

Kinetic parameters and thermal decomposition for Novel 1,1-malonyl-bis(4-p-Chlorophenylthiosemicarbazide) and Cu(II), Co(II), Zn(II) and Sn(II) complexes (H₄pCIMaTS) synthesized by electrochemical method

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ABSTRACT

Anodic oxidation of Co, Cu, Zn, and Sn metals in an acetone solution of 1,1-malonyl-bis(4-p-Chloro-phenylthiosemicarbazide) yields complexes of composition with general formula [Co₂(pCIMaTS)(H₂O)₆]-2H₂O, [Cu₂(pCIMaTS)(H₂O)₆], [Zn₂(pCIMaTS)(H₂O)₆] and [Sn₂(pCIMaTS)(H₂O)₆]-2H₂O. Chelation was investigated based on elemental analysis, conductivity, magnetic moment, spectral (UV-Vis, IR, Raman, ¹HNMR, mass), thermal, and ESR studies. The Raman and infrared 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 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 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. The kinetic thermodynamic parameters such as: E*, ΔH*, ΔS* and ΔG* are calculated from the DTG curves.

Keywords: Metal(II) Complexes; Electrochemical; Thermogravimetric; Bis-Thiosemicarbazide

1. INTRODUCTION

Thiosemicarbazide and their derivatives are of current

interest with respect to their uses as analytical reagents for high performance liquid chromatographic separations of metal(II) ions as metal chelates [1-3], potentiometric sensors [4], analytical determination of metal ions [5] and clinical analysis [6]. Most of these compounds have antifungal [7], antimicrobial [8], antitumor [9], biological activity [10,11] as well as hypoglycemic effects [12-14]. In addition, thiosemicarbazide derivatives have ability to form chelate complexes with transition metal ions [15-20]. Continuing our studies for the electrochemical synthesis of new metal complexes of ligands containing N, S and O atoms through the reaction of metal ions scarified from the anodic dissolution of metals [16,21,22]. In this paper we are reported a novel complexes isolated from the reaction between 1,1-Malonyl-bis(-4-p-chlorophenyl thiosemicarbazide) and the metal ions scarified from the dissolution of Cobalt, Copper, Zinc and Tin metals. The modern spectroscopic investigations are used to elucidate the structure of the prepared materials. The thermal decomposition is also used to infer the structure of the metal complexes and to calculate the different thermodynamic activation parameters [23,24].

2. EXPERIMENTAL

2.1. The Materials

All the chemicals (Aldrich) were subjected to purification before use. The solvents, DMF (BDH) (Analar), absolute acetone, ethanol and methanol (Fluka) used were reagent grade. The metals (Alfa Inorganics) used, Co, Cu, Zn, and Sn were purchased in the form of sheets (~2 cm × 2 cm, 2 - 3 mm thick). The oxide surface was removed by treating the metal with conc. HNO₃ for several minutes and then washing with distilled water. Tet-

raethylammonium perchlorate, Et_4NClO_4 , (BDH) was used as supplied [25].

2.2. The Organic Compounds

2.2.1. Preparation of 1,1-Malonyl-Hydrazide

1,1-Malonyl-dihydrazine was prepared by adding Malonyl Chloride (7 gm \approx 0.05 mol) to alcoholic solution of hydrazine hydrate (5 gm \approx 0.1 mole). The reaction mixture was exothermic and left to cool with stirring. A brown crystal precipitate was formed and washed with ethanol diethyl ether and left to dry. Yield (5 gm \approx 76%) and the melt point at 130°C.

2.2.2. Preparation of 1,1-Malonyl bis-4-(p-Chlorophenylthiosemi Carbazide)

1,1-Malonyl bis-4-(p-chlorophenylthiosemicarbazide) was prepared by adding 4-chloro-phenylisothiocyanate (3.4 gm, 0.02 mol) to an alcoholic solution of malonic acid dihydrazide (1.32 gm \approx 0.01 mole). The reaction mixture was refluxed for 1 hour 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 dist. water, EtOH and dried by Et_2O and finally dried in vacuo over silica gel. Yield (4.3 gm \approx 91%) and the melt point at 200°C [26] (Figure 1).

2.3. Electrochemical Procedure

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 was suspended and supported on a platinum wire. [21,22] 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 $E_f = 0.5 \pm 0.05 \text{ mol} \cdot \text{F}^{-1}$. [25].

Electrochemical Synthesis of 1,1-Malonyl bis-4-(p-Chlorophenyl Thiosemicarbazide) Metals Complexes

The ligand $\text{H}_4\text{pClMaTS}$ (0.236 gm, 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_4NClO_4 . When the current 40 mA was passed through the cell for 1 hour, the amount of Cobalt consumed is 59 mg and a dark brown precipitate was formed (the product is 0.364 gm, % yield 99.7 and $E_f = 0.51$). It was collected, washed with diethyl ether and dried. The resulting dark brown powder was collected and analyzed as $[\text{Co}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$. By the same way Cu, Zn, and Sn complexes were isolated.

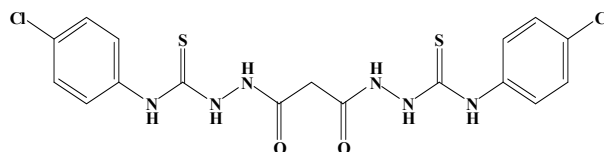


Figure 1. The structure of 1,1-malonyl-bis(4-p-chlorophenylthio semicarbazide).

2.4. Analytical Measurements

2.4.1. Spectral Measurements

The absorbances of solutions were measured in UV/Vis range at nano-Photoenergy 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.

2.4.2. $^1\text{H-NMR}$ Spectra

The ^1H NMR spectra were recorded on an Varian Mercury VX-300 NMR spectrometer. All the spectra were run at 300 MHz with ^2H lock. The ^1H NMR was run at 75.46 MHz in deuterated dimethylsulphoxide (DMSO-d_6). Chemical shifts were quoted in δ and were related to that of the solvents.

