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# Spectroscopic, thermogravimetric and antibacterial studies for some bivalent metal complexes of oxalyl-, malonyl- and succinyl-bis(4-*p*-chlorophenylthiosemicarbazide)

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# ABSTRACT

Anodic oxidation of Co, Cu, Zn, and Sn metals in an anhydrous acetone solution of 1,1-oxalyl-, malonyl- or succinyl-bis(4-*p*-chlorophenylthiosemicarbazide) yields a new polynuclear complexes. The isolated complexes have the general composition  $[M_2(L)(H_2O)_6]$ , L = pClSuTS and M = Co(II), Cu(II) or Sn(II),  $[M_2(L)(H_2O)_n] \cdot nH_2O$  where M = Cu(II), Co(II) or Sn(II), L = pClOxTS and *n* = 2 or 6, and  $[M_2(L)(ac)_2] \cdot nH_2O$  where M = Co(II) or Zn(II), L = pClOxTS or pClSuTS and *n* = 2. The thermogravimetry (TG) and derivative thermogravimetry (DTG) have been used to study the thermal decomposition of the investigated bisthiosemicarbazide ligands and their metal complexes. The kinetic thermodynamic parameters such as:  $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are calculated using Horowitz–Metzger (HM) and Coats–Redfern (CR) equations. The kinetic thermodynamic parameters such as:  $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are calculated using Horowitz–Metzger fully against four strains of Gram-negative bacteria; *Escherichia coli, Pseudomonas aeruginosa* species and Gram-positive bacteria; *Bacillus cereus* and *Staphylococcus aureus*.

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# 1. Introduction

During the last 20 years ago, there was a rapid growth and interest from the scientific researchers all over the world to discover, isolate, prepare new natural [1–5] and new synthetic compounds [6–9] that have a good potential activity against microorganisms. Spitteler et al. isolated new flavones from the Cameroonian medicinal plant Crotalaria lachnophora. They showed moderate inhibitory activities against Escherichia coli and Klebsiella pneumonia [10–12]. The antimicrobial efficiencies of this class of compounds were established by correlating the activity profile of each compound with its structure and by comparing the activities of all the compounds with each other based on their structure [1–5]. We have previously studied the antimicrobial, antifungal and hypoglycaemic effect of a series of bis and tetrakis-thiosemicarbazide and its Cu(II) complexes against some organisms and albino mice. These compounds were found to display significant decrease on plasma levels of glucose by 26–39% [8]. Interest in thiosemicarbazide chemistry has rapid growth for many years, largely as a result of its wide range of uses as antibacterial [9], antifungal [13], antitumor [14], biological activity [15,16], and its pharmacological applications [17–19]. 4-Ethyl-1-(pyridin-2-yl)thiosemicarbazide and its Cu(II) complexes

with different anions have been synthesized, characterized [20] and used as a chelating agent for the separation, preconcentration, and determination of Cu(II) ions in saturated saline solutions by a cloud point extraction technique [21]. In addition, the complexes of 4-ethyl and 4-(p-tolyl)-1-(pyridin-2-yl)thiosemicarbazides with Pd(II), Pt(II) and Ag(I) were [22] show antibacterial activity to some Gram-positive and Gram-negative bacterial strains. Thiosemicarbazide compounds have good ability to form complexes with metal ions [20–26]. In this paper, we report the synthesis, thermal, spectral and biological activity of new series of 1,1-oxalyl-, malonyl- and succinyl-bis(4-*p*-chlorophenylthiosemicarbazide) complexes formed during the electrochemical reaction through anodic dissolution of Co, Cu, Zn and Sn metals.

# 2. Experimental

# 2.1. Chemicals and materials

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<sub>4</sub> before use. The metals (Alfa Inorganics) used, Co, Cu, Zn, Sn and Au were purchased in the form of sheets ( $\sim$ 2 cm  $\times$  2 cm, 2–3 mm thick). The oxide surface was removed by treating the metal with conc. HNO<sub>3</sub> for several minutes



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and then washing with distilled water. Tetraethylammonium perchlorate, Et<sub>4</sub>NClO<sub>4</sub>, (BDH) was used as supplied [26].

## 2.2. General electrochemical procedures

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 1 mm diameter. In most cases, the metal (2–5 g) was suspended and supported on a platinum wire [27]. Measurements of the electrochemical efficiency,  $E_{fr}$  for the M/L system (where L = ligand used) gave  $E_f = 0.5 \pm 0.05$  - mol F-1 [28].

# 2.3. Preparation of 1,1-oxalyl-bis(4-p-chlorophenylthiosemicarbazide) (H<sub>4</sub>pClOxTS)

1,1-Oxalyl-bis(4-*p*-chlorophenylthiosemicarbazide) was prepared by adding 4-chloro-phenylisothiocynate (3.4 g, 0.02 mol) to an alcoholic solution of oxalic acid dihydrazide (1.18 g  $\approx$  0.01 mol). The reaction mixture was refluxed for 1 h and left to cool with stirring. The resulting white crystals were collected and washed with ethanol and diethyl ether, respectively. The resulting solids were filtered hot, washed with hot distilled water, EtOH and Et<sub>2</sub>O then dried under vacuum over silica gel. Yield (3.5 g  $\approx$  77%) with the melting point at 193 °C. 1,1-malonyl- and 1,1-succinyl-bis-4-(*p*-chlorophenylthiosemicarbazide) were prepared by the same way [29,30].

# 2.4. Electrochemical synthesis of 1,1-oxalyl-bis(4-pchlorophenylthiosemicarbazide) metal complexes

The ligand H<sub>4</sub>*p*ClOxTS (0.231 g, 0.5 mmol) was dissolved in the minimum amount of DMSO (0.5 mL) followed by the addition of 50 mL of acetone and 2.5 mg of Et<sub>4</sub>NClO<sub>4</sub>. When the current 40 mA was passed through the cell for 1 h, the amount of Cobalt consumed is 59 mg and a dark green precipitate was formed (the product is 0.3734 g, %yield 91 and  $E_f$  = 0.51). It was collected, washed with diethyl ether and dried. The resulting dark green powder was collected and analyzed as [Co<sub>2</sub>(*p*ClOxTS)(ac)<sub>2</sub> (H<sub>2</sub>O)<sub>4</sub>]·3H<sub>2</sub>O. By the same procedure, Cu, Zn, and Sn complexes were isolated and their data were gathered in Table 1.

