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Graphical Abstract

Two novel 1,3,4-thiadiazolethiosemicarbazone ligands were synthesized in addition to their Co(II) chelates which have been proved using various analysis tools. The synthesized ligands and their complexes were also investigated as inhibitors for the corrosion of carbon steel in 1.0 M HCl using different techniques. The obtained results revealed that such compounds act as good inhibitors.



Investigation of the inhibition efficiencies of novel synthesized cobalt complexes of 1,3,4-thiadiazolethiosemicarbazone derivatives for the acidic corrosion of carbon steel

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Abstract

Two novel thiosemicarbazone linked with 1,3,4-thiadiazole ligands were synthesized through the condensation reaction of the acetyl group at position 5 of 1,3,4-thiadiazole derivatives with thiosemicarbazide in acidic ethanol solution in addition to their Co(II)complexes. The divalent cobalt complexes of both ligands have been synthesized through the reaction of cobalt acetate with each ligand leading to the formation of the two complexes [(LH)Co(OAc)]0.5H₂O and [(LCl)Co(OAc)(H₂O)₂]; where LH and LCl are 1,3,4-thiadiazolethiosemicarbazone ligands. The two complexes have been proved to have tetrahedral and octahedral geometry from the results of UV-Vis spectra and magnetic moment. Analysis of the IR spectra of both ligands and complexes ascertained that the ligands behaved as monobasic tridentate coordinating to the metal ion center through azomethine-nitrogen atoms and thiadiazole ring in addition to deprotonated SH group. The synthesized ligands and their complexes were also investigated as inhibitors for the corrosion of carbon steel in 1.0 M HCl using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy techniques. The obtained results revealed that the inhibition efficiencies of the tested derivatives were found to depend on the concentrations and structures of such derivatives, and were decreased with raising temperature. At the same inhibitors concentration, the inhibition efficiencies are slightly increased in the order: LH > LCl > LH-Co > LCl-Co. The results derived from all applied techniques are harmonious with each other

Keywords: Thiadiazoles, Cobalt complexes, Corrosion, Inhibition, Carbon steel

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1. Introduction

Corrosion is considered as the most serious problem facing metals and their alloys, which in turn causes various industrial problems, such as deterioration of buildings and machinery, corrosion of boilers in factories and petroleum pipeline in oil refineries and others, causing short life of these facilities and low operational efficiency of them [1]. The application of corrosion inhibitors is the best way to control corrosion of the metal and alloy surfaces due to its facility of implementation and cost-effectiveness [1,2]. For this reason, numerous organic compounds particularly including heteroatoms (N, O, S) in the form of conjugated π -bond, polar groups, and aromatic rings, have been specified as perfect corrosion inhibitors [3-6].

1,3,4-Thiadiazoles have been extensively investigated for their applications in several fields as pharmaceutical, agrochemicals and industrial sectors [7-10]. For instance, methazolamide, acetazolamide and sulfamethazole are marketdrugs having a 1,3,4-thiadiazole nucleus [11]. In addition, they have found to be good oxidation inhibitors [12] and metal complexing agents [13] where 1,3,4-thiadiazoles and thiosemicarbazones play important roles in the synthesis of valuable metal-complexes [14-16] due to the presence of two nitrogen and sulfur donor atoms. A literature survey [17, 18] and through our previous research work [19, 20] showed that thiosemicarbazones have many biological applications and are also used as anticorrosion of mild steel and many minerals in the acidic medium. Furthermore, Bouraiou and coworkers have recently proved that cobalt complexes exhibited corrosion inhibition ability for steel in acidic medium [21].

Carbon steel is the most widely used steel alloy used in various industries including petroleum, automotive, channels, plates, cold-rolled sheets and power generation [22]. Due to its broad applications in industrial sectors, it predominantly exists immersed with acidic medium, mainly HCl which is exceedingly utilized for acid pressing for elimination of oxide level from it before undergoing next processing, decaling, and acidization of oil wells [22]. Carbon steel is extremely oversensitive towards corrosion in acidic media.

Motivation from all the above activities and extending our experience in the preparation of effective complexes [23-29], we interested herein to synthesize two 1,3,4-

thiadiazolethiosemicarbazone ligands and their divalent cobalt complexes. Further, these compounds were tested for their corrosion inhibition performance on the acidic corrosion of carbon steel in 1.0 M HCl solution with implementation of various techniques as weight loss (WL), potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM).