2.4.3. Microanalytical Techniques

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The copper, cobalt, zinc, and tin contents were determined gravimetrically by the direct ignition of the complexes at 1000°C for 3 hours till constant weight. The residue was then weighted in the forms of metal oxides. The melting point of ligand and their metal complexes were measured by the electro thermal melting point Stuart SMP3 made in UK.

2.4.4. Magnetic Measurements

Magnetic measurements were carried out on a Sherwood Scientific magnetic balance using Gouy method. Calibration: $\text{Hg}[\text{Co}(\text{CNS})_4]$ and $[\text{Ni}(\text{en})_3](\text{S}_2\text{O}_3)$ are easily prepared pure, do not decompose or absorb moisture and pack well. Their susceptibilities at 293 K are 16.44×10^{-6} and 11.03×10^{-6} c.g.s. Units, decreasing by 0.05×10^{-6} and 0.04×10^{-6} per degree temperature raise respectively, near room temperature. The cobalt compound, besides having the higher susceptibility, also packs rather densely and is suitable for calibrating low fields, while the nickel compound with lower susceptibility and density is suitable for higher field. Here we were used $\text{Hg}[\text{Co}(\text{CNS})_4]$ only as calibrant, Micro analytical Center, Cairo University, Egypt.

2.5. Thermal Investigation

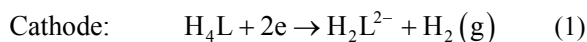
Thermogravimetric analysis (TGA and DTG) were

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

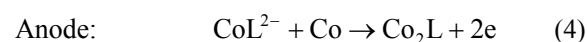
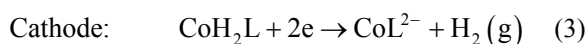
3. RESULTS AND DISCUSSION

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 $E_f = 0.5 \pm 0.05 \text{ mol} \cdot \text{F}^{-1}$. The values show that the reaction of the ligand with cobalt anode is compatible with the following steps 1 and 2.

1) The First step:



2) The Second step:



Anodic oxidation of Co, Cu, Zn, and Sn metals in an anhydrous acetone solution of 1,1-malonayl-bis (4-p-Chlorophenylthiosemicarbazide) yields complexes of composition with general formula $[\text{Co}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$, $[\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$ and $[\text{Sn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$. Structural investigation of the ligand and their complexes has been made based on elemental analysis, conductivity, magnetic moment, spectral (UV-Vis, IR, Raman, $^1\text{H-NMR}$, Mass), thermal studies. The elemental analysis and some physical data of the resulted compounds are given in **Table 1**. The complexes are air-stable, hygroscopic. All 1,1-malonayl-bis (4-p-chlorophenyl) thiosemicarbazide, Co(II), Cu(II), Zn(II) and Sn(II) complexes are paramagnetic in nature. They are white, dark brown, dark brown, yellowish white and page respectively; quite stable in atmospheric conditions; insoluble in water, ethanol and Diethylether but are completely soluble in DMF and DMSO the complexes have different melting points (200°C - 243°C).

3.1. Molar Conductivity

The molar conductivity values of the 1,1-malonayl-bis (4-p-chlorophenylthiosemicarbazide) and its complexes in DMSO solvent ($1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) were 20 μs for ($\text{H}_4\text{pClMaTS}$) ligand, 37 μs for $[\text{Co}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$, 35 μs for $[\text{Cu}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$, 38 μs for $[\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$ and 36 μs for $[\text{Sn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$ respectively. The molar conductivity measurements located in the range of non-electrolytic behavior (**Table 1**).

3.2. Infrared Spectra

Important IR spectral data of the ligands and complexes are summarized in **Table 2**. The IR spectrum of $[\text{H}_4\text{pClMaTS}]$ shows bands at 3310, 3196 and 3111 cm^{-1} for the three-NH groups present in the ligand. The bands occurring at 1657, 1400, 1341, 902 and 814 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$, thioamide I [$\beta(\text{NH}) + \nu(\text{CN})$], thioamide II [$\nu(\text{CN}) + \beta(\text{NH})$], $\nu(\text{N-N})$ and $\nu(\text{C}=\text{S})$, respectively. An exhaustive comparison of the IR spectra of the ligand and complexes gave information about the mode of bonding of the ligand in metal complexes. The IR spectrum of complexes $[\text{Co}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$, $[\text{Cu}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$, $[\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$ and $[\text{Sn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2(\text{H}_2\text{O})$ when compared with ligand $[\text{H}_4\text{pClMaTS}]$, indicates that bands due to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{S})$ are absent, but new bands appear at 1602 and 763 cm^{-1} due to $\nu(\text{N}=\text{C})$ and $\nu(\text{C-S})$, 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). Furthermore, the ligand bands due to thioamide I, thioamide II and $\nu(\text{N-N})$ undergo a positive shift of (16 - 40 cm^{-1}), (59 cm^{-1}) and (23 - 43 cm^{-1}) respectively. The magnitude of the positive shift supports that enolic oxygen, thiolato sulfur and both hydrazinic nitrogens are involved in coordination and $[\text{H}_4\text{pClMaTS}]$ behaves as tetranegatively charged hexadentate species in complexes $[\text{Co}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$, $[\text{Cu}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$, $[\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6]$ and $[\text{Sn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}$. IR spectral bands of complexes are appear of bands in the range (743 - 777 cm^{-1}) assigned to groups (C-S) vibrations. This is also confirmed by the appearance of bands in the range of 418 - 428 cm^{-1} , this has been assigned to the $\nu(\text{M-N})$ [27,28]. And the appearance of bands in the range of 490 - 501 cm^{-1} , this has been assigned to the $\nu(\text{M-O})$. It is due to the increase in the band strength, which again confirms the coordination via the azomethine nitrogen. The band appearing at ca. 814 cm^{-1} $\nu(\text{C}=\text{S})$ and at 1657 cm^{-1} $\nu(\text{C}=\text{O})$ in the IR spectral of ligand is shifted towards lower wave number. It indicates that thione sulphur and also the enolic oxygen coordinates to the metal ion [27]. Thus the ligand behaves as tridentate in bath saide chelating agent coordinating through azomethine nitrogen, thiolate sulphur and enolic oxygen. IR spectral of ligand and its metal complexes are shown in the **Figure 2**.

