Spectroscopic and thermal studies for Co(II), Cu(II), Zn(II) and Sn(II) metal complexes of Salicaldehydethiosemicarbazone synthesized by electrochemical technique

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ABSTRACT

A series of metal complexes of Co(II), Cu(II), Zn(II) and Sn(II) having the general composition [ML] where L = Salicaldehydethiosemicarbazone M = Co(II), Cu(II), Zn(II) and Sn(II) have been prepared by electrochemical method and characterized by elemental chemical analysis, magnetic susceptibility measurements, thermal analysis, molar conductance, and spectral (IR, Raman, electronic UV/Vis, IH-NMR, mass) The IR and Raman spectral data suggests the involvement of sulphur and azomethane nitrogen in coordination to the central metal ion. On the basis of spectral studies, a octahedral geometry has been assigned for Co(II), Cu(II), and tetrahedral geometry has been assigned for Zn(II), Sn(II) complexes. The IR spectra show that the Salicaldehydethiosemicarbazone free ligand is coordinated to the metal(II) as a neutral bidentate ligand through both of the lone pair of electrons of the C=O carbonyl group, C=N azomethine group and C=S group. The differential thermogravimetric analysis (DTG) curves were used to study the decomposition steps of the isolated complexes using Horowitz-Metzger (HM) and Coats-Redfern (CR) methods.

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INTRODUCTION

The chemistry of thiosemicarbazones has received considerable attention in view of their variable bonding modes, promising biological implications, structural diversity, and ion-sensing ability [1-3]. They have been used as drugs and are reported to possess a wide variety of biological activities against bacteria, fungi, and certain type of tumors and they are also a useful model for bioinorganic processes [4, 5]. As regards biological implications, thiosemicarbazone complexes have been intensively investigated for antiviral, anticancer, antitumoral, antimicrobial, antiamoebic, and anti-inflammatory activities, the inhibitory action is attributed due to their chelating properties [6-9]. In view of the above applications, the present work relates to the synthesis and spectroscopic studies of Co(II), Cu(II), Zn(II) and Sn(II) complexes with Salicaldehydethiosemicarbazone.

EXPERIMENTAL

All the chemicals (Aldrich) were subjected to purification before use. The solvents used were reagent grade. DMF (BDH) (Analar), absolute ethanol and methanol (Fluka) were used as supplied. Acetone was dried over anhydrous $MgSO_4$ before use. The metals (Alfa Inorganics) used, Co, Cu, Zn and Sn were purchased in the form of sheets (~2 cm x 2cm, 2-3 mm thick). The oxide surface was removed by treating the metal with conc. HNO_3 for several minutes and then washing with distilled water. Tetraethyl-ammonium perchlorate, Et_4NClO_4, (BDH) was used as supplied [10-12].

Synthesis of Salicaldehydethiosemicarbazone

The organic derivative was prepared by adding an alcoholic solution of Salisaldehyde (12ml ≈ 0.1 mol) to alcoholic solution of thiosemicarbazide (9.1gm ≈ 0.1mol). The reaction mixture was left under reflux over hotplate with stirring for 1h. The resulting yellowish white crystals were collected and washed with ethanol, diethyl ether and left to dry. Yield (18gm ≈ 95%) and the melt point at 133ºC. The structure of Salicaldehydethiosemicarbazone, (H_2STS) is shown in Fig.1.
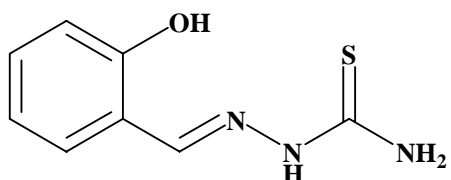

Fig. 1. The structure of Salicaldehydethiosemicarbazone Ligand, (H_2STS).

Electrochemical procedure

The preparative results show that the direct electrochemical oxidation of the metals in the presence of a ligand solution is a one-step process and represents a convenient and simple route to a variety of transition metal complexes. The apparatus used in the electrochemical reaction consists of a tall-form 100 mL Pyrex beaker containing 50 mL of the appropriate amount of the organic ligand dissolved in acetone solution. The cathode is a platinum wire of approximately 1mm diameter. The metal (2-5 g) was suspended and supported on a platinum wire. Measurements of the electrochemical efficiency, E_f, defined as moles of metal dissolved per Faraday of electricity, for the M/L system (where L = ligand used) gave $E_f = 0.5 \pm 0.05$ mol F^{-1} [10-12].

Electrochemical synthesis of Salicaldehydethiosemicarbazone metal complexes

Electrolysis of cobalt metal into 60 ml of anhydrous acetone solution of Salicaldehydethiosemicarbazone (H_2STS) ligand as an example, (0.4686gm, 5mmol), 1.5 mg Et_4NClO_4 dissolved in two drops of water and 20 V current led to dissolution of 59 mg of Co during 60 min. ($E_f = 0.5$ mol. F^{-1}). Since, most of the products are insoluble in the reaction mixture, the collection procedure involved filtration, after which the solid was washed with diethyl ether. The resulting faint beige powder (0.8gm, 53 %) was collected and analyzed as [Co(STS)(ac)(H_2O)]. By the same way Cu, Zn, and Sn complexes were isolated and all the data were gathered in Table 1.

Table 1. Electrochemical conditions for the synthesis of STS metal complexes.

Product Formula	Mol. Wt.	Metal consumed (mg)	Wt. of Product (gm)	E_f mol F^{-1}
[Co(STS)(ac) (H_2O)_2]	346.3	110	0.8	0.55
[Cu(STS)(ac) (H_2O)_2]	350.9	125	0.94	0.51
[Zn(STS) (H_2O)]	276.65	60	0.5	0.52
[Sn(STS) (H_2O)]	330	230	0.94	0.52

Spectral measurements

The spectra of solutions were measured in UV/Vis range at Central Laboratory, Ain Shams University. Infrared spectra for the samples were recorded by Perkin Elmer FTIR 1605 using KBr pellets at National Research Center, Cairo, Egypt. Raman spectra were measured on a Nicolet spectrometer using a laser line of Nd-YAG of wavelength = 1064 nm and a power of 200 mW at NRC in Egypt.

^{1}H-NMR spectra

The ^{1}H-NMR spectra were recorded on an Varian Mercury VX-300 NMR spectrometer. ^{1}H spectra were run at 300 MHz in deuterated dimethylsulphoxide (DMSO-d_6). Chemical shifts are quoted in δ and were related to that of the solvents.

Microanalytical techniques

Carbon and hydrogen contents were determined using a Perkin-Elmer CHN 2400 on micro analytical unit at Cairo University. The melting point of ligand and their metal complexes were measured by the electro thermal melting point Stuart SMP3 made in UK.

Magnetic measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method [13].

Thermal investigation

Thermogravimetric analysis (TGA and DTG) were carried out in dynamic nitrogen atmosphere (30 ml/min) with a heating rate of 10°C/min using a Schimadzu TGA-50H thermal analyzer.

RESULTS AND DISCUSSION

Measurements of the electrochemical efficiency, E_f, defined as moles of metal dissolved per Faraday of electricity, for the Co/L system (where L = ligand) gave $E_f = 0.5\pm0.05$ mol F^{-1}. The values listed in Table 1 show that the reaction of the thiosemicarbazide and Acetaldehydethiosemicarbazone ligands with cobalt anode is compatible with the following equations 1 and 2.

