^2$$

for $n \neq 1$ .... (1.10)

When $n = 1$, the LHS of equation 4 would be $\log[-\log (1-\alpha)]$. For a first-order kinetic process the Horowitz-Metzger equation may be written in the form:

$$\log[\log(w_\alpha / w_\gamma)] = E^*\theta/2.303RT_s^2 – \log 2.303 \quad .... (1.11)$$

Where $\theta = T - T_s$, $w_\gamma = w_\alpha − w$, w_α = mass loss at the completion of the reaction; w = mass loss up to time t. The plot of $\log[\log(w_\alpha / w_\gamma)]$ vs θ was drawn and found to be linear from the slope of which E^* was calculated. The pre-exponential factor, A, was calculated from the equation:

$$E^*/RT_s^2 = A/[\varphi \exp(-E^*/RT_s)] \quad .... (1.12)$$

The entropy of activation, ΔS^*, was calculated from equation 3. The enthalpy activation, ΔH^*, and Gibbs free energy, ΔG^*, were calculated from;

$$\Delta H^* = E^* – RT \text{ and } \Delta G^* = \Delta H^* – T\Delta S^*, \text{ respectively.}$$
.... (1.13)

ΔG is positive for reaction for which ΔH is positive and ΔS is negative. The reaction for which ΔG is positive and ΔS is negative considered as unfavorable or non spontaneous reactions.

Reactions are classified as either exothermic ($\Delta H < 0$) or endothermic ($\Delta H > 0$) on the basis of whether they give off or absorb heat. Reactions can also be classified as exergonic ($\Delta G < 0$) or endergonic ($\Delta G > 0$) on the basis of whether the free energy of the system decreases or increases during the reaction.

The thermodynamic data obtained with the two methods are in harmony with each other. The activation energy of Co^{+2}, Cu^{+2}, Zn^{+2} and Sn^{+2} complexes is expected to increase in relation with decrease in their radii (**Tunali and Ozkar 1993**). The smaller size of the ions permits a closer approach of the ligand. Hence, the E value in the first stage for the Zn^{+2} complex is higher than that for the other Zn^{+2}, Co^{+2} and Cu^{+2} complexes.

The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9949 to 0.9993, showing a good fit with linear function. It is clear that the thermal decomposition process of all HTS complexes is non-spontaneous, i.e, the complexes are thermally stable.
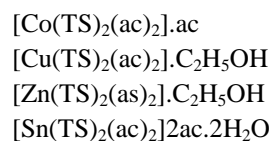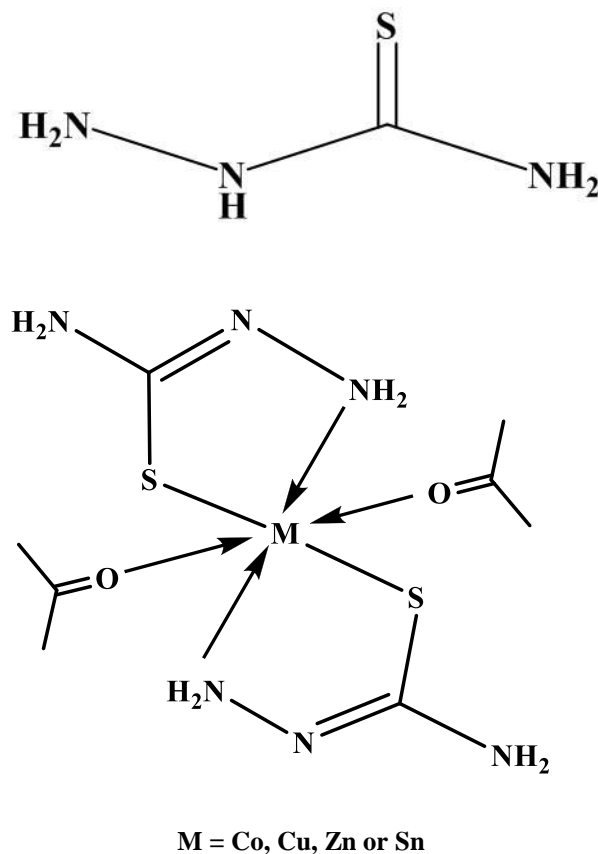

M = Co, Cu, Zn or Sn

$[Co(TS)_2(ac)_2].ac$
$[Cu(TS)_2(ac)_2].C_2H_5OH$
$[Zn(TS)_2(as)_2].C_2H_5OH$
$[Sn(TS)_2(ac)_2]2ac.2H_2O$

Fig.(1.1) The structures of thiosemicarbazide and its metals complexes

Table (1.1) Analytical results for the prepared complexes of thiosemicarbazide.