3.3. Raman Spectra

Important Raman spectral data of the ligands and its metal complexes are summarized in **Table 3**. The Raman spectrum of $[\text{H}_4\text{pClMaTS}]$ shows bands at 3201 cm^{-1} for

Table 1. Analytical Results for the Prepared Complexes of 1,1-malonayl-bis(4-p-chlorophenyl thiosemicarbazide) and their metal complexes.

Compound Empirical formula	Formula weight	Colour	m.p. (°C)	% Found (Calc.)			Am μ s
				C	H	N	
(H ₄ pClMaTS), I C ₁₇ H ₁₆ Cl ₂ N ₆ O ₂ S ₂	471.38	White	200	43.18 (43.32)	3.08 (3.42)	17.6 (17.83)	20
[Co ₂ (pClMaTS)(H ₂ O) ₆]·2(H ₂ O), Ia C ₁₇ H ₂₈ Cl ₂ Co ₂ N ₆ O ₁₀ S ₂	729.3	Dark Brown	220	27.7 (28)	4.25 (3.87)	11.35 (11.52)	37
[Cu ₂ (pClMaTS)(H ₂ O) ₆], Ib C ₁₇ H ₂₄ Cl ₂ Cu ₂ N ₆ O ₈ S ₂	702.54	Dark brown	210	29.86 (29.06)	3.39 (3.44)	11.5 (11.96)	35
[Zn ₂ (pClMaTS)(H ₂ O) ₆], Ic C ₁₇ H ₂₄ Cl ₂ Zn ₂ N ₆ O ₈ S ₂	706.3	Yellowish White	213	29.07 (28.91)	3.30 (3.43)	11.40 (11.9)	38
[Sn ₂ (pClMaTS)(H ₂ O) ₆]·2(H ₂ O), Id C ₁₇ H ₂₈ Cl ₂ Sn ₂ N ₆ O ₁₀ S ₂	848.9	Page	243	24.01 (24.05)	3.22 (3.32)	9.34 (9.9)	36

Table 2. Significant IR spectral bands (cm⁻¹) of the ligand of 1,1-malonayl-bis(4-p-chlorophenyl thiosemicarbazide) and its metal complexes.

Assignments	The compound				
	I	Ia	Ib	Ic	Id
ν (OH)	-	3407	3435	3429	3429
ν (N ⁴ H)	3310	3237	3238	3305	3305
ν (N ² H)	3196	3179	3180	3194	3197
ν (NH)	3111	3109	3111	3105	3111
CH-arom.	3005	3034	3053	3005	3007
CH-aliph.	2940	2980	2934	2938	2940
ν (C=O)/ ν (NCO)	1657	1595	1599	1591	1599
Thioamide I [β (NH)+ ν (CN)]	1400	1420	1431	1416	1440
Thioamide II [ν (CN)+ β (NH)]	1341	1400	1400	1400	1400
δ (OH)	-	1306	1310	1310	1308
ν (C-O)	-	1290	1219	1273	1246
ν (N-N)	902	935	945	924	925
ν (C=S)/ ν (C-S)	814	743	772	777	777
ν (M-O)	-	493	501	490	490
ν (M-N)	-	421	428	418	421

Table 3. Significant Raman spectral bands (cm⁻¹) of the ligand of 1,1-malonayl-bis(4-p-chlorophenyl thiosemicarbazide) and its metal complexes.

Assignments	The compound	
	I	Ic
ν (NH)	3201	3209
CH-arom.	3063	3062
CH-aliph.	2934	2933
ν (C=O)/ ν (NCO)	1635	1593
Thioamide I [β (NH)+ ν (CN)]	1405	1444
Thioamide II [ν (CN)+ β (NH)]	1355	1395
δ (OH)	-	1315
ν (N-N)	1088	1090
ν (C=S)/ ν (C-S)	824	779

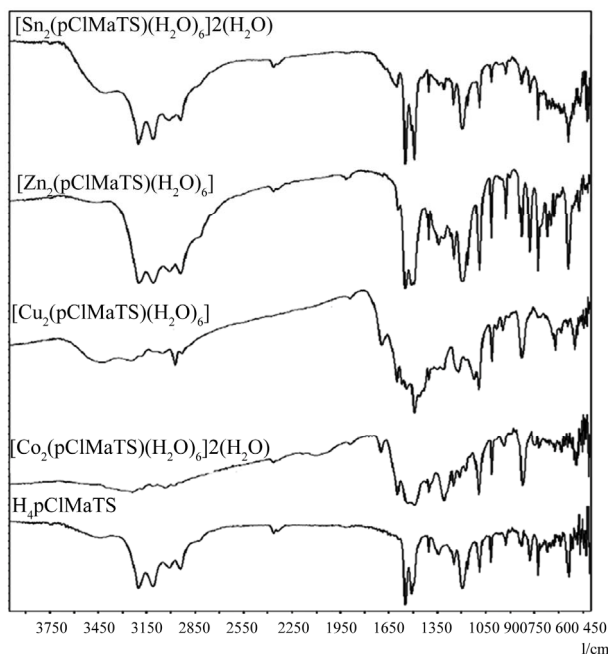


Figure 2. IR spectral of 1,1-Malonayl-bis(4-p-chloro phenyl-thiosemicarbazide) and its metal complexes.

