



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 bithiosemicarbazide ligands and their metal complexes. The kinetic thermodynamic parameters such as: E^* , ΔH^* , ΔS^* and ΔG^* are calculated using Horowitz–Metzger (HM) and Coats–Redfern (CR) equations. The kinetic thermodynamic parameters such as: E^* , ΔH^* , ΔS^* and ΔG^* are calculated from the DTG curves. The tested compounds show a reasonable activity 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 $MgSO_4$ before use. The metals (Alfa Inorganics) used, Co, Cu, Zn, Sn and Au 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. HNO_3 for several minutes

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and then washing with distilled water. Tetraethylammonium perchlorate, Et_4NClO_4 , (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_f , 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) ($H_4pClOxTS$)

1,1-Oxalyl-bis(4-p-chlorophenylthiosemicarbazide) was prepared by adding 4-chloro-phenylisothiocyanate (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 Et₂O 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-p-chlorophenylthiosemicarbazide) metal complexes

The ligand $H_4pClOxTS$ (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_4NClO_4 . 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 $[\text{Co}_2(pClOxTS)(ac)_2(H_2O)_4] \cdot 3H_2O$. 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 ¹H 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⁻¹ at National Research Center, Cairo, Egypt. The ¹H NMR spectra were recorded on an Varian Mercury VX-300 NMR spectrometer. ¹H NMR spectra were run at 300 MHz and ¹³C NMR spectra were run at 75.46 MHz in deuterated dimethyl sulphoxide (DMSO-d₆). Chemical shifts are quoted in δ 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 nano-central 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 1.0×10^{-3} mol L⁻¹ 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 1.0×10^{-3} mol/dm⁻³ 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 Shimadzu 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

Analytical results for the prepared complexes of oxalyl, malonyl and succinyl-bis(4-p-chlorophenylthiosemicarbazide) and its metal complexes.

Compounds empirical formula	Formula weight	Color	M.p. (°C)	% Found (calc.)			Am μ s
				C	H	N	
$H_4pClOxTS$, (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
$[\text{Co}_2(pClOxTS)(ac)_2(H_2O)_4] \cdot 3(H_2O)$, (Ia) $C_{22}H_{36}Cl_2Co_2N_6O_{11}S_2$	813.5	Dark Green	>300	32.12 (32.48)	3.97 (4.46)	9.89 (10.33)	38
$[\text{Cu}_2(pClOxTS)(H_2O)_6] \cdot 6(H_2O)$, (Ib) $C_{16}H_{24}Cl_2Cu_2N_6O_{14}S_2$	796.6	Brown	>300	24.1 (24.12)	4.03 (4.3)	10.32 (10.55)	40
$[\text{Zn}_2(pClOxTS)(ac)_2] \cdot 2(H_2O)$, (Ic) $C_{22}H_{26}Cl_2Zn_2N_6O_6S_2$	736.3	Faint Yellow	218	35.55 (35.89)	3.21 (3.56)	11.88 (11.41)	30
$[\text{Sn}_2(pClOxTS)(H_2O)_2]$, (IId) $C_{16}H_{14}Cl_2Sn_2N_6O_4S_2$	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
$[\text{Co}_2(pClMaTS)(H_2O)_6] \cdot 2(H_2O)$, (IIa) $C_{17}H_{28}Cl_2Co_2N_6O_{10}S_2$	729.3	Dark Brown	220	27.7 (28)	4.25 (3.87)	11.35 (11.52)	37
$[\text{Cu}_2(pClMaTS)(H_2O)_6]$, (IIb) $C_{17}H_{24}Cl_2Cu_2N_6O_8S_2$	702.54	Dark Brown	210	29.86 (29.06)	3.39 (3.44)	11.5 (11.96)	35
$[\text{Zn}_2(pClMaTS)(H_2O)_6]$, (IIc) $C_{17}H_{24}Cl_2Zn_2N_6O_8S_2$	706.3	Yellowish White	213	29.07 (28.91)	3.30 (3.43)	11.40 (11.9)	38
$[\text{Sn}_2(pClMaTS)(H_2O)_6] \cdot 2(H_2O)$, (IIId) $C_{17}H_{28}Cl_2Sn_2N_6O_{10}S_2$	848.9	Page	243	24.01 (24.05)	3.22 (3.32)	9.34 (9.9)	36
$H_4pClSuTS$, (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
$[\text{Co}_2(pClSuTS)(H_2O)_6]$, (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
$[\text{Cu}_2(pClSuTS)(H_2O)_6]$, (IIIb) $C_{18}H_{24}Cl_2Cu_2N_6O_{14}S_4$	1011.8	Green	>300	21.32 (21.37)	3.34 (3.39)	7.9 (8.31)	35
$[\text{Zn}_2(pClSuTS)(ac)_2] \cdot 2(H_2O)$, (IIIc) $C_{24}H_{30}Cl_2Zn_2N_6O_6S_2$	764.4	Page	235	37.84 (37.71)	3.84 (3.96)	11.04 (10.99)	32
$[\text{Sn}_2(pClSuTS)(H_2O)_6]$, (IIId) $C_{18}H_{26}Cl_2Sn_2N_6O_8S_2$	826.9	Pale Yellow	275	26.11 (26.15)	3.3 (3.17)	9.68 (10.16)	36

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