Compound Empirical formula	Formula weight	Colour	M.P., ºC	% Found (Calc.)			Λm μs
				C	H	N	
[Co(TS)$_2$(ac)$_2$].ac C$_{11}$H$_{26}$CoN$_6$O$_3$S$_2$	413.4	Green	160	31.61 (32.00)	5.80 (6.34)	20.00 (20.30)	30
[Cu(TS)$_2$(ac)$_2$].C$_2$H$_5$OH C$_{10}$H$_{26}$CuN$_6$O$_3$S$_2$	406.0	Faint Green	156	29.70 (29.60)	6.28 (6.45)	20.28 (20.70)	32
[Zn (TS)$_2$(ac)$_2$].C$_2$H$_5$OH C$_{10}$H$_{26}$ZnN$_6$O$_3$S$_2$	407.9	Yellowish White	164	28.90 (29.40)	6.14 (6.42)	20.30 (20.60)	40
[Sn (TS)$_2$(ac)$_2$]2ac.2H$_2$O C$_{14}$H$_{38}$SnN$_6$O$_6$S$_2$	568.0	Yellowish White	175	30.01 (29.6)	6.80 (6.40)	15.62 (14.80)	35

Table (1.2) Significant IR spectra bands (cm^{-1}) of thiosemicarbazide and its metal complexes.

Assignment	Compound				
	HTS	[Co(TS)$_2$(ac)$_2$].ac	[Cu(TS)$_2$(ac)$_2$].C$_2$H$_5$OH	[Zn(TS)$_2$(ac)$_2$].C$_2$H$_5$OH	[Sn(TS)$_2$(ac)$_2$]2ac.2H$_2$O
$\upsilon(N^1H_2)$	3366	3379	---	---	3370
$\upsilon(N^4H)$	3265	3234	3234	3234	3219
$\upsilon(N^2H)$	3163	---	---	---	---
$\upsilon(C=N)$	1533	1597	1597	1597	1600
$\upsilon(C=S)$	802	---	---	---	---
$\upsilon(C-S)$	---	634	634	632	634
$\delta(OH)$	---	1365	1363	1363	1365
$\upsilon(M-O)$	---	580	582	576	569
$\upsilon(M-N)$	---	496	490	500	500

Table (1.3) The electronic spectra data of thiosemicarbazide and its metal complexes

	π-π*	n-π*				CT–transition					
HTS	234 (42740)	321 (31150)	337 (29670)	305 (32790)	354 (28250)	------	------	------	-----	------	-----
[Co(TS)$_2$(ac)$_2$].ac	255 (39220)	352 (28410)	-----	-----	-----	393 (25450)	409 (24450)	422 (23700)	439 (22780)	461 (21 690)	486 (21370)
[Cu(TS)$_2$(ac)$_2$] .C$_2$H$_5$OH	261 (38310)	306 (32680)	342 (29240)	-----	-----	413 (24210)	423 (23640)	489 (20450)	------	------	-----
[Zn(TS)$_2$(ac)$_2$]. C$_2$H$_5$OH	266 (37590)	305 (32790)	323 (30960)	330 (30300)	344 (29070)	------	------	------	------	-------	-----
[Sn (TS)$_2$(ac)$_2$] 2ac.2H$_2$O	254 (39370)	325 (30770)	334 (29940)	316 (31650)	351 (28490)	------	------	------	------	------	-----

Table (1.4) The thermal data of thiosemicarbazide and its metal complexes.

Compound	steps	Temperature range (°C)	TG weight loss (%)		Assignments	T_{max} / °C
			Calc.%	Found%		
[Co(TS)$_2$(ac)$_2$].ac	1	25 – 205	28.100	29.00	2[O=C(CH$_3$)$_2$]	190
	2	205 – 260	27.60	26.50	2[O=C(CH$_3$)] and (C$_2$N$_2$H$_4$)	240 263 420 and 560
	3	260 – 655	30.00	30.00	(NH$_2$-NH$_2$) and S$_2$	
	4	More than 655	14.30	14.00	Residual Cobalt	
[Cu(TS)$_2$(ac)$_2$].C$_2$H$_5$OH	1	25 – 232	53.70	53.90	2[O=C(CH$_3$)$_2$], C$_2$H$_5$OH and (C$_2$N$_2$H$_4$)	107 195 365 530 And 760
	2,3	232 – 729	30.70	30.60	2(NH$_2$-NH$_2$), N$_2$ and S$_2$	
	4	More than 729	15.65	15.50	Residual Cooper	
[Zn(TS)$_2$(ac)$_2$].C$_2$H$_5$OH	1	25 – 250	62.30	63.60	2[O=C(CH$_3$)$_2$], C$_2$H$_5$OH, 2(NH$_2$- NH$_2$) and N$_2$	195 and 270
	2	250– 430	15.70	16.00	S$_2$	
	3	430– 605	5.90	5.70	C$_2$	
	4	More than 605	16.00	14.70	Residual Zinc metal	
[Sn(TS)$_2$(ac)$_2$]2ac.2H$_2$O	1	25 – 242	63.00	62.40	4[O=C(CH$_3$)$_2$], 2H$_2$O, (CH$_2$- CH$_2$) and 2N$_2$	195 and 270
	2	242 – 410	17.30	19.00	(NH$_2$- NH$_2$) and S$_2$	
	3	More than 410	19.70	18.60	Residual Tin	

Table 1.5: Kinetic parameters using the Coats–Redfern (CR) and Horowitz–Metzger (HM) operated for thiosemicarbazide and its Co(II), Cu(II), Zn(II) and Sn(II) complexes.