the NH groups present in the ligand. The bands occurring at 1635, 1405, 1355, 1088 and 824 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$, thioamide I [$\beta(\text{NH}) + \nu(\text{CN})$], thioamide II [$\nu(\text{CN}) + \beta(\text{NH})$], $\nu(\text{N}-\text{N})$ and $\nu(\text{C}=\text{S})$, respectively [29]. An exhaustive comparison of the Raman spectra of the ligand and complexes gave information about the mode of bonding of the ligand in metal complexes. The Raman spectrum of complexes [$\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6$] when compared with [$\text{H}_4\text{pClMaTS}$], indicates that bands due to $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{S})$ are absent, but new bands appear at ca. 1593 and 779 cm^{-1} due to $\nu(\text{N}=\text{C})$ and $\nu(\text{C}-\text{S})$, 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). Furthermore, the ligand bands due to thioamide I, thioamide II and $\nu(\text{N}-\text{N})$ undergo a positive shift of (39 cm^{-1}), (40 cm^{-1}) and (2 cm^{-1}) respectively. The magnitude of the positive shift supports that enolic oxygen, thiolato sulfur and both hydrazinic nitrogens are involved in coordination and [$\text{H}_4\text{pClMaTS}$] behaves as tetranegatively charged hexadentate species in complexes [$\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6$]. Raman spectral bands of complexes appear of bands at (779 cm^{-1}) assigned to groups (C-S) vibrations. It indicates that thione sulphur and also the enolic oxygen coordinates to the metal ion [30]. Thus, it may be concluded that the ligand behaves as hexadentate chelating agent coordinating through azomethine nitrogen and thiolate sulphur.

3.4. Electronic Spectra

The electronic spectra of both 1,1-malonayl-bis(4-p-chlorophenyl thiosemicarbazide) ligand and its complexes were performed in DMSO and the spectral data are listed in **Table 4**. There are two main absorption bands in the spectra of the free ligand and their complexes; the first band is exhibited at the range 284 - 308 nm and assigned to $\pi-\pi^*$ [31], and the second appeared at the range 330 - 358 nm due to $n-\pi^*$ intraligand transitions [32]. These absorptions also present in the spectra of the Co(II), Cu(II), Zn(II) and Sn(II) and [$\text{H}_4\text{pClMaTS}$] 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 **Figure 3**.

3.5. Magnetic Susceptibility

Co(II) has the electronic configuration $3d^7$ and should exhibit a magnetic moment higher than that expected for two unpaired electrons in octahedral (1 - 1.13 BM). The magnetic moment observed for the Co(II) complexes lies in the value of 1.3 BM which is consistent with the octahedral stereochemistry of the complexes. Room-temperature magnetic moment of the Cu(II) complexes lies in the range of 1 BM, corresponding to one unpaired electron. whatsoever the geometry of Cu(II) is, its complexes always show magnetic moment corresponding to one unpaired electron.

3.6. $^1\text{H-NMR}$ Spectra

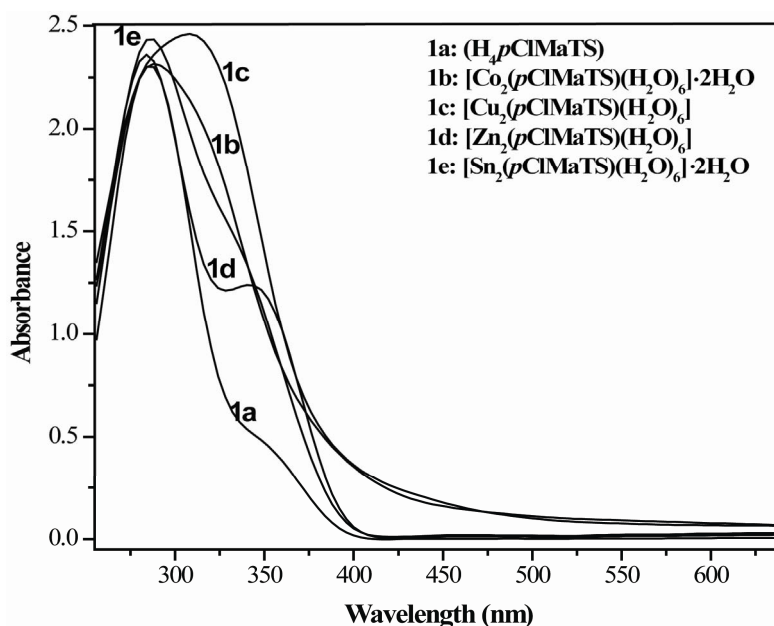
Thus, the $^1\text{H-NMR}$ spectra of the [$\text{Zn}_2(\text{pClMaTS})(\text{H}_2\text{O})_6$] complex on comparing with those of spectrum of the free 1,1-malonayl-bis(4-p-chlorophenylthiosemicarbazide) ligand (L) indicate that L ligand act as hexadentate ligand through the nitrogen atom of C=N azomethine group, oxygen atom of C=O carbonyl group and sulfur atom of C=S group. $^1\text{H-NMR}$ spectra of zinc(II) complex was carried out in DMSO- d_6 as a solvent, the data obtained are in agreement with the suggested coordination through the C=N and C=S groups by presence of the signals of NH, the complexes formed due to loss four protons (two from 2NH amine groups and two protons from 2NH amide groups).

($\text{H}_4\text{pClO} \times \text{TS}$) $^1\text{H-NMR}$ δ (ppm): 9.75(6,18NH amide group), 1.95(7,19NH amine group), 3.35(CH_2) 6.6 - 7.75 (CH-aromatic)

[$\text{Zn}_2(\text{pClO} \times \text{TS})(\text{ac})_2$] $2(\text{H}_2\text{O})$ $^1\text{H-NMR}$ δ (ppm): 1.15 (H_2O), (NH amide groups disappeared), (NH amine groups disappeared), 3.35(CH_2), 5.2(10,22CNH aromatic), 6.6 - 7.75(CH-aromatic shifted).