Cathode: H_2L + 2e $\rightarrow$ L^{2-} + H_2 (g)   (1)

Anode: L^{2-} + Co $\rightarrow$ CoL + 2e   (2)
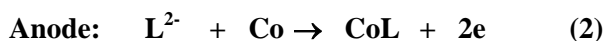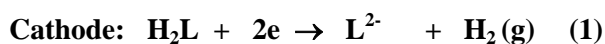
The elemental analysis and some physical data of the resulted compounds are given in Table 2. The complexes are air-stable, hygroscopic, with higher melting points, insoluble in H_2O and most of organic solvents, but soluble in DMSO and DMF. The ligand behaves as tridentate coordinate through sulphur and nitrogen donor atoms, Fig. 2. By using electrochemical method the ligand reacted with Co(II), Cu(II), Zn(II) and Sn(II) metal ions give a yield complexes corresponding

Table 2. Analytical results for the prepared complexes of salicaldehydethiosemicarbazone and their metal complexes.

| Compound Empirical formula	Formula weight	Colour	m.p. (ºC)	% Found (Calc.)			Am µs
				C	H	N	
H$_2$STS C$_8$H$_9$N$_3$OS	195.24	Yellowish White	221ºC	49.02 (49.21)	5.48 (4.65)	21.1 (21.52)	**7**
[Co(STS)(ac)(H$_2$O)$_2$] C$_{11}$H$_{17}$Co 0N$_3$O$_4$S	346.3	Deep brown	285ºC	38.27 (38.15)	5.08 (4.95)	12.94 (12.14)	40
[Cu(STS)(ac)(H$_2$O)$_2$] C$_{11}$H$_{17}$CuN$_3$O$_4$S	350.9	Brownish green	165ºC	39.03 (37.7)	4.22 (4.88)	12.08 (11.98)	51
[Zn(STS)(H$_2$O)] C$_8$H$_9$ZnN$_3$O$_2$S	276.65	Yellow	275ºC	34.45 (34.73)	3.81 (3.28)	15.27 (15.19)	28
[Sn(STS)(H$_2$O)] C$_8$H$_9$SnN$_3$O$_2$S	330	Greenish yellow	235ºC	29.02 (29.12)	3.18 (2.75)	11.96 (12.74)	77
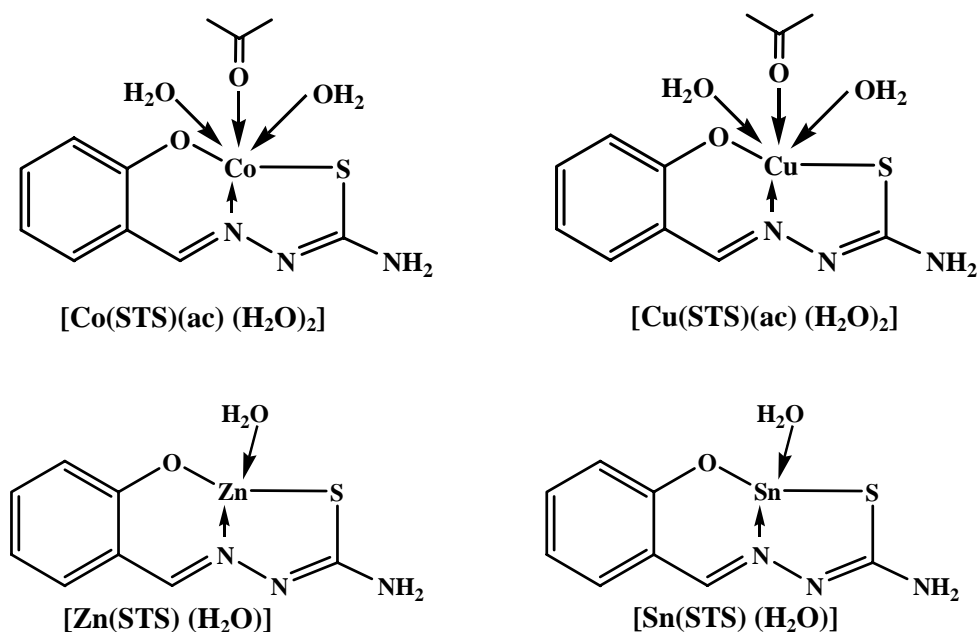
Fig. 2. The structures of Salicaldehydethiosemicarbazone metals complexes.

Table 3. Significant IR spectral bands, cm^{-1} of Salicaldehydethiosemicarbazone and it's metal complexes.

Compound	υNH_2	υOH	υN^4H	υN^2H	$\upsilon C=N$	$\upsilon C=S$	$\upsilon C-S$	δOH	$\upsilon M-O$	$\upsilon M-N$
H_2STS	3321	3445	----	3172	1603	777	----	1368	----	----
[Co(STS)(ac)(H$_2$O)$_2$]	----	3447	----	----	1601	----	645	1312	495	455
[Cu(STS)(ac)(H$_2$O)]	----	3447	3280	3152	1601	----	645	1312	495	455
[Zn(STS)H$_2$O)]	3319	3447	----	3181	1601	----	615	1319	495	446
[Sn(STS)(H$_2$O)]	3319	3442	3248	3172	1602	----	630	1313	522	448

to the formulas: [Co(STS)(ac)(H$_2$O)$_2$], [Cu(STS)(ac)(H$_2$O)$_2$], [Zn(STS)(H$_2$O)] and [Sn(STS)(H$_2$O)]. The newly synthesized complexes are very stable at room temperature in the solid state. The analytical data are in a good agreement with the proposed stoichiometry of the complexes.

Molar conductivity

Conductivity measurements have frequently been used in structural of metal chelates (mode of coordination) within the limits of their solubility. They 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 [16-20]. The molar conductivity values of the Salicaldehydethiosemicarbazone and its complexes in DMSO solvent (1.0 x 10^{-3} mol L^{-1}) were 7μs for H$_2$STS ligand, 40μs for [Co(STS)(ac) (H$_2$O)$_2$] (I), 51μs for [Cu(STS)(ac) (H$_2$O)] (II), 28μs for [Zn(STS) (H$_2$O)] (III) and 77μs for [Sn(STS) (H$_2$O)] (IV). The molar conductivity measurements located in the range of non-electrolytic concerning Co(II), Cu(II), Zn(II) and Sn(II) complexes (Table 2).