Complex	Stage	Method	Parameter					r
			E $(J\ mol^{-1})$	A (s^{-1})	ΔS $(J\ mol^{-1}\ K^{-1})$	ΔH $(J\ mol^{-1})$	ΔG $(J\ mol^{-1)}$	
Co(II)	1st	CR	1.03×10^5	4.02×10^9	-6.47×10	9.94×10^4	1.31×10^5	0.9975
		HM	1.16×10^5	2.03×10^{11}	-3.21×10	1.12×10^5	1.27×10^5	0.9966
Cu(II)	1st	CR	9.22×10^4	1.93×10^8	-9.01×10	8.9×10^4	1.31×10^4	0.9987
		HM	1.17×10^5	1.88×10^{11}	-3.29×10	1.13×10^5	1.29×10^4	0.9985
Zn(II)	1st	CR	1.85×10^5	3.22×10^{18}	1.06×10^2	1.81×10^5	1.32×10^5	0.9963
		HM	1.97×10^5	3.43×10^{20}	1.45×10^2	1.93×10^5	1.26×10^5	0.9935
Sn(II)	1st	CR	1.75×10^5	3.62×10^{17}	8.76×10	1.71×10^5	1.31×10^5	0.9992
		HM	1.92×10^5	1.19×10^{20}	1.36×10^2	1.88×10^5	1.25×10^5	0.9993
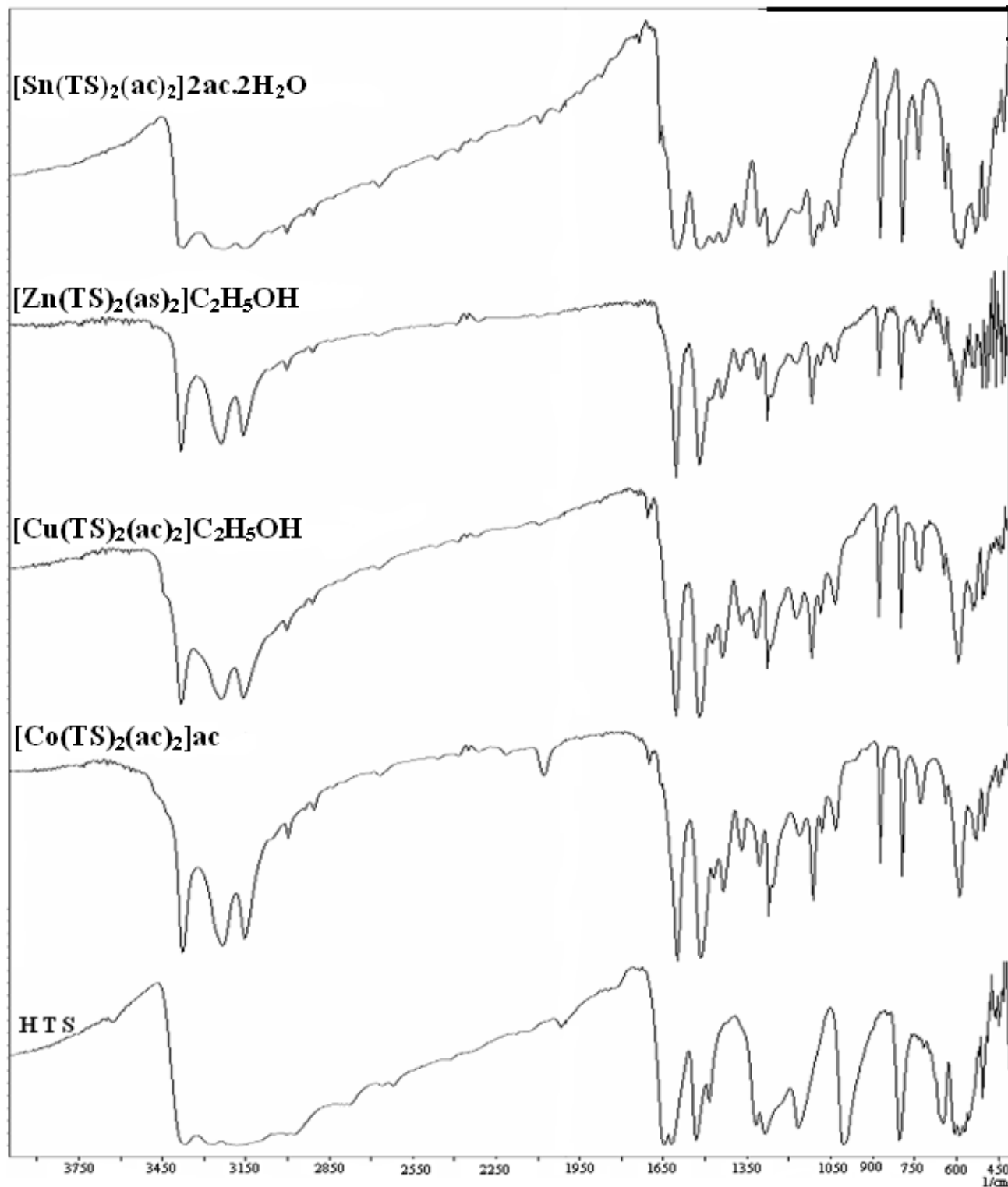
Fig. (1.2) IR spectra of thiosemicarbazide and its metal complexes