Table 4. The electronic spectral data of 1,1-malonayl-bis(4-p-chlorophenylthiosemicarbazide) and its metal complexes.

Compound	λ_{\max} nm (cm^{-1})				
	$\pi-\pi^*$ C=S	$n-\pi^*$ C=S	CT-transition		
H ₄ pClMaTS	287 (34840)	344 (29070)			
[Co ₂ (pClMaTS)(H ₂ O) ₆]·2(H ₂ O)	288 (34720)	342 (29240)	462 (21650)	485 (20620)	522 (19160)
[Cu ₂ (pClMaTS)(H ₂ O) ₆]	308 (32470)	358 (27930)	466 (21460)	493 (20280)	524 (19080)
[Zn ₂ (pClMaTS)(H ₂ O) ₆]	284 (35210)	344 (29070)			
[Sn ₂ (pClMaTS)(H ₂ O) ₆]·2(H ₂ O)	288 (34720)	330 (30300)			

**Figure 3.** The electronic spectral of 1,1-malonayl-bis(4-p-chloro phenylthiosemicarbazide) and its metal complexes.

3.7. Mass Spectrum

The electronic impact mass spectrum of the complex [Cu₂(pClMaTS)(H₂O)₆] {1,1-malonayl-bis(4-p-chlorophenylthiosemicarbazide) copper trihydrate} is fragment to half molecule species at $m/z = 304$ amu corresponding to species {4-methylene-p-chlorophenylthiosemicarbazide copper} [C₉H₇ClN₃OSCu], which confirms the proposed formula. It also shows series of peaks at 36, 50, 75, 90, 111, 138, 152, 184, 229, 263, and 300 amu corresponding to various fragments. The electronic impact mass spectrum of the [Sn₂(pClMaTS)(H₂O)₆]·2(H₂O) complex shows fragment molecular ion (M^+) peak at $m/z = 421$ amu corresponding to species [C₁₀H₉ClN₃O₄SSn], which confirms the proposed formula. It also shows series of peaks at 75, 111, 127, 169, 218, 302 and 336 amu corresponding to various fragments. The intensities of these peaks give the idea of the stabilities of the fragments.

3.8. Thermogravimetric Analysis

Thermogravimetric analysis curves (TGA and DTG)

of the 1,1-malonayl-bis-(4-p-chlorophenyl thiosemicarbazide) ligand and its complexes are shown in **Figure 4** and all the data are summarized in **Table 5**. 1,1-Malonayl-bis-(4-p-chlorophenylthiosemicarbazide) ligand was thermally decomposed in mainly decomposition steps within the temperature range successive decomposition steps within the temperature range 25°C - 700°C. The first decomposition step (obs. = 39.14%, calc. = 39%) within the temperature range 25°C - 245°C, may be attributed to the liberation of the 2(HNCO), 2H₂S and 2(NH) fragments. The second decomposition steps found within the temperature range 245°C - 345°C (obs. = 32.8%, calc. = 32.5%), which is reasonably accounted by the removal of 2(HCN), (C₂H₂) and Cl₂. The decomposition of the ligand molecule ended with a final (C₁₇H₂) residue (obs. = 28%, calc = 28.3%).

The complex [Co₂(pClMaTS)(H₂O)₆]2(H₂O) was thermally decomposed in five successive decomposition steps within the temperature range 25°C - 1000°C. The first decomposition step (obs. = 5.2%, calc. = 4.94%) within the temperature range 25°C - 188°C, may be attri-