#### 2.5. Spectral, analytical and physical measurements

#### 2.5.1. IR, Raman and <sup>1</sup>H NMR spectra

Infrared spectra for the samples were recorded by Perkin Elmer FTIR 1605 using KBr pellets. Raman spectra of ligand and metal complexes were recorded in the solid state on T-Nicolet FT-Raman (USA) with a wavelength 1064 nm power according sample resolution was 8 cm<sup>-1</sup> at National Research Center, Cairo, Egypt. The <sup>1</sup>HNMR spectra were recorded on an Varian Mercury VX-300 NMR spectrometer. <sup>1</sup>HNMR spectra were run at 300 MHz and <sup>13</sup>CNMR spectra were run at 75.46 MHz in deuterated dimethyl sulphoxide (DMSO-d<sub>6</sub>). Chemical shifts are quoted in  $\delta$  and were related to that of the solvents.

# 2.5.2. Electronic and mass spectra

The electronic spectra of solutions were measured in UV/Vis range (190–1100) nm using Helios UV Spectrometer at nanocentral laboratory of photo energy, Ain-Shams University. Mass spectra were recorded at SHIMADZU GC MS-QP 1000 EX Micro analytical Center, Cairo Universal, Giza and Al-Azher University, Egypt.

#### 2.5.3. Magnetic and molar conductance measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Molar conductivities of freshly prepared  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> DMSO solutions were measured using Jenway 4010 conductivity meter.

# 2.5.4. Microanalytical, magnetic and molar measurements

Carbon and hydrogen contents were determined using a Perkin–Elmer CHN 2400 analyzer [28]. Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Molar conductivities of freshly prepared  $1.0 \times 10^{-3}$  mol/ dm<sup>-3</sup> solutions of the complexes in DMSO were measured using Jenway 4010 conductivity meter.

# 2.6. Thermal investigation

Thermogravimetric analysis (TG/DTG) were carried out in the temperature range from 25 to 800 °C in a steam of nitrogen atmosphere using Schimadzu TGA-50H thermal analyzer. The experimental conditions were: platinum crucible, nitrogen atmosphere with a 30 mL/min flow rate and a heating rate 10 °C/min.

## 2.7. Antibacterial investigation

Bacterial cultures and growth conditions: Gram-negative E. Coli, Pseudomonas aeruginosa species and Gram-positive Bacillus cereus,

#### Table 1

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Analytical results for the prepared complexes of oxalyl, malonyl and succinyl-bis(4-p-chlorophenylthiosemicarbazide) and its metal complexes.
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Compounds empirical formula	Formula weight	Color	M.p. (°C)	% Found (calc.)			Am µs
				С	Н	Ν	
$H_4$ pClOxTS, (I) $C_{16}H_{14}Cl_2N_6O_2S_2$	457.4	White	193	41.61 (42.02)	3.28 (3.09)	17.8 (18.38)	17
[Co <sub>2</sub> (pClOxTS)(ac) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]3(H <sub>2</sub> O), ( <b>Ia</b> ) C <sub>22</sub> H <sub>36</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>11</sub> S <sub>2</sub>	813.5	Dark Green	>300	32.12 (32.48)	3.97 (4.46)	9.89 (10.33)	38
[Cu <sub>2</sub> (pClOxTS) (H <sub>2</sub> O) <sub>6</sub> ]6(H <sub>2</sub> O), ( <b>Ib</b> ) C <sub>16</sub> H <sub>24</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>14</sub> S <sub>2</sub>	796.6	Brown	>300	24.1 (24.12)	4.03 (4.3)	10.32 (10.55)	40
[Zn <sub>2</sub> (pClOxTS) (ac) <sub>2</sub> ]2(H <sub>2</sub> O), ( <b>Ic</b> ) C <sub>22</sub> H <sub>26</sub> Cl <sub>2</sub> Zn <sub>2</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub>	736.3	Faint Yellow	218	35.55 (35.89)	3.21 (3.56)	11.88 (11.41)	30
$[Sn_2(pClOxTS) (H_2O)_2], (Id) C_{16}H_{14}Cl_2Sn_2 N_6O_4S_2$	726.8	Yellow	205	26.33 (26.44)	2.2 (1.94)	11 (11.56)	35
$(H_4pClMaTS)$ , (II) $C_{17}H_{16}Cl_2N_6O_2S_2$	471.38	White	200	43.18 (43.32)	3.08 (3.42)	17.6 (17.83)	20
[Co <sub>2</sub> (pClMaTS) (H <sub>2</sub> O) <sub>6</sub> ]2(H <sub>2</sub> O), (IIa) C <sub>17</sub> H <sub>28</sub> Cl <sub>2</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>10</sub> S <sub>2</sub>	729.3	Dark Brown	220	27.7 (28)	4.25 (3.87)	11.35 (11.52)	37
[Cu <sub>2</sub> (pClMaTS) (H <sub>2</sub> O) <sub>6</sub> ], ( <b>IIb</b> ) C <sub>17</sub> H <sub>24</sub> Cl <sub>2</sub> Cu <sub>2</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub>	702.54	Dark Brown	210	29.86 (29.06)	3.39 (3.44)	11.5 (11.96)	35
[Zn <sub>2</sub> (pClMaTS) (H <sub>2</sub> O) <sub>6</sub> ], (IIc) C <sub>17</sub> H <sub>24</sub> Cl <sub>2</sub> Zn <sub>2</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub>	706.3	Yellowish White	213	29.07 (28.91)	3.30 (3.43)	11.40 (11.9)	38
[Sn <sub>2</sub> (pClMaTS) (H <sub>2</sub> O) <sub>6</sub> ]2(H <sub>2</sub> O), (IId) C <sub>17</sub> H <sub>28</sub> Cl <sub>2</sub> Sn <sub>2</sub> N <sub>6</sub> O <sub>10</sub> S <sub>2</sub>	848.9	Page	243	24.01 (24.05)	3.22 (3.32)	9.34 (9.9)	36
$H_4$ pClSuTS, (III) $C_{18}H_{18}Cl_2N_6O_2S_2$	485.41	White	197	44.76 (44.54)	3.79 (3.74)	17.01 (17.31)	10
$[Co_2(pClSuTS) (H_2O)_6], (IIIa) C_{18}H_{26}Cl_2Co_2N_6O_8S_2$	707.34	Dark Brown	217	31.05 (30.56)	4.25 (3.7)	11.3 (11.88)	38
[Cu <sub>2</sub> (pClSuTS) (H <sub>2</sub> O) <sub>6</sub> ], (IIIb) C <sub>18</sub> H <sub>34</sub> Cl <sub>2</sub> Cu <sub>4</sub> N <sub>6</sub> O <sub>14</sub> S <sub>4</sub>	1011.8	Green	>300	21.32 (21.37)	3.34 (3.39)	7.9 (8.31)	35
[Zn <sub>2</sub> (pClSuTS)(ac) <sub>2</sub> ] 2(H <sub>2</sub> O), (IIIc) C <sub>24</sub> H <sub>30</sub> Cl <sub>2</sub> Zn <sub>2</sub> N <sub>6</sub> O <sub>6</sub> S <sub>2</sub>	764.4	Page	235	37.84 (37.71)	3.84 (3.96)	11.04 (10.99)	32
$[Sn_2(pClSuTS) (H_2O)_6], (IIId) C_{18}H_{26}Cl_2Sn_2 N_6O_8S_2$	826.9	Pale Yellow	275	26.11 (26.15)	3.3 (3.17)	9.68 (10.16)	36