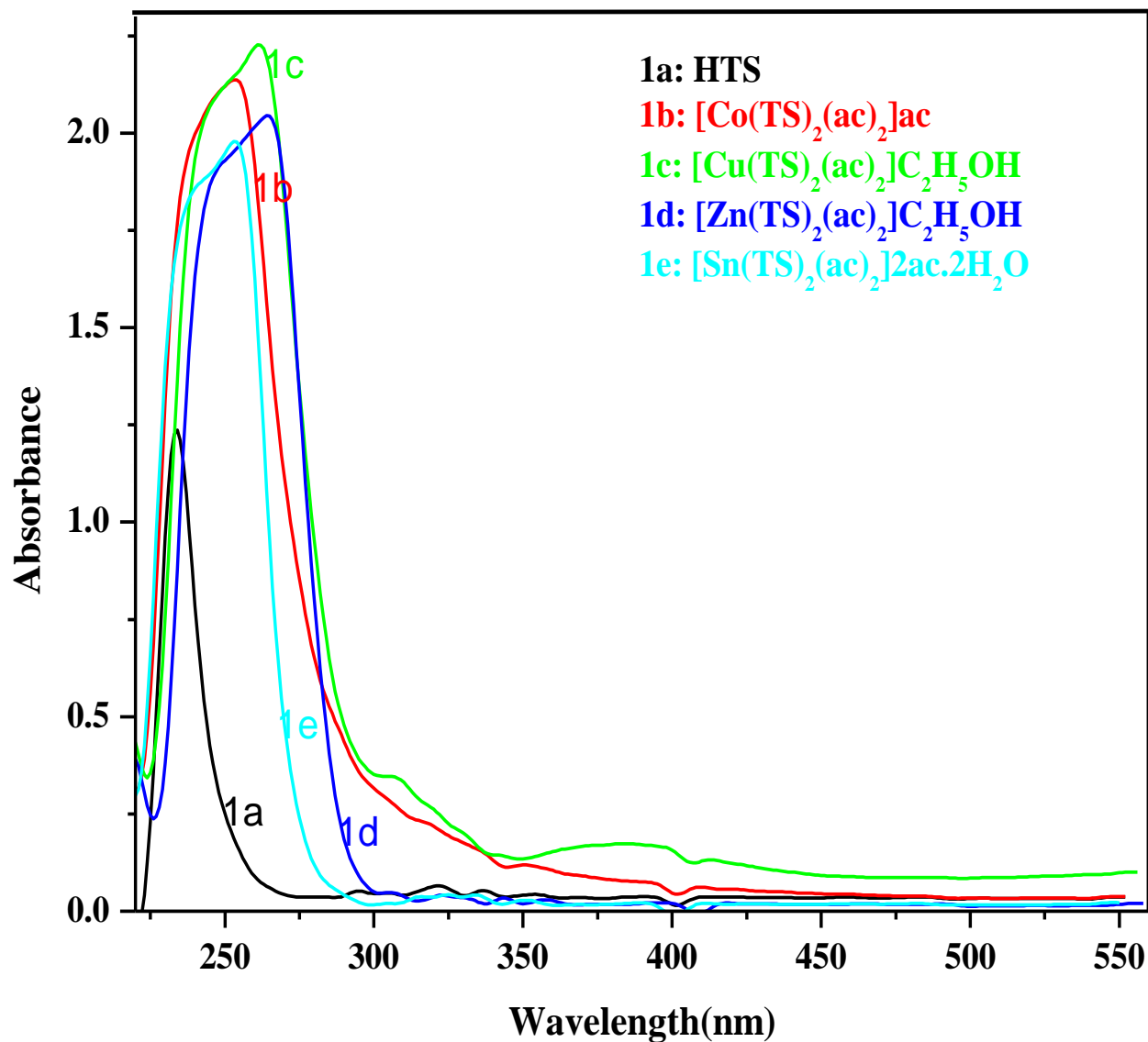
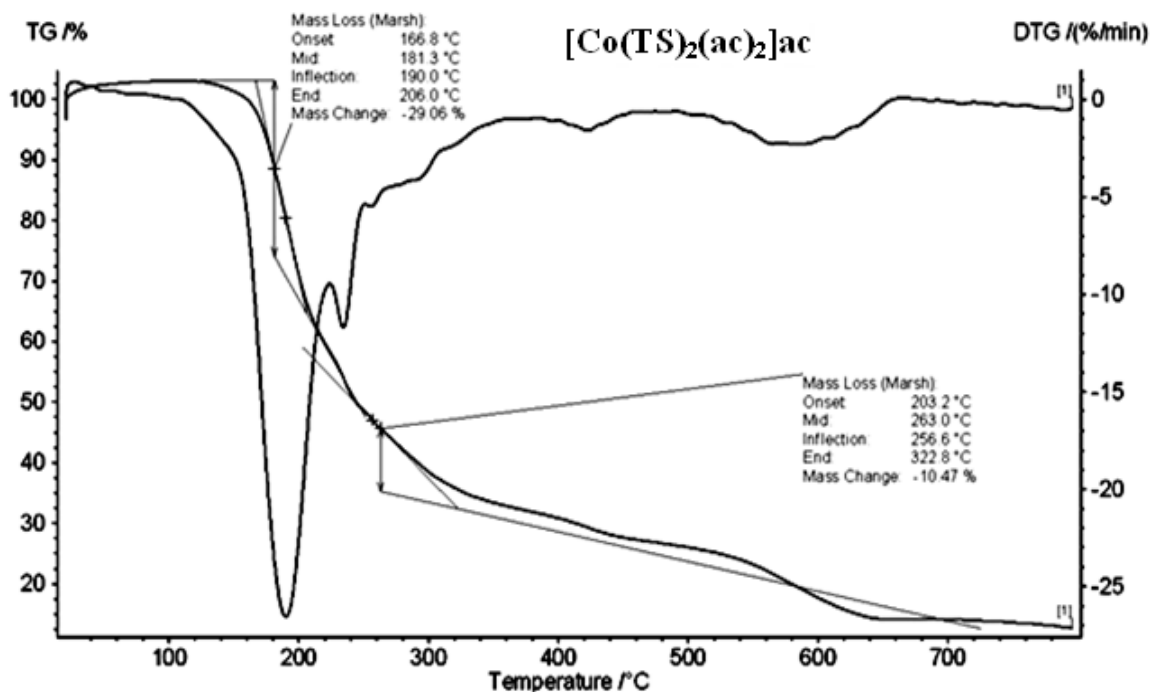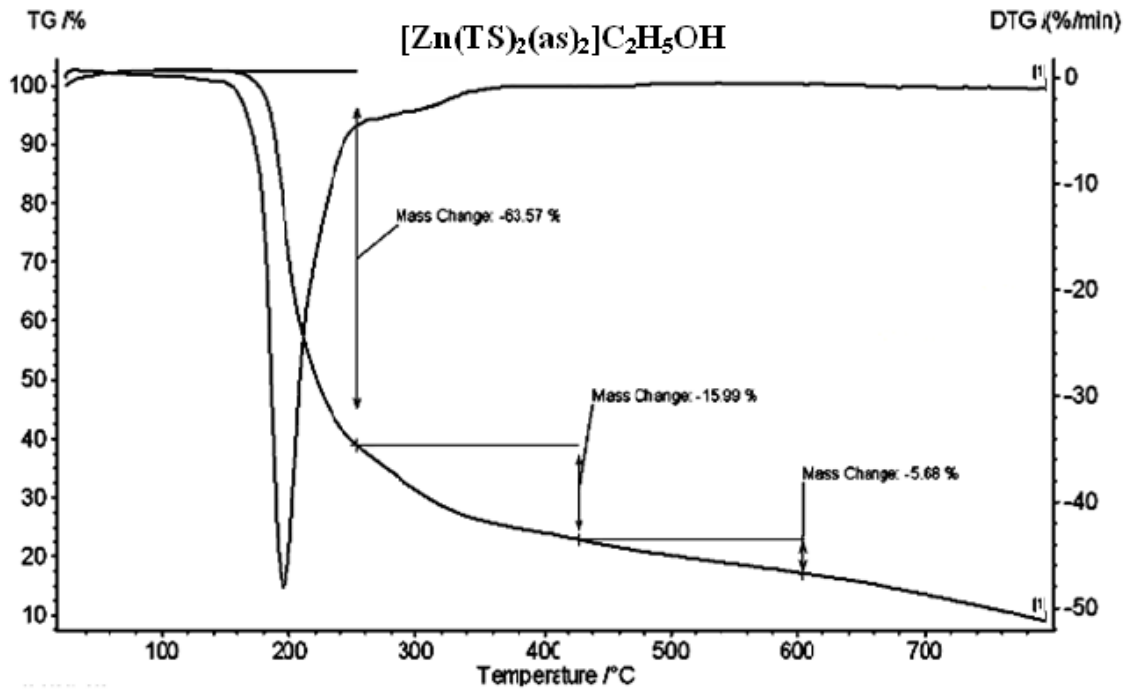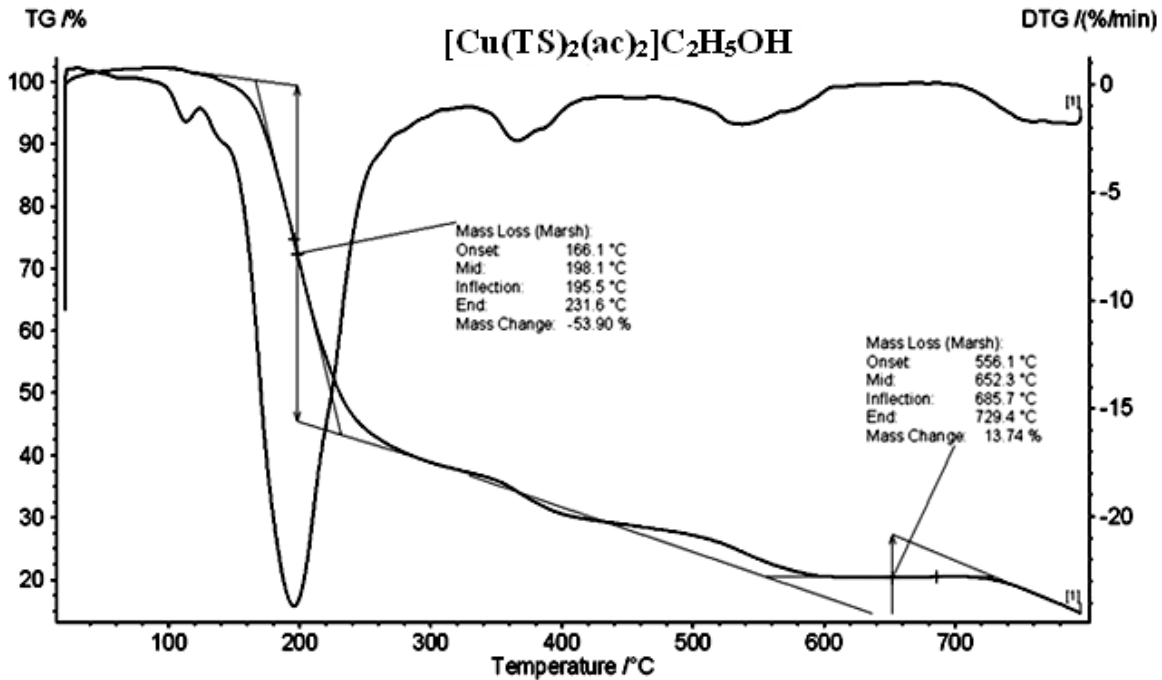**Fig. (1.3)** The electronic spectra of thiosemicarbazide and its metal complexes