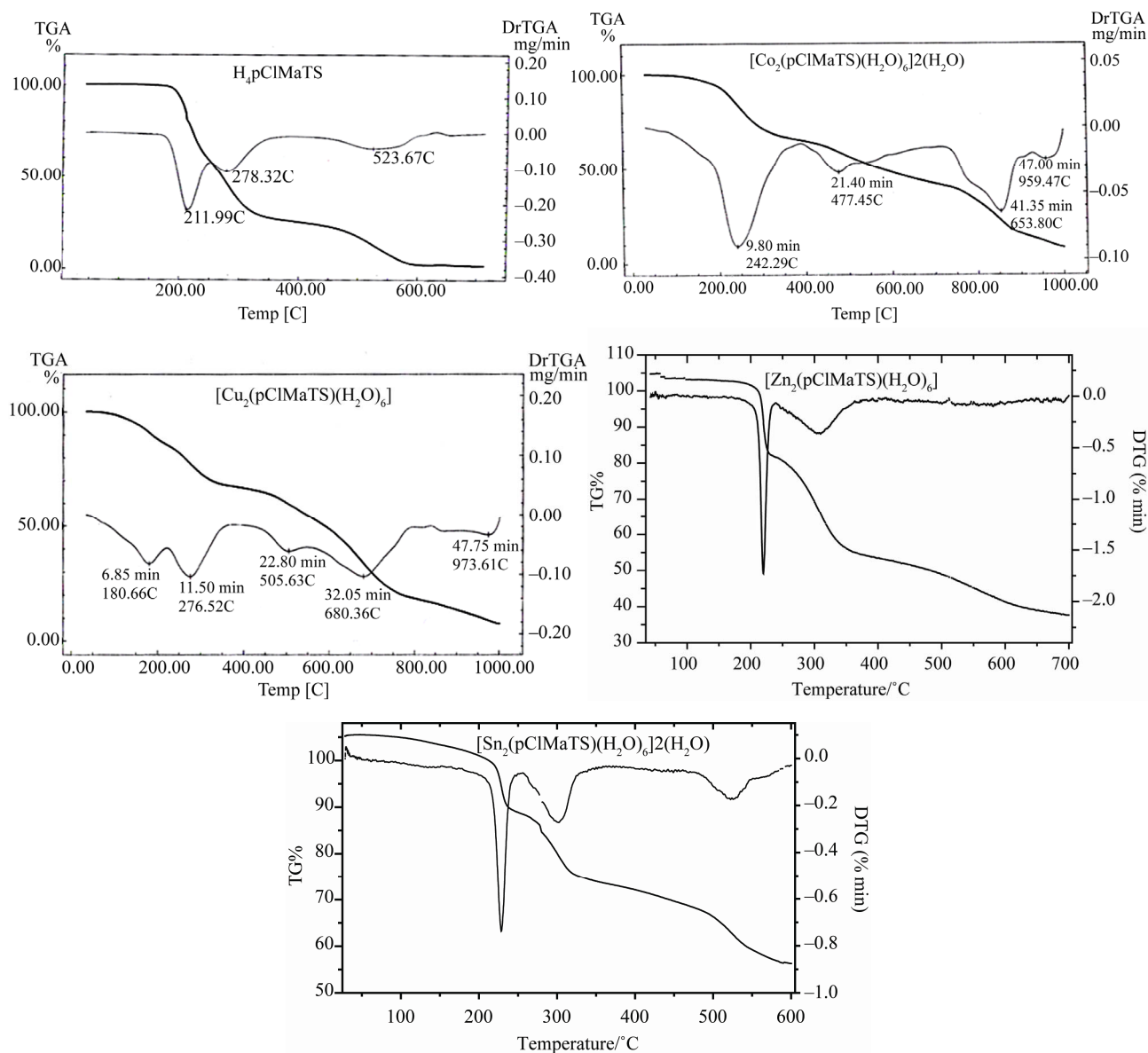


Figure 4. TGA and DrTGA diagram of 1,1-malonoyl-bis(4-p-chlorophenylthiosemicarbazide) and its metal complexes.

buted to the liberation of the two water molecules. The second decomposition steps found within the temperature range 188°C - 448°C (obs. = 33.1%, calc. = 33.5%), which is reasonably accounted by the removal of 6 water molecules $2N_2$, $2(HCN)$, and C_2H_2 fragments. The decomposition third step found within the temperature 448°C - 760°C (obs. = 23.4%, calc = 22.9%) which is reasonably accounted for by the removal of S_2 , Cl_2 and O_2 molecules. The decomposition fourth step found within the temperature 760°C - 885°C (obs. = 21.8%, calc = 22.5%) which is reasonably accounted for by the removal of CH_4 and $C_{12}H_4$ fragments. The rest of the ligand molecule was removed and fifth the decomposition of the Co(II) complex molecule ended with a final

Co₂ molecule is cobalt residue (obs. = 17.3%, calc = 16.5%).

The TG curve of $[Cu_2(pClMaTS)(H_2O)_6]$ 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 6 water molecules (obs. = 16.4%, calc = 15.4%) within the temperature range 25°C - 245°C. The third decomposition step occurs in the range 245°C - 475°C and corresponds to the loss of N_2 , $2(HCN)$, N_2H_2 , and O_2 (obs. = 20.6%, calc = 20.5%). The decomposition fourth step found within the temperature 475°C - 765°C (obs. = 42.4%, calc = 42.5%) which is reasonably accounted for by the removal of ($C_{13}H_8$, S_2 and Cl_2) fragments. The fifth decomposition

Table 5. The thermal data of 1,1-Malonayl-bis(4-p-chlorophenyl thiosemicarbazide) and their metal complexes.

Compound	Steps	Temperature range (°C)	TG weight loss (%)		Assignments	T _{max} °C
			Calc.	Found		
I	1	25 - 245	39	39.1	2(HNCO), 2H ₂ S and 2(NH) fragments	212
	2	245 - 345	32.5	32.8	2(HCN), (C ₂ H ₂) and Cl ₂	278
	3	More than 345	26.8	27.5	(C ₁₇ H ₂) residual	524
Ia	1	25 - 188	4.94	5.2	2water	
	2	188 - 448	33.5	33.1	6water molecules, 2N ₂ , 2(HCN), and C ₂ H ₂ fragments	242
	3	448 - 760	22.9	23.4	S ₂ , Cl ₂ and O ₂ molecules	477
	4	760 - 885	22.5	21.8	CH ₄ and C ₁₂ H ₄ fragments	854
	5	More than 885	16.5	17.3	CO ₂ molecule is cobalt residue	959
Ib	1,2	25 - 245	15.4	16.4	6water	181
	3	245 - 475	20.5	20.6	N ₂ , 2(HCN), N ₂ H ₂ , and O ₂	277
	4	475 - 765	42.5	42.4	C ₁₃ H ₈ , S ₂ and Cl ₂ fragments	506
	5	More than 765	21.5	20.6	C ₂ and Cu ₂ metal residual	680
Ic	1	25 - 224	15.3	15.5	6water molecules	974
	2	224 - 338	26.9	26.5	2N ₂ , S ₂ , 1/2O ₂ and 2(HCN) fragment	219
	3	338 - 643	18.2	18.6	1/2O ₂ , Cl ₂ , CH ₄ and C ₂ H ₂ molecules	309
	4	More than 643	39.5	39.4	residue metal of Zn ₂ and C ₁₂ H ₄ fragment	
Id	1, 2	25 - 321.7	25.2	24.7	8 water and HNCO and HCN molecules	
	3	321.7 - 505.6	8.8	9.3	1/2S ₂ and HNCO	229
	4	505.6 - 589	9.1	9.56	NH ₃ , N ₂ and 1/2S ₂ molecules	301
	5	More than 589	56.8	56.44	Cl ₂ , C ₁₄ H ₆ and Sn ₂ the residual metal	518

steps are final decomposition organic ligand to the C₂ and Cu₂ metal residual. (obs. = 20.6%, calc = 21.5%).