Staphylococcus aureus species and fungal Aspergillus fumingatus, Candida albicans were used as test microorganisms. The surface of the medium was inoculated and covered with the tested organisms using Swab. The agar surface was allowed to dry from 3 to 5 min before applying disks. The disks were dipped into a beaker of the chemicals using sterile forceps and placed them in the previous medium. Cultures plates of bacteria were incubated for grown at 37 °C for 48 h. Chloramphenicol was used as a standard antibacterial agent and Terbinafin was used as a standard antifungal agent. The test was done using the diffusion agar technique, at Al-Azher University, Egypt.

# 3. Results and discussion

## 3.1. Electrochemical reaction mechanism

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  $E_f = 0.5 \pm 0.05$  mol F<sup>-1</sup>. The values show that the reaction of the ligand with cobalt anode is compatible with the following steps 1 and 2 [26–28].

(1) The first step:

 $\label{eq:cathode: H4L+2e \rightarrow H_2L^{2-} + H_2(g) \tag{1}$ 

Anode :  $H_2L^{2-} + Co \rightarrow CoH_2L + 2e$  (2)

(2) The second step:

 $Cathode:\ CoH_2L+2e \rightarrow CoL^{2-}+H_2(g) \eqno(3)$ 

Anode : 
$$\operatorname{CoL}^{2-} + \operatorname{Co} \to \operatorname{Co}_2 L + 2e$$
 (4)

Anodic oxidation of Co, Cu, Zn, and Sn metals in an anhydrous acetone solution of 1,1-oxalyl-bis(4-*p*-chlorophenylthiosemicar-bazide yields complexes have a general formula  $[Co_2(pCl-OxTSC)(a-c)_2(H_2O)_4]$ ,  $[Cu_2(pCl-OxTSC)(H_2O)_6]$ ,  $[Zn_2(pCl-OxTSC)(ac)_2]$ ,  $[Sn_2(pCl-OxTSC)(H_2O)_2]$  chelation was investigated based on elemental analysis, conductivity, magnetic moment, spectral (UV *Vis* IR, Raman, <sup>1</sup>HNMR, mass) and thermal studies. The elemental analysis and some physical data of the resulted compounds are given in Table 1. The molar conductivity values for all the isolated complexes, in DMF or DMSO indicate non-electrolytes nature.

#### 3.2. Infrared and Raman spectra

The infrared and Raman spectral assignments of the ligands, pCl-OxTSC, pCl-MaTSC and pCl-SuTSC, and its reported complexes are listed in Table 2. They has the characteristic thioamide moiety (-HN-C(S)NH-), which can be present in either thione or thiol form [31]. The IR and Raman spectra of the discussed ligands show the absence of absorption bands in 2500–2600 cm<sup>-1</sup> regions indicating the presence of the free ligands in thione form [32]. The Molecular modeling structure of 1,1-oxalyl-, malonyl- and succinyl-bis(4-p-chlorophenylthiosemicarbazide were shown as in Figs. 1–3. The NH vibration of compounds I, II and III has bands appears in IR spectra at 3306–3310, 3196, and 3092–3111 cm<sup>-1</sup> ranges, (at 3301–3307, 3199 and 3095 cm<sup>-1</sup> in Raman). The bands occurring at 1651-1670, 1400-1402, 1341-1342, 902-923 and 814–831 cm<sup>-1</sup> ranges are assigned to v(C=0), thioamide I  $[\beta(NH) + v(CN)]$ , thioamide II  $[v(CN) + \beta(NH)]$ , v(N-N) and v(C=S), respectively in IR, (at 1650, 1405, 1355, 1090 cm<sup>-1</sup> Raman) [20]. pCl-OxTSC, pCl-MaTSC and pCl-SuTSC shows a strong IR band at  $1651-1670 \text{ cm}^{-1}$ , observed at  $1635-1650 \text{ cm}^{-1}$  in the Raman, which is corresponding to the carbonyl, v(C=0), group [33]. In the spectra of the complexes, the shift of these bands to lower frequency

is observed at  $1591-1601 \text{ cm}^{-1}$  and  $1593-1596 \text{ cm}^{-1}$  in IR and Raman, respectively, suggesting the participation of carbonyl group in the coordination to metal ions during the enolization [34,35]. This feature is further supported by the shift of *v*(N–N) band in the free ligand from 902-923 cm<sup>-1</sup> in IR to higher frequencies, 924-975 cm<sup>-1</sup> upon complexation [32,36]. On the other hand, the participation of the deprotonated thiol sulfur in coordination was indicated by the shift of the IR bands at 814–831 cm<sup>-1</sup> (at 824 cm<sup>-1</sup> in the Raman) in the free ligands to lower frequencies in the IR bands of the metal complexes at 755–777  $\text{cm}^{-1}$  (at 779–780  $\text{cm}^{-1}$  in the Raman) [33,37]. The spectra of the complexes show that new bands in the IR and Raman near 395-428 and 490-505 cm<sup>-1</sup> range may assign to v(M–N) and v(M–O), respectively [38,39]. The IR and Raman spectra of the complexes compared with ligands, indicates that bands due to v(NH), v(C=O) and v(C=S) are absent and new bands appear at due to v(N=C) and v(C-S), respectively, suggesting removal of both the hydrazinic protons via enolisation and thioenolisation and bonding of the resulting enolic oxygen and thiolato sulfur takes place with Co(II), Cu(II), Zn(II) and Sn(II). As an example, the Raman spectrum of complex IIc when compared with ligand II indicates that bands due to v(NH), v(C=0) and v(C=S) are absent, but new bands appear at ca. 1593 and 779 cm<sup>-1</sup> due to v(N=C) and v(C-S), respectively suggesting removal of both the hydrazinic protons via enolisation and thioenolisation and bonding of the resulting enolic oxygen and thiolato sulfur takes place with Zn(II). The spectra of all the complexes show that new bands in the IR and Raman near 395–428 and 490–505 cm<sup>-1</sup> range may assign to v(M-N) and v(M—O), respectively [38–40].

#### 3.3. Electronic spectra

The electronic spectra for all three ligands and their metal complexes were recorded in DMSO (Figs. 4–6) and the spectral data are listed in Table 3. There are two main absorption bands in the spectra of the ligands and their complexes; the first band at 256–296 nm and assigned to  $\pi$ – $\pi$ \* [20–23] and the second at 304– 356 nm due to n– $\pi$ \* intraligand transitions [26–28]. These absorptions also present in the spectra of the Co(II), Cu(II), Zn(II) and Sn(II) complexes but they are shifted.