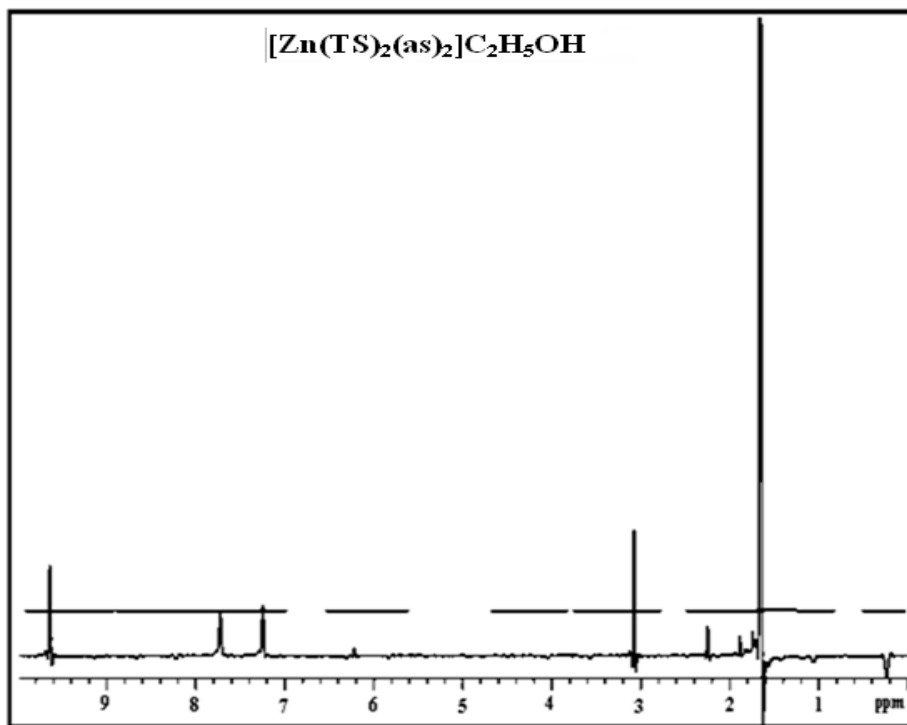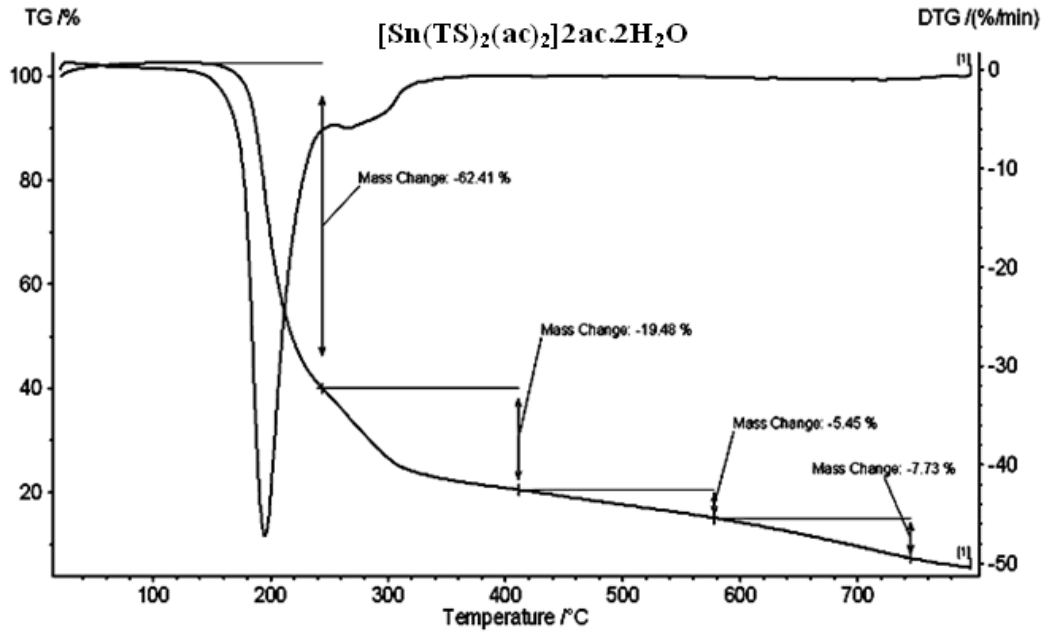
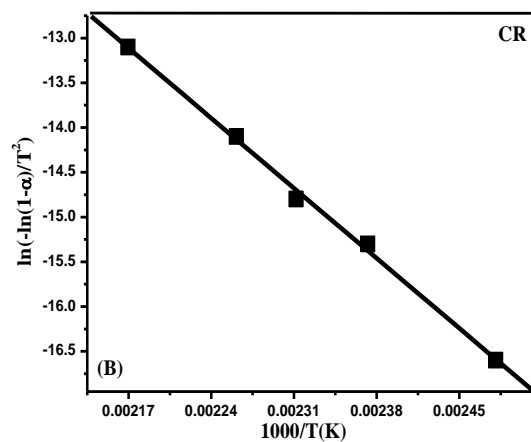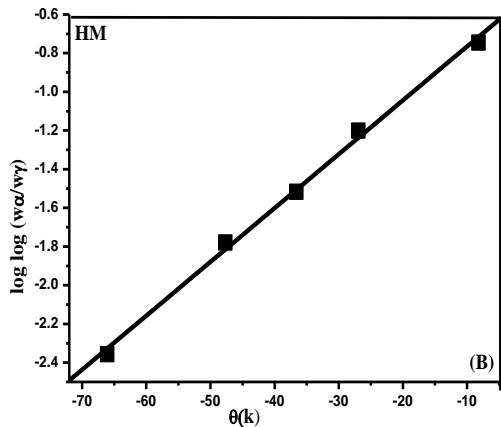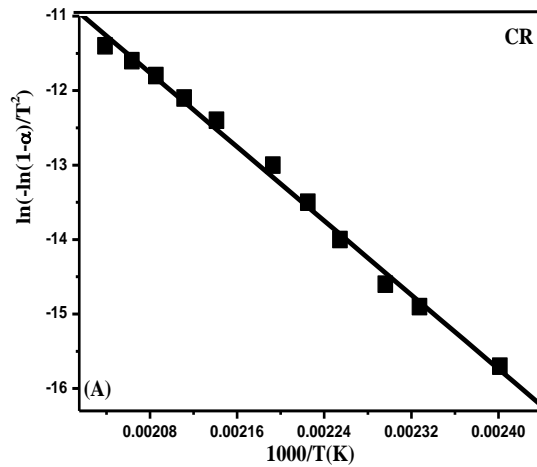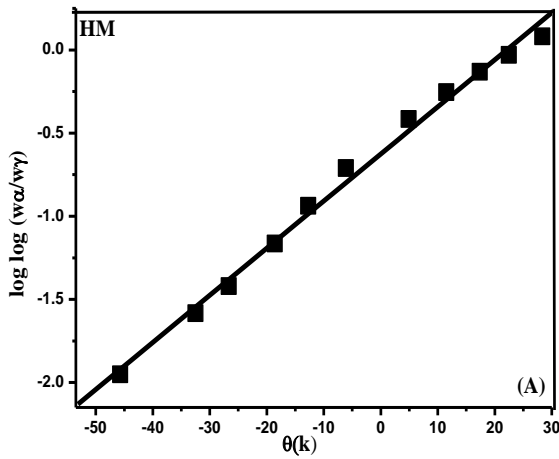**Fig. (1.4)** NMR spectra of zinc thiosemicarbazide complex