The complex [Zn₂(pClMaTS)(H₂O)₆] was thermally decomposed in mainly four decomposition steps within the temperature range 25°C - 700°C. The first decomposition step (obs. = 15.5%, calc = 15.3%) within the temperature range 25°C - 224°C, may be attributed to the liberation of 6water molecules. The decomposition second step found within the temperature 224°C - 338°C (obs. = 26.5%, calc = 26.9%) which is reasonably accounted for by the removal of 2N₂, S₂, 1/2O₂ and 2(HCN) fragment. The decomposition third step found within the temperature 338°C - 643°C (obs. = 18.6%, calc = 18.2%) which is reasonably accounted for by the removal of 1/2O₂, Cl₂, CH₄ and C₂H₂ molecules. The rest of the ligand molecule was removed and fourth the decomposition of the ligand molecule ended with a final residue metal of Zn₂ and C₁₂H₄ fragment (obs. = 39.4%, calc = 39.5%).

[Sn₂(pClMaTS) (H₂O)₆]:2(H₂O) the complex 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 step, the mass loss at 321.7°C corresponds to the loss of 8 water and

HNCO and HCN molecules (obs. = 24.7%, calc = 25.2%). Continuous mass loss in the TG curve from 321.7°C to 503.6°C corresponds to the loss of 1/2S₂ and HNCO molecules (obs. = 9.3%, calc = 8.8%). The rest of organic moiety NH₃, N₂ and 1/2S₂ molecules was removed on the fourth step within the temperature range 503.6°C - 589°C (obs. = 9.56%, calc = 9.1%). The final decomposition of the Cl₂, C₁₄H₆ and Sn₂ the residual metal (obs. = 56.44%, calc = 56.8%).

3.9. Kinetic Studies

The thermodynamic activation parameters of decomposition processes of hydrated Co(II), Cu(II), Zn(II) and Sn(II) complexes, namely activation energy (E*), enthalpy (ΔH*), entropy (ΔS*), and Gibbs free energy change of the decomposition (ΔG*), were evaluated graphically (**Figure 5**) by employing the Coats-Redfern and Horowitz-Metzger relations.

$$\Delta H^* = E^* - RT$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

The data are summarized in **Table 6**. The activation energies of decomposition were in the range 56.9 - 461 kJ·mol⁻¹. The high values of the activation energy illus-

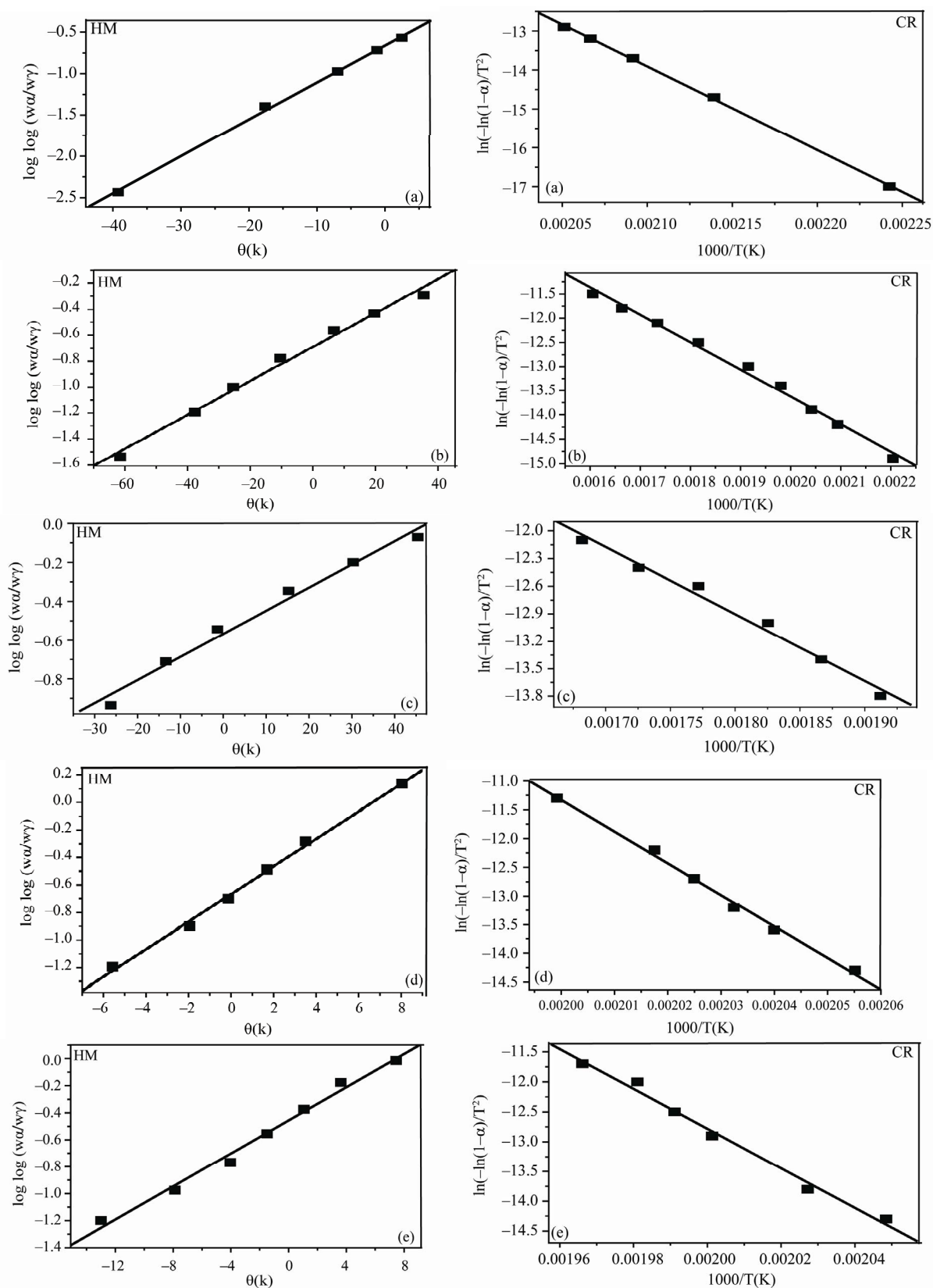
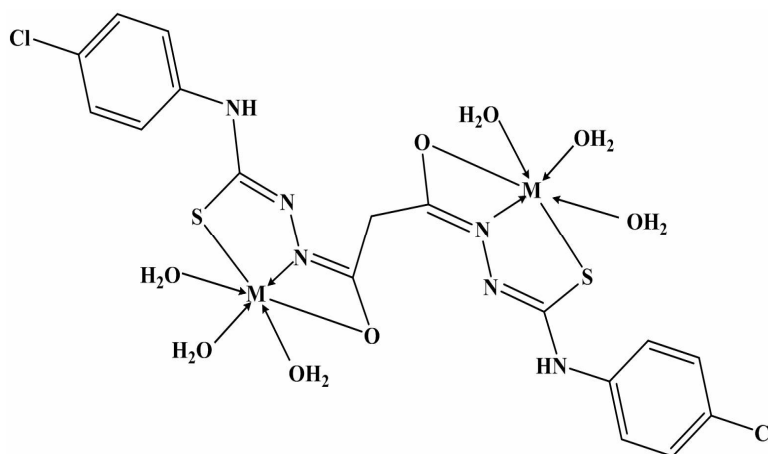