The electronic spectrum of  $[Co_2(pClOxTS)(ac)_2(H_2O)_4]\cdot 3H_2O$  has bands characteristic for an octahedral geometry [26-30]. The spectrum shows two bands at 20,600 and 31,950 cm<sup>-1</sup> assigned to the  ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}(\nu_2)$  and  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P)(\nu_3)$  transitions, respectively, in an octahedral structure. These bands were used to calculate the third spin-allowed band,  ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}[26-30]$ . The ligand field parameters, B,  $\beta$  and the  $\nu_2/\nu_1$  were calculated to be 1060 cm<sup>-1</sup>, 1.2 and 2.2, respectively, and are in good agreement with those reported for octahedral Co(II) complexes. The electronic spectrum of  $[Cu_2(pClOxTS)(H_2O)_6]\cdot 6H_2O$ , shows shoulders at 32,260 and 20,600 cm<sup>-1</sup>. The observed bands are due to  ${}^{2}B_{1g} \rightarrow {}^{2}Eg$  and  ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ , on the basis of octahedral geometry [20-23].

# 3.4. Magnetic susceptibility

The observed values of the magnetic moment for the complexes are generally diagnostic of the coordination geometry about the metal ion. Co(II) has  $3d^7$  and should exhibit a magnetic moment expected for three unpaired electrons. The magnetic moment observed for the Co(II) complexes is 3.2 BM which is consistent with the octahedral stereochemistry of the complexes.

## 3.5. <sup>1</sup>H NMR spectra

The <sup>1</sup>HNMR spectra of compounds **Ic** and **IIc** on comparing with those of the ligands indicate that the ligands acts as a hexadentate through the nitrogen atom of C=N oxygen atom of C=O and sulfur

# Table 2 Significant IR and Raman spectral bands, cm<sup>-1</sup>, of the ligand oxalyl, malonyl, succinyl-bis(4-p-chlorophenylthiosemicarbazide) and the metal complexes.

The compounds	Assignr	nents											
	vN <sup>4</sup> H	$\nu N^2 H$	vNH	vCH-arom.	vCH-aliph.	vC=0	$\beta NH/vCN$	vCN/βNH	$\delta OH$	vN-N	vC=S/vC-S	vМ—О	vM—N
H <sub>4</sub> pClOxTS, I	3306	3196	3092	3064	2940	1651	1402	1342	-	902	831	-	-
	3307	3199		3063	2935								
Co-complex, <b>Ia</b>	3234	3181	3111	3055	2932	1595	1422	1398	1307	934	755	505	415
Cu-complex, <b>Ib</b>	3230	3175	3109	3030	2941	1601	1443	1375	1306	941	756	500	420
Zn-complex, <b>Ic</b>	3211	3174	3100	3046	2940	1593	1425	1362	1308	924	777	495	415
	3205			3062	2931	1594					77 <b>9</b>		395
Sn-complex, <b>Id</b>	3300	3198	3000	3005	2940	1595	1435	1398	1308	924	775	490	417
		3205			2925	1595					780		416
H <sub>4</sub> pClMaTS, <b>II</b>	3310	3196	3111	3005	2940	1657	1400	1341	-	902	814	-	-
		3201			2934	1635	1405	1355			824		
Co-complex, <b>IIa</b>	3237	3179	3109	3034	2980	1595	1420	1400	1306	935	743	493	421
Cu-complex, IIb	3238	3180	3111	3053	2934	1599	1431	1400	1310	945	772	501	428
Zn-complex, <b>IIc</b>	3305	3194	3105	3005	2938	1591	1416	1400	1310	924	777	490	418
		3209			2933	1593		1395	1315		77 <b>9</b>		
Sn-complex, IId	3305	3197	3111	3007	2940	1599	1440	1400	1308	925	777	490	421
H <sub>4</sub> pClSuTS, III	3310	3196	3107	3005	2940	1670	1400	1341	-	923	827	-	-
		3201	3095	3005	2934	1650	1405	1355					
Co-complex, IIIa	3237	3220	3115	3032	2943	1595	1418	1368	1307	975	755	500	415
Cu-complex, IIIb	3238	3202	3115	3039	2938	1597	1450	1379	1319	960	775	490	425
Zn-complex, IIIc	3305	3200	3109	3001	2938	1595	1418	1400	1310	966	777	492	421
				3004	2931	1596		1390	1319				
Sn-complex, IIId	3305	3198	3115	3007	2940	1599	1445	1400	1308	964	773	495	415
	3300		3100	3005	2925	1593	1450	1390	1294				

Raman data are in bolds and italic.



Fig. 1. Molecular modeling of 1,1-oxalyl-bis(4-p-chlorophenylthiosemicarbazide).



**Fig. 2.** Molecular modeling of 1,1-malonayl-bis(4-*p*-chlorophenylthiosemicarbazide).

atom of C=S. <sup>1</sup>HNMR spectrum of zinc(II) complex is in agreement with the suggested coordination through the C=N and C=S groups by the presence of the signals of (two from 2NH amine groups and two protons from 2NH amide groups).

- (H<sub>4</sub>pClOxTS), <sup>1</sup>HNMR of 1,1-oxalyl-bis(4-*p*-chlorophenylthiose-micarbazide), <sup>1</sup>δ (ppm): 9.75(N5,17H amide group), 1.95(N6,18H amine group), 3.6(CN9,21H, 6.6–7.5 aromatic).



**Fig. 3.** Molecular modeling of 1,1-succinyl-bis(4-*p*-chlorophenylthiosemicarbazide).



**Fig. 4.** The electronic spectra of 1,1-oxalyl-bis(4-*p*-chlorophenylthiosemicarbazide), H<sub>4</sub>pClOxTS, and its metal complexes.



**Fig. 5.** The electronic spectra of 1,1-malonyl-bis(4-*p*-chlorophenylthiosemicarbazide), H<sub>4</sub>pCIMaTS, and its metal complexes.



**Fig. 6.** The electronic spectra of 1,1-succinyl bis(4-*p*-chlorophenylthiosemicarbazide), H<sub>4</sub>pClSuTS, and its metal complexes.