Infrared and Raman spectra

The assignments of the significant IR spectral bands of ligand and its metal complexes are presented in Table 3. In principle, the ligand can
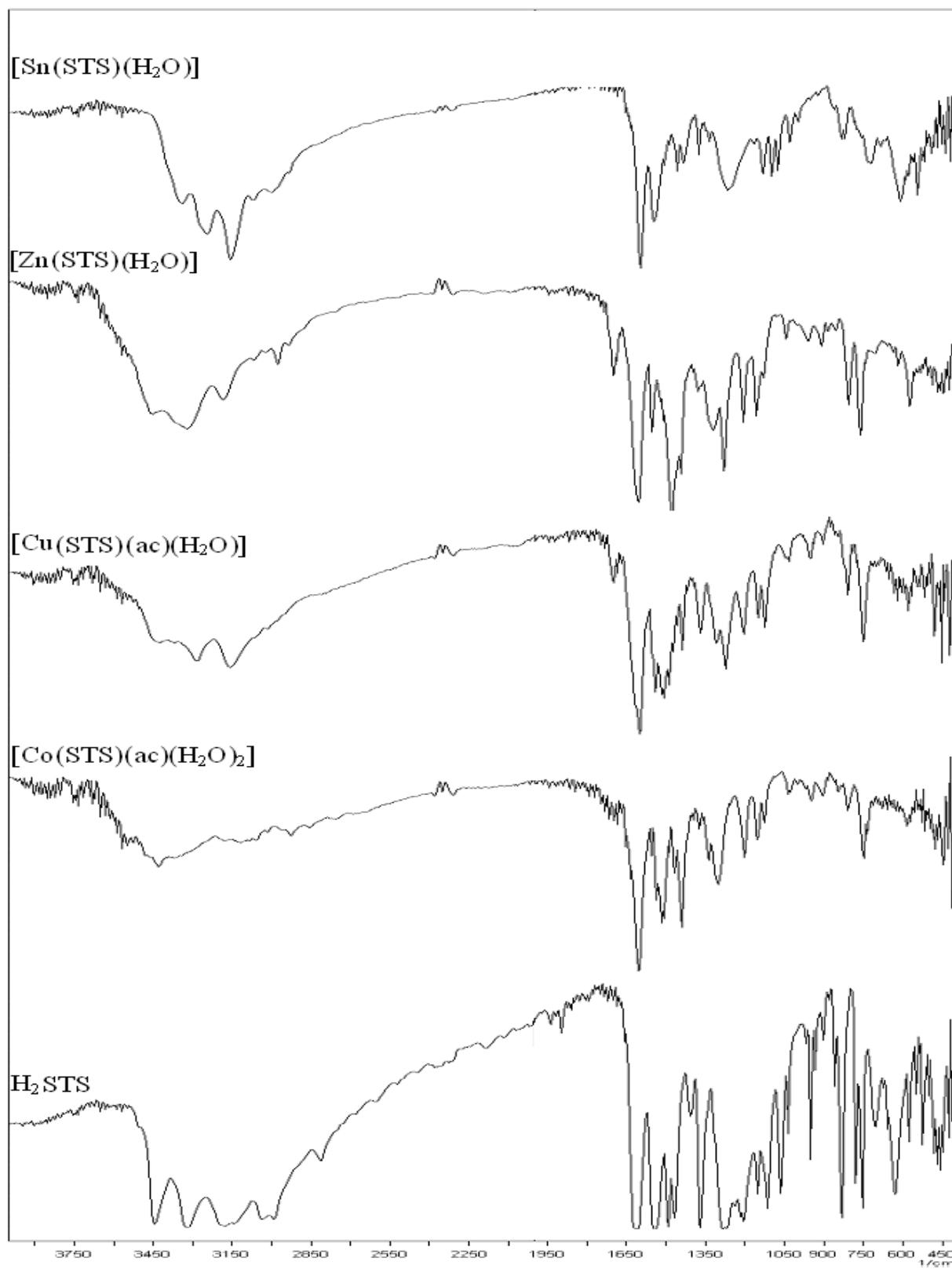
Fig. 3. IR spectral of the ligand of Salicaldehydethiosemicarbazone and it's metal complexes.

exhibit thione-thiol tautomerism since it contains a thioamide –NH–C=S functional group. The v(S–H) band at 2596 cm⁻¹ is present in the IR spectrum of ligand but v(N–H) band at ca. 3237 cm⁻¹ is absent, indicating that in the solid state, the ligand remains as the thione tautomer. The position of v(C=N) band of the Salicaldehydethiosemicarbazone appeared at 1602cm⁻¹ is shifted towards lower wave number in the complexes indicating coordination via the azomethane nitrogen [13, 14]. This is also confirmed by the appearance of bands in the range of 446–455 cm⁻¹, this has been assigned to the v(M–N) [15]. The appearance of bands in the range of 495–520cm⁻¹ has been assigned to the v(M–O) [16]. A strong band found at 1113 cm⁻¹ is due to the v(N–N) group of the Salicaldehydethiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the increase in the bund strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at ca. 777 cm⁻¹ v(C=S) in the IR spectral of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to the metal ion [17]. Thus, it may be concluded that the ligand behaves as tridentate chelating agent coordinating through azomethane nitrogen and thiolate sulphur. IR spectral of ligand and its metal complexes are shown in the Fig. 3.

Raman spectra

The assignments of the significant Raman spectral bands of ligand and its metal complexes are presented in Table 4. The position of v(C=N) band of the Salicaldehydethiosemicarbazone appeared at 1603cm⁻¹ is shifted towards lower wave number in the complexes indicating coordination via the azomethane nitrogen [18]. The appearance of bands at 344cm⁻¹, this has been assigned to the v(M–S). This is also confirmed by the appearance of bands in the range of 442 - 449 cm⁻¹, this has been assigned to the v(M–N) [16]. The appearance of bands in the range of 618 - 629cm⁻¹ has been assigned to the v(M–O) [17]. A strong band found at 1112 cm⁻¹ is due to the v(N–N) group of the Salicaldehydethiosemicarbazone. The position of this band is shifted towards higher wave number in the spectra of complexes. It is due to the

Table 4. Significant raman spectral bands (cm⁻¹) of the ligand of salicaldehydethiosemicarbazone and their metal complexes.

Assignments	The compound		
	H₂STS	[Zn(STS)(H₂O)]	[Sn(STS)(H₂O)]
v(C=N)	1603	1600	1601
δ(OH)	1317	1324	1323
v(N–N)	1112	1154	1117
v(C=S)	778	----	----
v(C-S)	----	618	629
v(M-O)	----	495	521
v(M-N)	----	449	442
v(M-S)	----	360	355

increase in the bund strength, which again confirms the coordination via the azomethane nitrogen. The band appearing at ca. 778 cm⁻¹ v(C=S) in the Raman spectra of ligand is shifted towards lower wave number. It indicates that thione sulphur coordinates to the metal ion. Raman spectra of ligand and its metal complexes are shown in the Fig. 4.