Figure 5. Kinetic data curves of: (a) 1,1-Malonayl-bis(4-p-chlorophenyl thiosemicarbazide)(H₄pClMaTS), (b) Co(II), (c) Cu(II), (d) Zn(II) and (e) Sn(II) complexes.

Table 6. Kinetic parameters using the Coats-Redfern (CR) and Horowitz-Metzger (HM) operated for 1,1-malonayl-bis(4-p-Chlorophenylthiosemicarbazide) ($H_4pClMaTS$) and its Co(II), Cu(II), Zn(II) and Sn(II) complexes.

Compound	Stage	Method	Parameter					R
			E ($J \cdot mol^{-1}$)	A (s^{-1})	ΔS ($J \cdot mol^{-1} \cdot K^{-1}$)	ΔH ($J \cdot mol^{-1}$)	ΔG ($J \cdot mol^{-1}$)	
I	1 st	CR	1.79×10^5	1.94×10^{17}	8.20×10^1	1.75×10^5	1.35×10^5	0.9997
		HM	1.54×10^5	7.15×10^{14}	3.54×10^1	1.50×10^5	1.33×10^5	0.9992
		Average	1.66×10^5	9.74×10^{16}	5.87×10^1	1.62×10^5	1.34×10^5	0.9995
Ia	1 st	CR	4.70×10^4	1.40×10^2	-2.08×10^2	4.27×10^4	1.50×10^5	0.9963
		HM	6.65×10^4	4.13×10^4	-1.61×10^2	6.22×10^4	1.45×10^5	0.9956
		Average	5.67×10^4	2.07×10^4	-1.85×10^2	5.25×10^4	1.48×10^5	0.9960
Ib	1 st	CR	6.07×10^4	2.32×10^3	-1.86×10^2	5.61×10^4	1.58×10^5	0.9931
		HM	6.87×10^4	2.35×10^4	-1.66×10^2	6.42×10^4	1.55×10^5	0.9918
		Average	6.47×10^4	1.29×10^4	-1.76×10^2	6.02×10^4	1.57×10^5	0.9925
Ic	1 st	CR	4.58×10^4	1.17×10^{47}	6.52×10^2	4.54×10^5	1.33×10^5	0.9977
		HM	4.65×10^5	1.20×10^{48}	6.70×10^2	4.61×10^5	1.30×10^5	0.9982
		Average	4.61×10^5	6.57×10^{47}	6.62×10^2	4.57×10^5	1.32×10^5	0.9980
Id	1 st	CR	2.76×10^4	1.68×10^{27}	2.72×10^2	2.72×10^5	1.36×10^5	0.9950
		HM	2.95×10^5	1.77×10^{29}	3.11×10^2	2.90×10^5	1.35×10^5	0.9945
		Average	2.85×10^5	8.94×10^{28}	2.91×10^2	2.81×10^5	1.35×10^5	0.9948

**Figure 6.** The suggested Octahedral structure of 1,1-malonayl-bis (4-p-chlorophenylthiosemicarbazide) Metal trihydrate Complex. M = Co(II), Cu(II), Zn(II) and Sn(II).

trated to the thermal stability of the complexes. 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 All

1,1-Malonayl-bis(4-p-Chlorophenyl) thiosemicarbazide and its 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 ($H_4pClMaTS$). Hence, the E value in the first stage for the Zn^{+2} complex is higher than that for the other Sn^{+2} , Cu^{+2} and Co^{+2} complex. The correlation coefficients of the Arrhenius plots of the thermal decomposition steps were found to lie in the range 0.9925 to 0.9995 showing a good fit with linear function. It is clear that the thermal decomposition process of all ($H_4pClMaTS$) complexes is non-spontaneous, *i.e.*, the

complexes are thermally stable.

4. CONCLUSIONS

We can concluded from the above discussions on the (H₄pClMaTS) ligand and its Co(II), Cu(II), Zn(II) and Sn(II) complexes using the elemental analysis, molar conductivity, IR, Raman, UV, ¹HNMR, mass spectra and magnetic properties, as well as TG/DTG, that. Thus the ligand behaves as tridentate in bath saide chelating agent coordinating through azomethine nitrogen, thiolate sulphur and enolic oxygen as shown in **Figure 6**.

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