- $[Zn_2(pClOxTS)(ac)_2]\cdot 2H_2O^1HNMR \delta$  (ppm): 1.19(CH<sub>3</sub> acetone), 2.7(H<sub>2</sub>O) (NH amide groups disappeared), (NH amine groups disappeared), 3.5(9,21CNH aromatic), 6.6–7.5(CH-aromatic shifted).
- $(H_4pCISuTS)$  <sup>1</sup>HNMR  $\delta$  (ppm): 9.7(7,19NH amide group), 1.95(8,20NH amine group),4(11,23CNH aromatic), 2.5(3,4CH<sub>2</sub>) 6.6-7.75(CH-aromatic).
- $[Zn_2(pClSuTS)(ac)_2]2(H_2O)$  <sup>1</sup>H NMR  $\delta$  (ppm): 1.1(H<sub>2</sub>O), 1.2(CH<sub>3</sub> acetone) (NH amide groups disappeared), (NH amine groups disappeared), 2.5(CH<sub>2</sub>), 4(CNH aromatic), 6.6–7.75(CH-aromatic shifted).

#### 3.6. Thermogravimetric analysis

Thermogravimetric analysis curves (TGA and DTG) of **I**, **Ia**, **Ib**, **Ic** and **Id** are discussed as mentioned in Table 4. Compound **I** was thermally decomposed within the temperature range 25–700 °C. The first step with weight loss of 42.5% (calc. 42.4%) at 25–237 °C may be attributed to the liberation of  $2(N_2H_2)$ , 2(HCNS) and  $1/2O_2$ . The second step at 237–337 °C (obs. = 30.2%, calc. = 30.4%), is accounted for the removal of  $1/2O_2$ , Cl<sub>2</sub> and C<sub>4</sub>H<sub>4</sub>. The decomposition ended with C<sub>10</sub>H<sub>4</sub> residue (obs. = 27.3%, calc. = 27.1%).

The complex **Ia** was thermally decomposed in five steps. The first step (obs. = 6%, calc. = 6.6%) at 25-175 °C may be attributed to the

#### Table 3

The electronic spectra data of oxalyl, malonyl and succinyl-bis(4-p-chlorophenylthiosemicarbazide) and its metal complexes.

Compounds	$\lambda_{\rm max}  {\rm nm}  ({\rm cm}^{-1})$							
	$\pi - \pi^*$	$n-\pi^*$	d–d Transit	ion				
I	256	314	-	-	-			
	(39,060)	(31,850)						
Ia	260	313	494	559	578			
	(38,460)	(31,950)	(20,240)	(17,889)	(17,300)			
Ib	268	310	486	540	-			
	(37,300)	(32,260)	(20,600)	(18,520)				
Ic	265	317	-	-	-			
	(37,740)	(31,550)						
Id	266	324	-	-	-			
	(37,600)	(30,860)						
П	287	344	-	-	-			
	(34,840)	(29,070)						
IIa	288	342	462	485	522			
	(34,720)	(29,240)	(21,650)	(20,620)	(19,160)			
IIb	308	358	466	493	524			
	(32,470)	(27,930)	(21,460)	(20,280)	(19,080)			
llc	284	344	-	-	-			
	(35,210)	(29,070)						
IId	288	330	-	-	-			
	(34,720)	(30,300)						
III	264	328	-	-	-			
	(37,880)	(30,490)						
IIIa	296	356	540	600	622			
	(33,780)	(28,090)	(18,520)	(16,670)	(16,080)			
IIIb	256	320	543	610	-			
	(39,060)	(31,250)	(18,420)	(16,390)				
IIIc	280	332	-	-	-			
	(35,710)	(30,120)						
IIId	260	304	-	-	-			
	(38,460)	(32,890)						

liberation of  $3H_2O$ . The second step at 175-390 °C (obs. = 29.2%, calc. = 28.6%) is due to the removal of 2 acetone, 4 water and  $N_3H_3$  fragments. The third step at 390-707 °C (obs. = 18.3%, calc. = 18.9%) is accounted for the removal of ( $C_4N_3S_2$ ) fragment. The fourth step at 707-990 °C (obs. = 22.8%, calc. = 22.8%) is accounted for the removal of ( $C_9H_7Cl_2$ ) fragment. The decomposition ended with 2CoO and 3/ 2C<sub>2</sub> (obs. = 23.7%, calc. = 22.9%) (see Table 4).

The TG curve of **Ib** complex indicates that the mass change begins at 25 °C and continuous up to 1000 °C. The first and second mass loss corresponds to the liberation of the 12water molecules and two (HCN) fragment (obs. = 34.4%, calc. = 33.9%) at 25–342 °C. The third step occurs in the range 342–475 °C and corresponds to the loss of (CN<sub>4</sub>S) (obs. = 12.8%, calc. = 12.6%). The fourth and fifth decomposition step are final decomposition organic ligand to the (C<sub>13</sub>H<sub>8</sub>Cl<sub>2</sub>), 1/2S<sub>2</sub>, O<sub>2</sub> fragments and 2Cu metal residual atoms. (obs. = 52.8%, calc. = 53.4%). From the previous discussion, the structure of **Ib** complex may have the octahedral bi-nuclear complex as shown in Scheme 1.

Ic complex was thermally decomposed in mainly five decomposition steps within the temperature range 25–700 °C. The first decomposition step (obs. = 20.64%, calc. = 20.64%) at 25–245 °C, may be attributed to the liberation of two water and two acetone molecules. The second step at 245–386 °C (obs. = 23.4%, calc. = 23.6%) is accounted for the removal of the 2(HCN), 2N<sub>2</sub> and S<sub>2</sub> fragments. The third step found within the temperature 386–700 °C (obs. = 19.7%, calc. = 19.96%) is accounted for the removal of Cl<sub>2</sub> and C<sub>6</sub>H<sub>4</sub> molecule. The rest of the ligand molecule was removed with a final residue of (C<sub>8</sub>H<sub>4</sub>), (ZnO) and zinc metal (obs. = 36.3%, calc. = 35.7%).

**Id** complex is thermally stable up to 50 °C and decomposition beyond this temperature as indicated by the first loss step in the TG curve. First step, the mass loss at 226 °C corresponds to the loss of two water and 2(HCN) molecules (obs. = 12.6%, calc. = 12.4%).

Table 4		
The thermal data of 1,1-oxalyl-bis(4-p-chlorophenylthiosemicarbazide)	and its metal c	complexes.