Electronic spectra

The electronic spectra of both Salicaldehydethiosemicarbazone ligand and its complexes were performed in DMSO and the spectral data are listed in Table 5. There are two main absorption bands in the spectra of the free ligand and their complexes; the first band is exhibited at the range 260-290 nm and assigned to π-π* [15-17] and the second appeared at the range 314-383 nm due to n-π* intraligand transitions [18]. These absorptions were also present in the spectra of the Co(II), Cu(II) , Zn(II) and Sn(II) and L ligand complexes, but they are shifted. In the spectra of all complexes attributed to the complexation behavior of the ligand towards metal ions which was supported the coordination of the Ligand-to-metallic ions, shown as the Fig. 5.
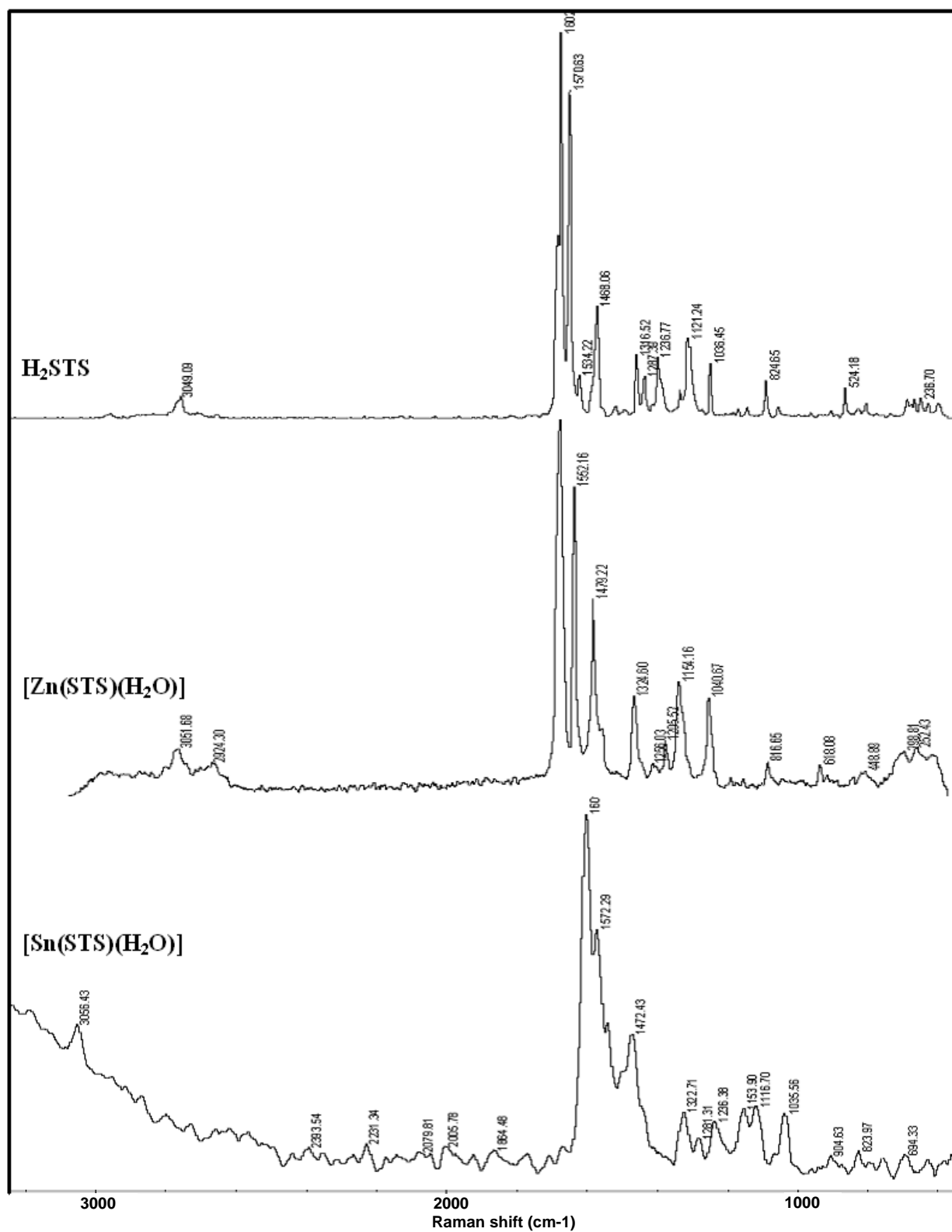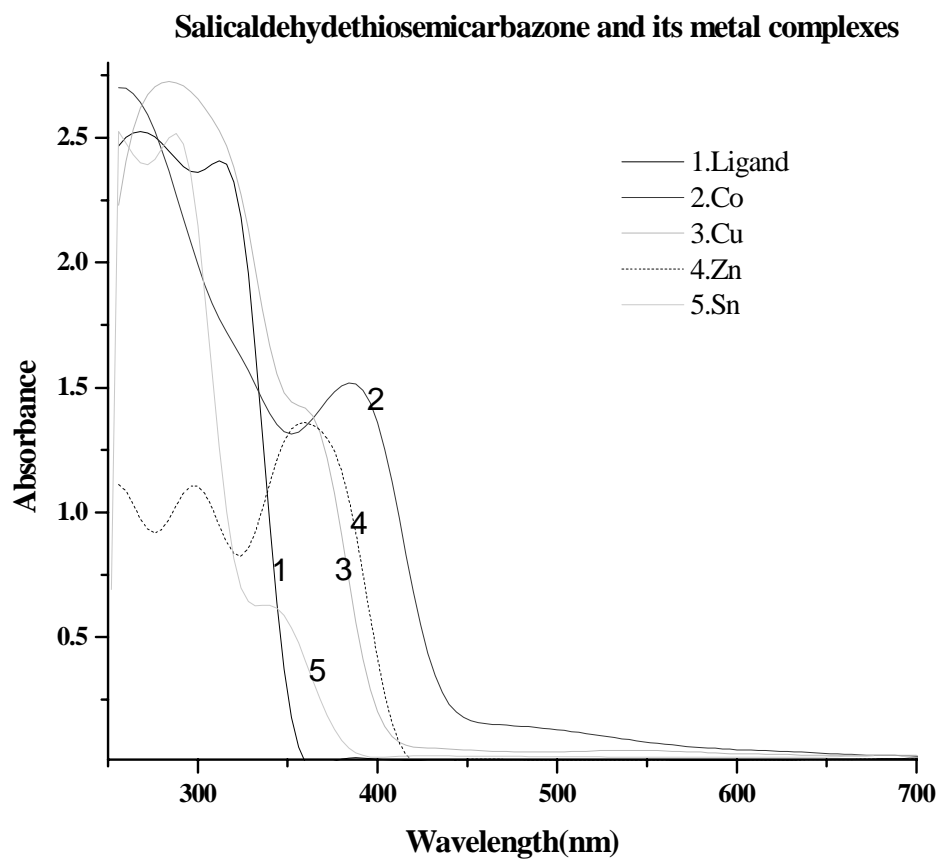
Fig. 4. Raman spectral of the ligand Salicaldehydethiosemicarbazone and it's metal complexes.

Table 5. The electronic spectral data of Salicaldehydethiosemicarbazone and it's metal complexes.

Compound	λ_{max} nm (cm^{-1})							
	π-π^* C=S	n-π^* C=S	CT - transition					
H$_2$STS	265 (37740)	314 (31850)	----	----	----	----	----	----
[Co(STS)(ac)(H$_2$O)$_2$]	260 (38460)	383 (26110)	488 (20490)	573 (17450)	633 (15800)	653 (15310)	675 (14810)	696 (14370)
[Cu(STS)(ac)(H$_2$O)$_2$]	280 (35710)	360 (27780)	544 (18380)	580 (17240)	601 (16640)	656 (15240)	668 (14970)	----
[Zn(STS)(H$_2$O)]	290 (34400)	360 (27780)	468 (21370)	----	----	----	----	----
[Sn(STS)(H$_2$O)]	285 (35090)	342 (29240)	420 (23810)	----	----	----	----	----

Fig. 5. The electronic spectral of Salicaldehydethiosemicarbazone and it's metal complexes.
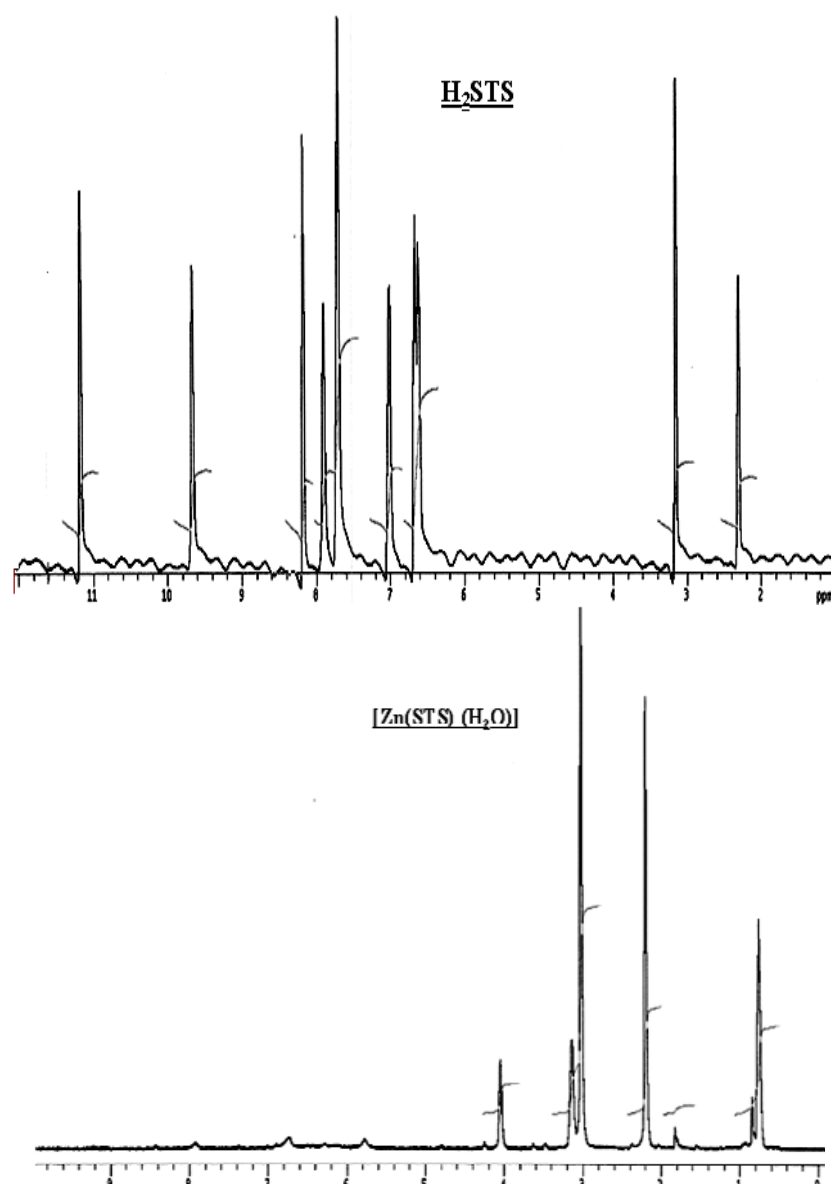
Fig. 6. NMR of Salicaldehydethiosemicarbazone and its Zinc complex.