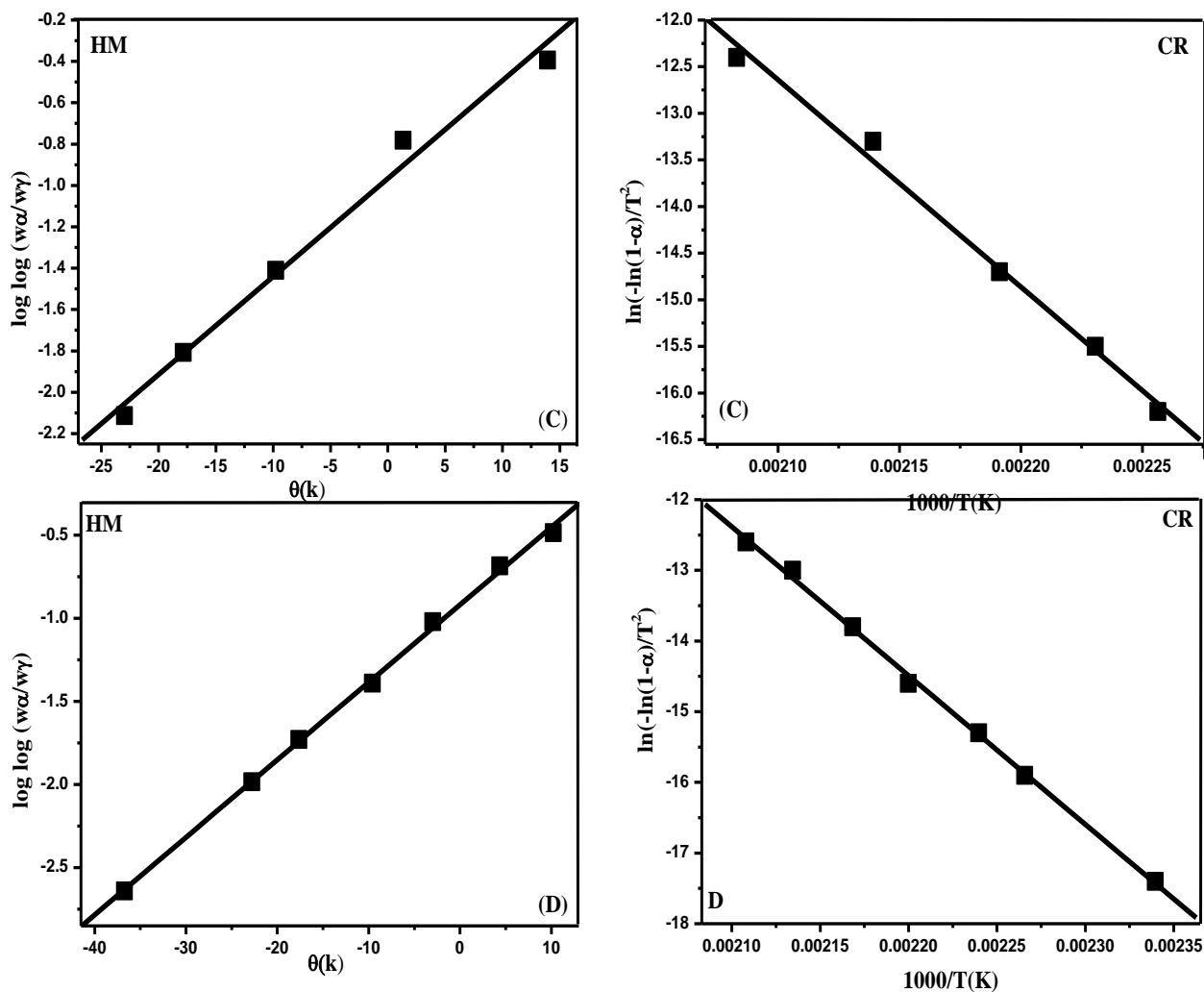**Fig. (1.5)** TGA and DTG diagram of thiosemicarbazide and its metal complexes.

Fig. (1.6): Kinetic data curves of: (A) $[Co(TS)_2(ac)_2]ac$,
(B) $[Cu(TS)_2(ac)_2]C_2H_5OH$, (C) $[Zn(TS)_2(as)_2]C_2H_5OH$ and
(D) $[Sn(TS)_2(ac)_2]2ac.2H_2O$ complexes.

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