Compound	Steps	Temperature range (°C)	TG weight loss (%)		Assignment	$T_{\rm max}$
			Calc.%	Found%		
I	1 2 3	25–237 237–337 More than 337	42.40 30.40 27.10	42.50 30.20 27.30	2(N <sub>2</sub> H <sub>2</sub> ), 2(HCNS) and 1/2O <sub>2</sub> fragments 1/2O <sub>2</sub> , Cl <sub>2</sub> and C <sub>4</sub> H <sub>4</sub> $C_{10}H_4$	205 280 565
Ia	1 2 3 4 5	25–175 175–390 390–707 707–990 More than 990	6.60 28.50 18.90 22.80 22.90	6 .00 29.20 18.30 22.80 23.70	3 Water 2 Acetone, 4 water and N <sub>3</sub> H <sub>3</sub> (C <sub>4</sub> N <sub>3</sub> S <sub>2</sub> ) (C <sub>9</sub> H <sub>7</sub> Cl <sub>2</sub> ) 2CoO and residual carbon 3/2C <sub>2</sub>	166 278 777 869
Ib	1,2 3 4,5	25–342 342–475 More than 475	33.90 12.60 53.40	34.40 12.80 52.80	12 Water and 2(HCN) (CN <sub>4</sub> S) (C <sub>13</sub> H <sub>8</sub> Cl <sub>2</sub> ), (S), (O <sub>2</sub> ) molecules and 2Cu(II)metal	187, 271 405, 480 840 978
Ic	1 2 3 4	25–245 245–386 386–700 More than 700	20.64 23.60 19.96 35.70	20.64 23.40 19.70 36.30	Two water and two acetone molecules $2(HCN)$ , $2N_2$ and $S_2$ $Cl_2$ and $C_6H_4$ $(C_8H_4)$ , (ZnO) and zinc metal residue	228 319 493 649
Id	1 2 3 4	25–226 226–322 322–560 More than 560	12.40 16.50 16.90 54.10	12.60 16.20 17.20 54.00	Two water and 2(HCN) molecules $S_2$ and $2N_2$ $Cl_2$ and $C_4H_4$ $Cl_0 And C_4H_4$ (SnO) and Sn metal residue	224 301 530

Table 5Kinetic parameters using the Coats-Redfern (CR) and Horowitz-Metzger (HM) operated for (H<sub>4</sub>pClOxTS) and its complexes.

Compound	Stage	Method	Parameter						
			E (J mol <sup>-1</sup> )	$A(s^{-1})$	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H$ (J mol <sup>-1</sup> )	$\Delta G$ (J mol <sup>-1)</sup>		
I	1st	CR HM	$\begin{array}{c} 1.12\times10^5\\ 1.28\times10^5\end{array}$	$\begin{array}{c} 1.07\times 10^{10} \\ 1.50\times 10^{12} \end{array}$	$\begin{array}{c} -5.68 \times 10^{1} \\ -1.58 \times 10^{1} \end{array}$	$\begin{array}{c} 1.08\times10^5\\ 1.24\times10^5\end{array}$	$\begin{array}{c} 1.35\times10^5\\ 1.32\times10^5\end{array}$	0.9981 0.9961	
Ia	1st	CR HM	$\begin{array}{c} 5.14\times10^{4}\\ 6.33\times10^{4}\end{array}$	$\begin{array}{c} 7.99\times10^3 \\ 6.60\times10^3 \end{array}$	$\begin{array}{c} -1.75\times 10^2 \\ -1.77\times 10^2 \end{array}$	$\begin{array}{l} 4.68\times10^{4}\\ 5.87\times10^{4}\end{array}$	$\begin{array}{c} 1.43\times10^5\\ 1.56\times10^5\end{array}$	0.9920 0.9929	
Ib	1st	CR HM	$\begin{array}{c} 1.10\times10^5\\ 1.31\times10^5\end{array}$	$\begin{array}{c} 7.01 \times 10^9 \\ 2.96 \times 10^{12} \end{array}$	$\begin{array}{c} -6.04 \times 10^{1} \\ -1.01 \times 10^{1} \end{array}$	$\begin{array}{c} 1.06\times10^5\\ 1.27\times10^5\end{array}$	$\begin{array}{c} 1.35\times10^5\\ 1.31\times10^5\end{array}$	0.9995 0.9991	
Ic	1st	CR HM	$\begin{array}{c} 8.04\times10^{4}\\ 1.07\times10^{5}\end{array}$	$\begin{array}{c} 7.21\times10^5 \\ 2.29\times10^8 \end{array}$	$\begin{array}{c} -1.38 \times 10^2 \\ -8.98 \times 10^1 \end{array}$	$\begin{array}{c} 7.59\times10^{4}\\ 1.02\times10^{5}\end{array}$	$\begin{array}{c} 1.50\times10^5\\ 1.51\times10^5\end{array}$	0.9968 0.9985	
Id	1st	CR HM	$\begin{array}{c} 8.61\times10^4\\ 1.71\times10^5\end{array}$	$\begin{array}{c} 1.65 \times 10^{7} \\ 32.75 \times 10^{9} \end{array}$	$\begin{array}{c} -1.11 \times 10^2 \\ -6.59 \times 10^1 \end{array}$	$\begin{array}{c} 8.2\times10^4\\ 1.05\times10^5\end{array}$	$\begin{array}{c} 1.37\times10^5\\ 1.38\times10^5\end{array}$	0.9938 0.9955	



**Scheme 1.** Suggested octahedral structure for, **Ia**, *copper oxalyl-bisthiosemicarbazide complex*.

Continuous mass loss in the TG curve from 226 to 322 °C corresponds to the loss of S<sub>2</sub> and 2N<sub>2</sub> molecules (obs. = 16.2%, calc. = 16.5%). The decomposition third step found within the temperature 322–560 °C (obs. = 17.2%, calc. = 16.9%) which is reasonably accounted for by the removal of Cl<sub>2</sub> and C<sub>4</sub>H<sub>4</sub> molecule. The rest of organic moiety and the final decomposition of the organic ligand to the C<sub>10</sub>H<sub>4</sub>, (SnO) and Sn metal residue molecules was re-

moved on the fourth step within the temperature of more than  $560 \degree C$  (obs. = 54%, calc. = 54.1%).

Ligand **II** was thermally decomposed in mainly decomposition steps, Table S1, within the temperature range successive decomposition steps at 25–700 °C. The first decomposition step (obs. = 39.14%, calc. = 39%) at 25–245 °C, may be attributed to the liberation of the 2(HNCO), 2H<sub>2</sub>S and 2(NH) fragments. The second decomposition step at 245–345 °C (obs. = 32.8%, calc. = 32.5%), is accounted for the removal of 2(HCN), (C<sub>2</sub>H<sub>2</sub>) and Cl<sub>2</sub>. The decomposition of the ligand molecule ended with a final (C<sub>17</sub>H<sub>2</sub>) residue (obs. = 28%, calc. = 28.3%).