Magnetic susceptibility

The observed values of magnetic moment for complexes are generally diagnostic of the coordination geometry about the metal ion. Co(II) has the electronic configuration $3d^8$ and should exhibit a magnetic moment higher than that expected for two unpaired electrons in octahedral (2.61BM). The magnetic moment observed for the Co(II) complexes are consistent with the octahedral stereochemistry of the complexes. Room- temperature magnetic moment of the

Cu(II) complexes lies in the range of 1.74BM, corresponding to one unpaired electron whatsoever the geometry of Cu(II) is, its complexes always show magnetic moment corresponding to one unpaired electron.

^{1}H-NMR spectra

The ^{1}H-NMR spectra presented the persuasive confirmation of the coordination modes. Thus, the ^{1}H-NMR spectra of the $[Zn(STS)_2(H_2O)_2]. 2(H_2O)$ complex on comparing with those of spectrum of
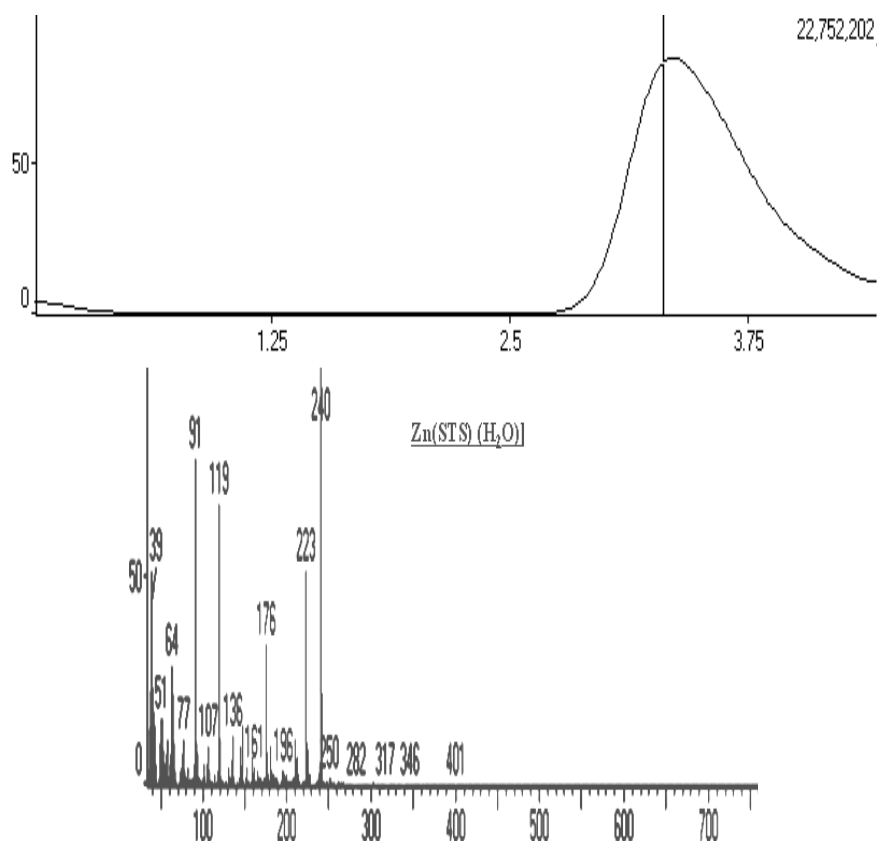
Fig. 7. The Electron impact mass spectrum of the [Zn(STS)(H₂O)] complex.

the free salicaldehydethiosemicarbazone ligand (L) indicate that, the ligand acts as tridentate ligand through the nitrogen atom of C=N azomethine group, sulfur atom of C=S group and oxygen atom of C-O group. ^{1}H-NMR spectra of zinc(II) complex was carried out in DMSO-d_6 as a solvent, the data obtained are in agreement with the suggested chelating by presence of the protons of OH and NH group at shown Fig. 6.

(H₂STS) ^{1}H-NMR δ (ppm): 2.3(NH), 6.6(OH-aromatic), 7, 7.6, 7.9, 8.15(CH-aromatic), 9.6(NH₂), 11.2(CH)

[Zn(STS)(H₂O)₂] ^{1}H-NMR δ (ppm): 0.8(H₂O), 2.2(NH₂), 4.2(CH) 5.8(OH-aromatic was shifted), 7-8(CH-aromatic was shifted), NH was disappeared.

Mass spectrum

The electronic impact mass spectrum, Fig. 7, of the complex Zn(STS) [Zinc

Salicyaldehydethiosemicarbazone] shows a molecular ion (M+) peak at *m/z* = 280 amu corresponding to species [C₈H₉N₃O₂SZn], peak at *m/z* = 257 amu corresponding to species [C₈H₇N₃OSZn], which confirms the proposed formula. It also shows series of peaks at 39, 51*,* 64, 77, 91, 107, 119, 136, 161, 176, 181, 191, 210, 223, 240 and 250 amu corresponding to various fragments. The intensities of these peaks give the idea of the stabilities of the fragments.

Thermogravimetric analysis

Thermogravimetric analysis curves (TGA and DrTGA) of the Salicaldehydethiosemicarbazone ligand and its complexes are shown in Fig. (8-12). The thermo analytical results are summarized in Table 6.

Salicaldehydethiosemicarbazone ligand, (Fig. 8), was thermally decomposed in mainly three decomposition steps within the temperature range from 25ºC up to 800ºC. The first decomposition

Table 6. The thermal data of Salicaldehydethiosemicarbazone and it's metal complexes.

Compound	steps	Temperature ring (ºC)	TG weight loss (%)		Assignments	T_{max}
			Calc.	**Found**		
HSTS	1	25ºC – 338ºC	71.8%	72%	$C_5H_6N_3S$	161ºC 193ºC 238ºC 281ºC 671ºC
	2	338ºC – 567ºC	8.72%	9.1%	hydroxyl group	
	3	More than 567ºC	19.5%	18.9%	C_3H_2 residue	
[Co(STS) (ac)(H$_2$O)$_2$]	1	25ºC – 395ºC	38.7%	38.7%	2 H_2O and (N=C–NH$_2$)	102ºC 280ºC 405ºC 480ºC 530ºC 790ºC
	2	395ºC – 750ºC	35.4%	34.4%	(O – C$_6$H$_5$ – CH = N)	
	3	More than 750ºC	26.3%	25.9%	(sulphur) atom and cobalt(II) residue	
[Cu(STS) (as)(H$_2$O)$_2$]	1	25ºC – 276ºC	30.9%	30.5%	tow water, acetone and NH$_2$ molecules	180ºC 225ºC 250ºC 345ºC
	2	267ºC – 415ºC	11.4%	11.5%	(N – N = C)	
	3	More than 415ºC	57.7%	58%	(O – C$_6$H$_4$ – CH), (sulphur) atom and copper(II) metal residual atoms	
[Zn(STS)(H$_2$O)]	1	25ºC – 287ºC	6.5%	7%	waters molecule	160ºC 260ºC 333ºC 515ºC 790ºC
	2	287ºC – 355ºC	20.3%	19.4%	(N=N–C–NH$_2$)	
	3	355ºC – 558ºC	13.8%	14%	(CH–C–CH)	
	4	558ºC – 790ºC	9.5%	9.8%	(CH=CH)	
	5	More than 790ºC	49.8%	49.8%	Zn(II) and (CH =C –O– Zn – S)	
[Sn(STS)(H$_2$O)]	1	25ºC – 330ºC	32.1%	32.1%	H$_2$O and (N–N=CS –NH$_2$)	190ºC 233ºC 272ºC 450ºC 790ºC
	2	330ºC– 607ºC	11.5%	10.5%	(CH= C–CH)	
	3	607ºC – 795ºC	15.5%	15.2%	(C= CH– CH=CH)	
	4	More than 795ºC	41%	42.23%	(Sn=O)	

step (obs. = 72%, calc. = 71.8%) within the temperature range 25ºC – 338ºC, may be attributed to the liberation of the C$_5$H$_6$N$_3$S molecule. The second decomposition steps found within the temperature range 338ºC – 567ºC (obs. = 9.1%, calc. = 8.72%), which is reasonably accounted by the removal of hydroxyl group.

The decomposition of the ligand molecule ended with a final C$_3$H$_2$ residue (obs. = 18.9%, calc = 19.5%).

[Co(STS)(ac)(H$_2$O)$_2$] complex, (Fig. 9), was thermally decomposed in four successive decomposition steps within the temperature range 25ºC – 800ºC. The first decomposition step
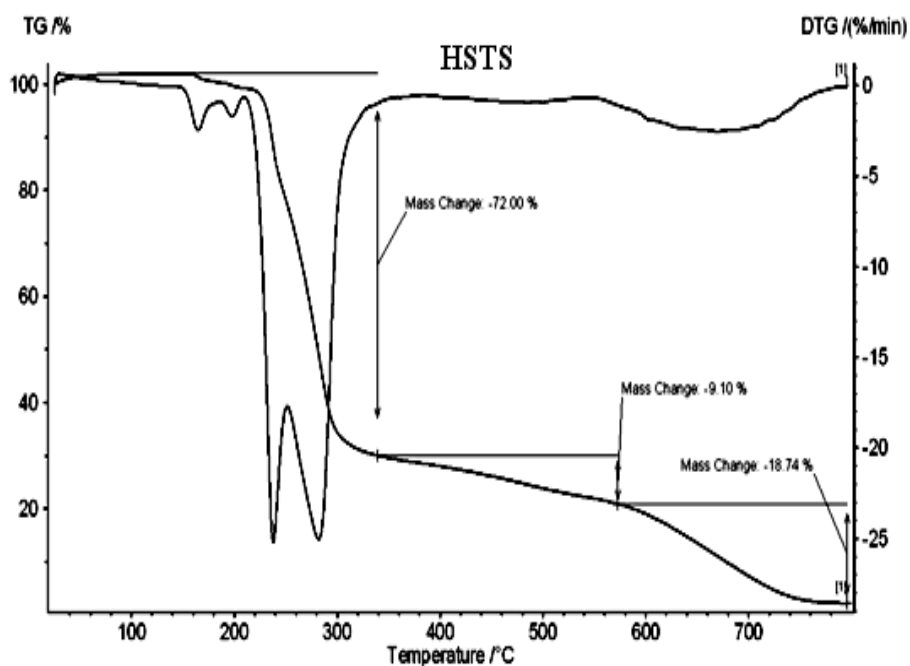
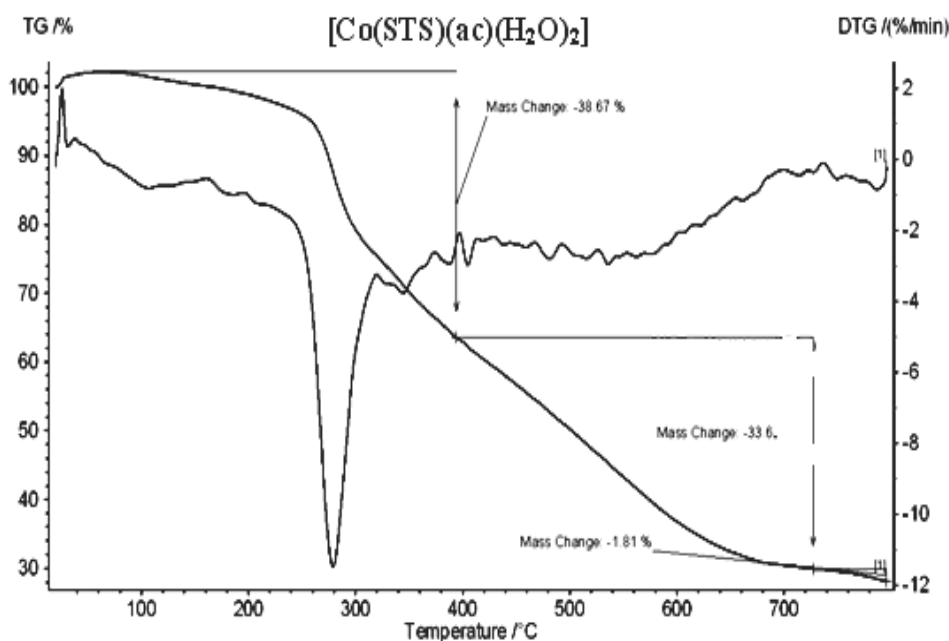**Fig. 8.** TGA and DrTGA diagram for Salicaldehydethiosemicarbazone.

Fig. 9. TGA and DrTGA diagram for [Co(STS)(ac)(H$_2$O)] complex.

(obs. = 38.7%, calc. = 38.7%) within the temperature range 25ºC-395ºC, may be attributed to the liberation of the acetone, 2 H$_2$O and (N = C – NH$_2$) molecules. The second decomposition steps found within the temperature range 395ºC-750ºC (obs. = 34.4%, calc.=35.4%), which is reasonably accounted by the removal of (O – C$_6$H$_5$ – CH = N) molecule The decomposition of the Co(II)/L complex
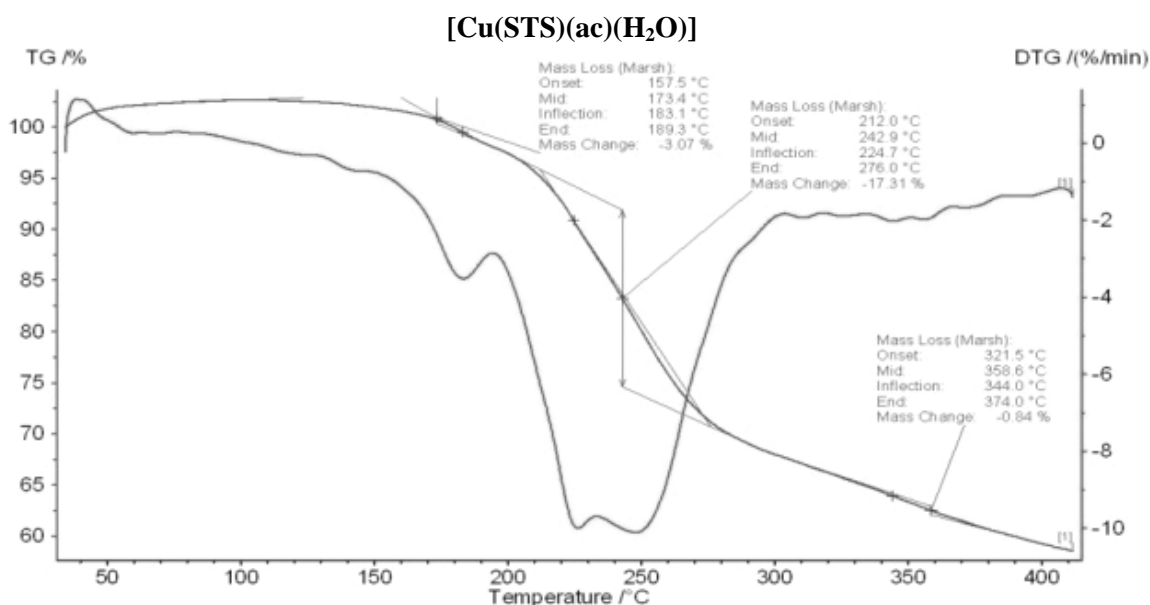
[Cu(STS)(ac)(H₂O)]