The complex **IIa** was thermally decomposed in five steps within the temperature range 25–1000 °C. The first step (obs. = 5.2%, calc. = 4.94%) at 25–188 °C, may be attributed to the liberation of the two H<sub>2</sub>O molecules. The second step at 188–448 °C (obs. = 33.1%, calc. = 33.5%), is accounted for the removal of 6H<sub>2</sub>O, 2N<sub>2</sub>, 2(HCN), and C<sub>2</sub>H<sub>2</sub> fragments. The decomposition third step at 448–760 °C (obs. = 23.4%, calc. = 22.9%) is accounted for the removal of S<sub>2</sub>, Cl<sub>2</sub> and O<sub>2</sub> molecules. The fourth step found at 760–885 °C (obs. = 21.8%, calc. = 22.5%) is accounted for the removal of CH<sub>4</sub> and C<sub>12</sub>H<sub>4</sub> fragments. The rest of the ligand molecule was removed with a final 2Co atom (obs. = 17.3%, calc. = 16.5%).

The TG curve of **IIb** complex indicates that the mass change begins at 25 °C and continuous up to 1000 °C. The first and second mass loss corresponds to the liberation of the  $6H_2O$  molecules (obs. = 16.4%, calc. = 15.4%) at 25–245 °C. The third step occurs in the range 245–475 °C and corresponds to the loss of N<sub>2</sub>, 2(HCN), N<sub>2</sub>H<sub>2</sub>, and O<sub>2</sub> (obs. = 20.6%, calc. = 20.5%). The fourth step at 475–765 °C (obs. = 42.4%, calc. = 42.5%) is accounted for the removal of (C<sub>13</sub>H<sub>8</sub>, S<sub>2</sub> and Cl<sub>2</sub>) fragments. The fifth steps are final decomposition organic ligand to the C<sub>2</sub> and 2Cu residual. (obs. = 20.6%, calc. = 21.5%).

The complex **IIc** was thermally decomposed in mainly four steps within the temperature range 25–700 °C. The first decomposition step (obs. = 15.5%, calc. = 15.3%) at 25–224 °C, may be attributed to the liberation of 6H<sub>2</sub>O. The second step at 224–338 °C (obs. = 26.5%, calc. = 26.9%) is accounted for the removal of 2N<sub>2</sub>, S<sub>2</sub>, 1/2O<sub>2</sub> and 2(HCN) fragment. The decomposition third step found within the temperature 338–643 °C (obs. = 18.6%, calc. = 18.2%) is accounted for the removal of 1/2O<sub>2</sub>, Cl<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> fragments. The rest of the molecule was removed with a final residue metal of 2Zn and C<sub>12</sub>H<sub>4</sub> fragment (obs. = 39.4%, calc. = 39.5%).

The complex **IId** is thermally stable up to 50 °C and decomposition beyond this temperature as indicated by the first and second loss steps in the TG curve. First and second steps, the mass loss at 322 °C corresponds to the loss of 8H<sub>2</sub>O and HNCO and HCN molecules (obs. = 24.7%, calc. = 25.2%). Continuous mass loss in the TG curve from 322 to 504 °C corresponds to the loss of 1/2S<sub>2</sub> and HNCO molecules (obs. = 9.3%, calc. = 8.8%). The rest of organic moiety NH<sub>3</sub>, N<sub>2</sub> and 1/2S<sub>2</sub> molecules was removed on the fourth step at 504–589 °C (obs. = 9.56%, calc. = 9.1%). The final decomposition of the Cl<sub>2</sub>, C<sub>14</sub>H<sub>6</sub> and Sn<sub>2</sub> the residual (obs. = 56.44%, calc. = 56.8%).

All the steps of decomposition for the ligand **III** and its metal complexes were described in Table S3. Ligand **III** was thermally decomposed in mainly decomposition steps within the temperature range successive decomposition steps within the temperature range 25–700 °C. The first decomposition step (obs. = 36%, calc. = 35.8%) within the temperature range 25–234 °C, may be attributed to the liberation of the 2(HCN), 2N<sub>2</sub> and S<sub>2</sub> fragments. The second decomposition steps found within the temperature range 234–334 °C (obs. = 32.1%, calc. = 32.3%), which is reasonably accounted by the removal of Cl<sub>2</sub>, O<sub>2</sub> and C<sub>4</sub>H<sub>6</sub>. The decomposition of the ligand molecule ended with a final C<sub>12</sub>H<sub>10</sub> residue (obs. = 31.86%, calc. = 31.7%).

The complex **IIIa** was thermally decomposed in four successive decomposition steps within the temperature range 25–1000 °C. The first decomposition step (obs. = 31.9%, calc. = 32%) within the temperature range 25–332 °C, may be attributed to the liberation of the 6water molecules, 2(HCN) and N<sub>2</sub>H<sub>2</sub> fragments. The second decomposition steps found within the temperature range 332–550 °C (obs. = 16.9%, calc. = 16.8%), which is reasonably accounted by the removal S<sub>2</sub>, O<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> fragments. The decomposition third step found within the temperature 550 °C (obs. = 24.6%, calc. = 24.5%) which is reasonably accounted for by the removal of Cl<sub>2</sub>, and C<sub>8</sub>H<sub>6</sub> fragments. The rest of the ligand molecule was removed and fourth the decomposition of the Co(II)/L complex molecule ended with a final 3/2C<sub>2</sub> and Co<sub>2</sub> metal is cobalt residue (obs. = 26.6%, calc. = 26.8%).

The TG curve of complex **IIIb** indicates that the mass change begins at 25 °C and continuous up to 1000 °C. The first mass loss corresponds to the liberation of the 10water molecules (obs. = 17.8%, calc. = 17.8%) within the temperature range 25–465 °C. The second decomposition steps found within the temperature range 465– 700 °C (obs. = 15%, calc. = 14.8%), which is reasonably accounted by the removal of 2(HCN), 2N<sub>2</sub> and 2(CH<sub>2</sub>) fragments. The third decomposition step occurs in the range 700–910 °C and corresponds to the loss of Cl<sub>2</sub>, 2(C<sub>6</sub>H<sub>4</sub>) and 2S<sub>2</sub> (obs. = 33.9%, calc. = 34.7%). The fourth and fifth steps are the final decomposition (obs. = 33.3%, calc. = 32.6%) which is reasonably accounted for by the removal of carbon and 4CuO.



Scheme 2. Suggested structure for succinyl bisthiosemicarbazide metals complexes.

The complex **IIIc** was thermally decomposed in mainly three decomposition steps within the temperature range 25–700 °C. The first decomposition step (obs. = 20%, calc. = 19.9%) within the temperature range 25–236.8 °C, may be attributed to the liberation of two water and two acetone molecules. The decomposition second step found within the temperature 236.8–365 °C (obs. = 25.3%, calc. = 25.38%) which is reasonably accounted for by the removal of 2(HCN) 2(HNCO) 2CH and N<sub>2</sub> fragment. The decomposition of the ligand molecule ended with a final residue metal of Zn(II) and contaminated 2Cl<sub>2</sub>, S<sub>2</sub>, (C<sub>6</sub>H<sub>4</sub>) and 2Zn (obs. = 54.7%, calc. = 54.66%).