Fig. 10. TGA and DrTGA diagram for [Cu(STS)(ac)(H₂O)] complex.
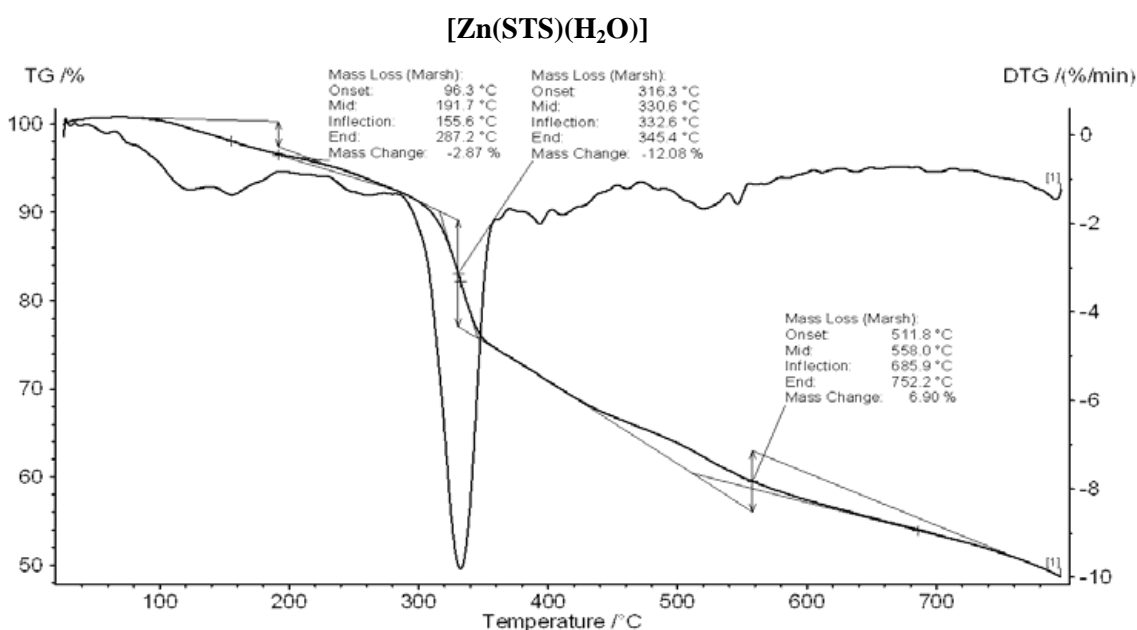
[Zn(STS)(H₂O)]

Fig. 11. TGA and DrTGA diagram for [Zn(STS)H₂O] complex.

molecule ended with a final (sulphur) atom and cobalt(II) residue (obs. = 25.9%, calc = 26.3%) [18, 19].

The TG curve of [Cu(STS)(as)(H₂O)₂] complex, (Fig. 10), indicates that the mass change begins at 25ºC up to 415ºC. The first mass loss corresponds to the liberation of the tow water, acetone and NH_2 molecules (obs. = 30.5%, calc = 30.9%) within the temperature range 25ºC – 276ºC. The second decomposition step occurs in the range 267ºC – 415ºC and corresponds to the loss of (N – N = C) (obs. = 11.5%, calc = 11.4%). The final
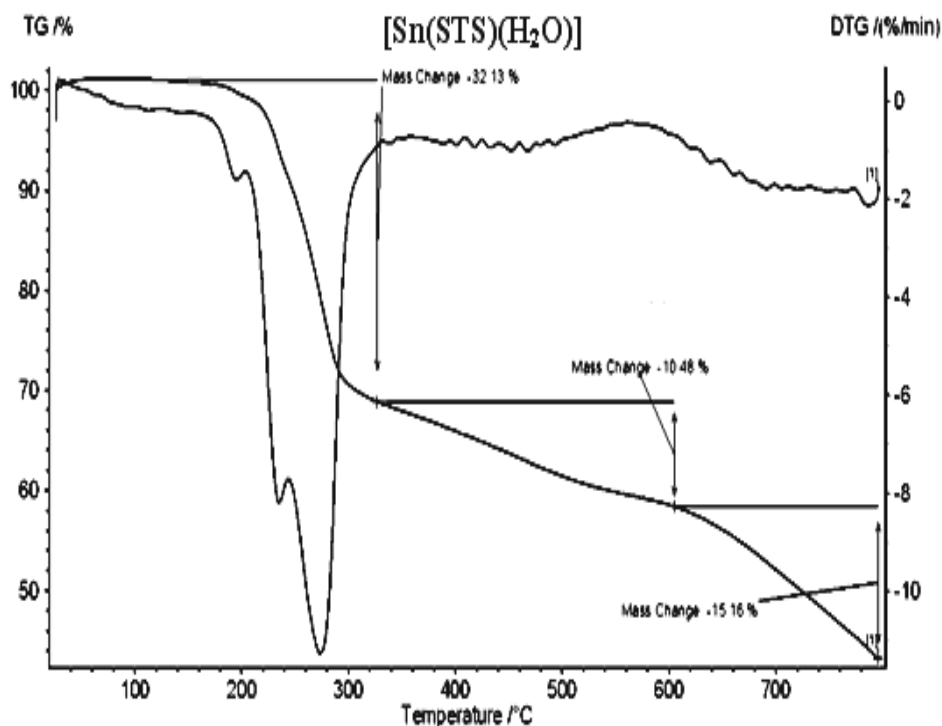
Fig. 12. TGA and DrTGA diagram for [Sn(STS).H_2O] complex.

step is the decomposition of the organic ligand to the $(O – C_6H_4 – CH)$, (sulphur) atom and copper(II) metal residual atoms. (obs. = 58%, calc = 57.7%).

[Zn(STS) (H_2O)] complex, (Fig. 11), was thermally decomposed in mainly five decomposition steps within the temperature range 25ºC – 800ºC. The first decomposition step (obs. = 7%, calc = 6.5%) within the temperature range 25ºC – 287ºC, may be attributed to the liberation of waters molecule. The decomposition second step found within the temperature 287ºC – 355ºC (obs. = 19.4%, calc = 20.3%) accounted by the removal of $(N=N–C–NH_2)$ molecule. The decomposition third step found within the temperature 355ºC – 558ºC (obs. = 14%, calc = 13.8%) is accounted for the removal of (CH–C–CH) molecule. The decomposition fourth step found within the temperature 558ºC – 790ºC (obs. = 9.8%, calc = 9.5%) indicate the removal of (CH=CH) molecule. The rest of the ligand molecule was removed and fifth the decomposition of the ligand molecule ended with a final residue metal of Zn(II) and contaminated, (CH =C –O– Zn – S) atoms (obs. = 49.8%, calc = 49.8%).

[Sn(STS)(H_2O)] the complex, (Fig. 12), is thermally stable up to 50ºC and decomposition beyond this temperature as indicated by the first loss step in the TG curve. First step, the mass loss at 330ºC corresponds to the loss of hydrated water and (N–N=CS –NH_2) molecules (obs. = 32.1%, calc = 32.1%). Continuous mass loss in the TG curve from 330ºC to 607ºC corresponds to the loss of (CH= C–CH) molecule (obs. = 10.5%, calc = 11.5%). The rest of organic moiety(C= CH– CH=CH) molecule was removed on the third step within the temperature range 607ºC – 795ºC (obs. = 15.2%, calc = 15.5%). The final decomposition of the organic ligand to the tin metal Oxide (Sn=O) the residual atoms (obs. = 42.23%, calc = 41%) [18-20].

Kinetic studies

In the present investigation, the general thermal behaviors of the H_2STS and its Metal complexes in terms of stability ranges, peak temperatures and values of kinetic parameters, are discussed. The kinetic parameters have been evaluated using the Coats-Redfern equation as shown in Fig. 13 [21-23].
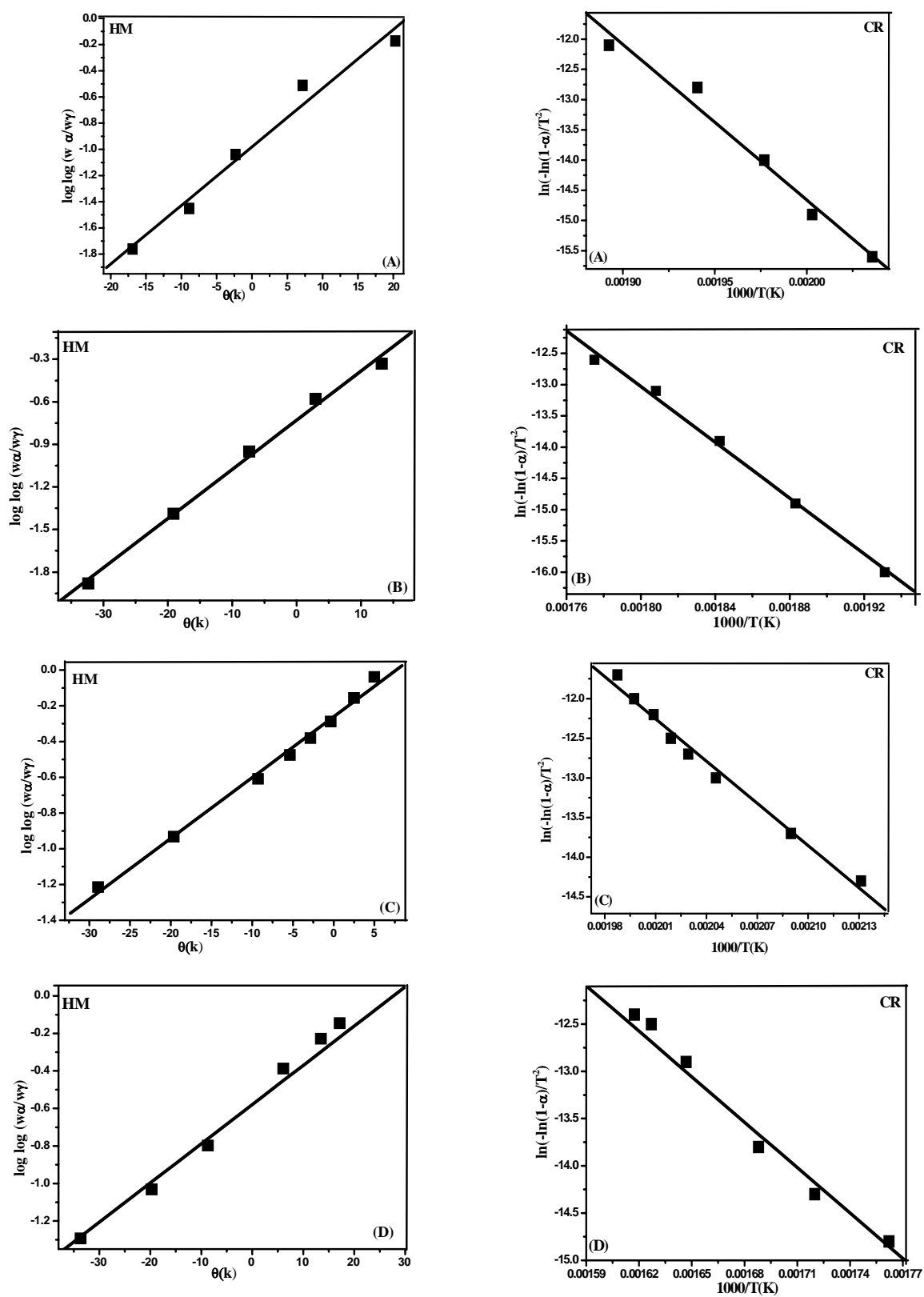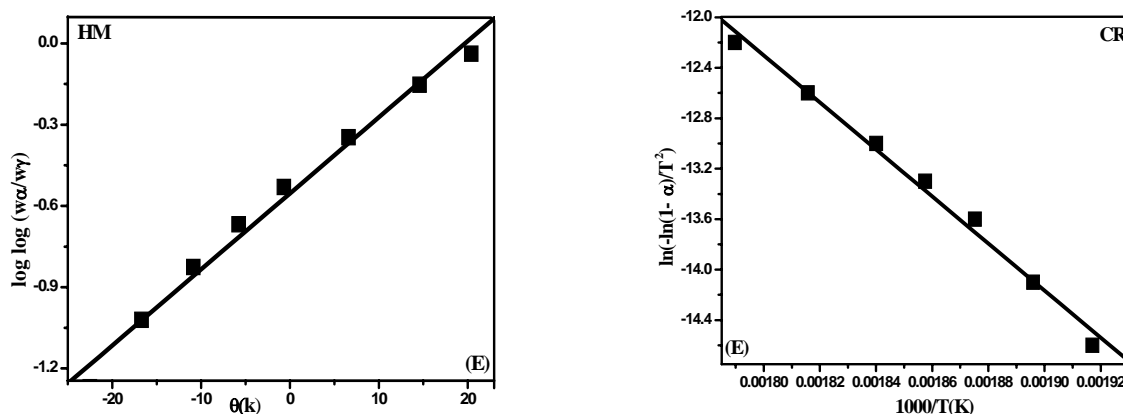
Fig. 13

Fig. 13. continued..

Fig. 13. Kinetic data curves of: (A) Salicyaldehydethiosemicarbazone (H₂STS), (B) Co(II), (C) Cu(II), (D) Zn(II) and (E) Sn(II) complexes.

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. The smaller size of the ions permits a closer approach of the ligand. Hence, the E value in the first stage for the Co^{+2} complex is higher than that for the other Sn^{+2}, Cu^{+2} and Zn^{+2} complexes. The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9885 to 0.9975, showing a good fit with linear function. It is clear that the thermal decomposition process of all H₂STS complexes is non spontaneous, i.e, the complexes are thermally stable.

CONCLUSION

We can concluded from the above discussions on the H₂STS ligand and its Co(II), Cu(II), Zn(II) and Sn(II) complexes using the elemental analysis, molar conductivity, IR, Raman, UV, ¹HNMR, and magnetic properties, as well as TG/DTG, that. In IR the band appearing at ca. 777 cm⁻¹ ν(C–S) in the IR spectral of ligand is absent. It indicates that thione sulfur coordinates to the metal ion. Thus, it may be concluded that the ligand behaves as tridentate chelating agent coordinating through azomethine nitrogen and thiolate sulphur. The structures are shown at (Fig. 2).

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