The complex **IIId** is thermally stable up to 50 °C and decomposition beyond this temperature as indicated by the first loss step in the TG curve. First step, the mass loss at 239 °C corresponds to the loss of six water molecules (obs. = 13%, calc. = 13.1%). Continuous mass loss in the TG curve from 239 °C to 321 °C corresponds to the loss of 2HCN and 2N<sub>2</sub> fragments (obs. = 12.7%, calc. = 13.3%). The rest of the ligand molecule was removed and fifth step the decomposition of the ligand molecule ended with a final residue metal of two Tin atoms and contaminated of, C<sub>16</sub>H<sub>12</sub>, fragments (obs. = 53.5%, calc. = 53.4%). From the previous discussion, the structure of Co(II) and Sn(II) *succinyl bisthiosemicarbazide metals complexes* may have the octahedral bi-nuclear structure as shown in Scheme 2.

#### 3.7. Kinetic studies

1,1-Oxalyl-, malonyl- and succinyl-bis(4-p-chlorophenylthiosemicarbazide) ligand and its Co(II), Cu(II), Zn(II) and Sn(II) complexes thermodynamic activation parameters of decomposition processes of hydrated complexes, namely activation energy, E\*, enthalpy,  $\Delta H^*$ , entropy,  $\Delta S^*$ , and Gibbs free energy change of the decomposition,  $\Delta G^*$ , were evaluated graphically, Figs. S1–S15, by employing the Coats-Redfern and Horowitz-Metzger relations [41–46]. The thermodynamic parameters for oxalyl-thiosemicarbazide complexes were calculated and summarized in Table 5. All the thermodynamic parameters for the rest of materials were also calculated. The data are summarized in Tables S2 and S4. The high values of the activation energy illustrated to the thermal stability of the complexes.  $\Delta G$  is positive for reaction for which  $\Delta H$ is positive and  $\Delta S$  is negative. The reaction for which  $\Delta G$  is positive and  $\Delta S$  is negative considered as unfavorable or non spontaneous reactions.

The activation energies of decomposition of ligand **I** and its metal complexes were in the range **57.3–120** kJ mol<sup>-1</sup>. The high values of the activation energy illustrated to the thermal stability of the complexes. The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9925–0.9993 showing a good fit with linear function. It is clear that the thermal decomposition process of ligand I and its complexes are thermally stable. The entropy of activation had negative values in all the complexes, which indicates that the decomposition reactions proceed with a lower rate than the normal ones. The activation energy of ligand **II** and its Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup> and Sn<sup>2+</sup> complexes is expected to increase in relation with decrease in their radii. The activation energies of decomposition were in the range **56.9–461** kJ mol<sup>-1</sup>. The high values of the activation energy illustrated to the thermal stability of the complexes. The smaller size of the ions permits a closer approach of the ligand (H<sub>4</sub>pClMaTS). Hence, the *E* value in the first stage for the  $Zn^{2+}$  complex is higher than that for the other Sn<sup>2+</sup>, Cu<sup>2+</sup> and Co<sup>2+</sup> complex. The activation energies of ligand III and its metal complexes were in the range **50.2–337** kJ mol<sup>-1</sup>. The high values of the activation energy illustrated to the thermal stability of the complexes. It is clear that the thermal decomposition process of compounds I. II. III and Co<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Sn<sup>2+</sup> metal complexes are non-spontaneous, i.e., the materials are thermally stable.

#### 3.8. Antibacterial activity

The inhibition zones of antibacterial and antifungal activities at different concentration (1.0, 2.5 and 5.0 mg/mL) are presented in Tables S5-S7. The data indicate that some metal complexes show an appreciable activity against E. Coli, P. aeruginosa species and Gram-positive bacteria; B. cereus and S. aureus. It has been observed that Zn(II) and Sn(II) complexes have much toxicity. This is expected because the Tin and Zinc salts are mostly used as fungicides. Such increased activity of the metal chelates can be explained on the effect of binding of the metal complexes to DNA [47] and the basis of the Tweedy's chelation theory [48]. The increase in antimicrobial activity is due to faster diffusion of metal complexes as a whole through the cell membrane or due to the combined activity of the metal and ligand. Thus, according to chelation theory, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups [49]. Further, it increases the delocalization of the  $\pi$  electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and thus blocks the metal binding sites on enzymes of microorganisms [50]. These metal complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restricts further growth of the organism [50]. The variation in the activity of different complexes against different organisms depend either on the impermeability of the cells of the microbes or difference in ribosomes of microbial cells.

# 4. Conclusions

The structures of the complexes of oxalyl, malonyl and succinylbis(4-*p*-chlorophenylthiosemicarbazide) were interpretive by elemental analyses, IR, Raman, <sup>1</sup>HNMR, molar conductance, UV–Vis, mass, and thermal analysis data. The Infrared and Raman spectral studies suggests the tridentate behavior of the ligand from each tail. Since the ligand has two thiosemicarbazide groups, it may acts in an SNO tridentate fashion from each side with one of the two metal ions forming a polynuclear complex coordinating through both of the lone pair of electrons on the enolic oxygen of the carbonyl group (C=O), the azomethine nitrogen (C=N) and the thioenol form of the thiocarbonyl group(C=S). The <sup>1</sup>HNMR spectra of Zn(II) complexes indicate that the bis-thiosemicarbazide ligands under investigation acts as a hexadentate through the nitrogen atom of azomethine (C=N), oxygen atom of carbonyl (C=O) and sulfur atom of thioketo (C=S) groups. On the basis of the magnetic measurements octahedral geometry are suggested for all investigated complexes. The thermodynamic activation parameters of decomposition processes of the materials were evaluated graphically. It is clear that the thermal decomposition process of compounds I, II, III and  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Sn^{2+}$  metal complexes are non-spontaneous, i.e., the materials are thermally stable. The synthesized ligands in comparison to their metal complexes were also screened for their antibacterial and antifungal activities against some bacterial species. The activity data show the metal complexes to be more potent antibacterials than the parent ligands against two or more bacterial species.

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#### **Appendix A. Supplementary material**

Provided with this paper some supporting information concerned with the following topics:

- 1. The thermal decomposition steps for ligands **II**, III and their metal complexes (Tables S1 and S3).
- 2. The thermodynamic parameters for the ligands **II**, III and their metal complexes (Tables S2 and S4).
- 3. The inhibition zones of antibacterial and antifungal activities at different concentrations (Tables S5 S6 and S7).
- 4. Kinetic data curves for 1,1-oxalyl-, malonyl- and succinyl-bis(4*p*-chlorophenylthiosemicarbazide) ligands and the corresponding metal complexes by employing the Coats–Redfern and Horowitz–Metzger relations (Figs. S1–S15).

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.11.024.

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