2. Experimental

2.1. Materials and Methods

All used reagents in this study were of very pure and obtained from BDH, Aldrich or Sigma. The utilized solvents for recording all spectral investigations in this text were bought with high purity from Aldrich. The elemental microanalyses [C, H, N] of the synthesized derivatives were carried out at Cairo University, in the microanalytical center on Perkin-Elmer 2400 CHN Elemental analyzer. The Infrared (IR) spectra were performed on a 1430-Perkin-Elmer infrared-spectrophotometer ranging from 4000 to 200 cm⁻¹ as sample-KBr discs. The NMR spectra were carried out in dimethyl sulfoxide (DMSO- d_6) on ¹H-NMR (Varian operating at 400 MHz) and ¹³CNMR (Varian operating at 100 MHz). A Shimadzu UV-Vis 240 spectrophotometer was used to record the electronic absorption spectra. The solid complexes magnetic susceptibility was recorded at ordinary temperature by using magnetic susceptibility instrument via the Gouy's technique. TGA (thermogravimetric analysis) of the two prepared solid complexes were recorded on the TG-50-Schimadzu thermogravimetric analyzer under 10°C /min heating rate/nitrogen atmosphere with temperature ranging from 25 to 800 °C. The electrochemical corrosion measurements, potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS), were conveyed out using a thermostated PGSTAT30 potentiostat/galvanostat using a three-electrode electrochemical cell with carbon steel as the working electrode (WE), saturated calomel electrode (SCE) as the reference electrode (RE) and the platinum counter electrode (CE). The morphology of carbon steel surface before and after addition of the synthesized compound was investigated using scanning electron microscopy (SEM) using JEOL Scanning Electron Microscope (SEM) model T-200. A carbon steel rod which was the working electrode (its composition, wt. %: C = 0.11%, Si = 0.25%, S = 0.05%, P = 0.04%, Mn = 0.45%and the remainder is iron) and was contemporized before each experiment as reported earlier [2,3], then it was placed immediately into 1.0 M HCl (corrosive medium, blank) and/or the desired inhibitor concentration at open circuit potential (OCP) until a steady

state was reached. The 1.0 M HCl solution was prepared by diluting the analytical reagent (37% HCl, AR grade) with double-distilled water.

2.2. Synthesis of 5-acetyl-3-aryl-2-imino-1,3,4-thiadiazole (3a and 3b)

Thiadiazole derivatives **3a** and **3b** have been prepared as previously described [30] as follows: A solution of 0.01 mole = 1g of potassium thiocyanate **2** in 10 mL water has been added, while stirring, to suspensions of hydrazonoyl chloride derivatives **1** (0.005 mol) in ethanol (50 mL). The mixture has been then stirred for 5 hours at room temperature, during which dissolution took place and new solids have been formed. The latter have been collected, washed was water, and methanol was used to recrystallized to give products **3a** and **3b**.

2.2.1. 5-Acetyl-3-phenyl-2-imino-1,3,4-thiadiazole (3a)

Yellow solid, (0.19 g, 90 %), mp, 70-72 ⁰C (EtOH), (Lit. mp. 74- 76 °C) [30].

2.2.2. 5-Acetyl-3-(4-chlorophenyl)-2-imino-1,3,4-thiadiazole (3b)

Yellow solid, (0.2 g, 80 %), mp. 126-128 °C (EtOH), (Lit. mp 127 °C) [30].

2.3. Synthesis of compounds 5a and 5b (LH and LCl ligands)

A mixture of 0.01 mole of 5-acetyl-3-aryl-2-imino-1,3,4-thiadiazolederivatives (**3a** or **3b**), 0.01mole of thiosemicarbazide and a few drops of conc. HCl in ethanol (30 mL) have been refluxed for 5 h. The solid products, which formed after cooling, have been collected and recrystallized from ethanol/dioxane to give the thiosemicarbazone derivatives **LH** and **LCl** (Scheme 1).

¹H NMR of **LH** (DMSO-d₆) δ 2.30 (s) (CH₃, 3H,), 7.62-8.14 (m) (Ar-H and NH, 6H), 8.15 (s) (NH, 1H), 8.40 (s) (NH, 1H), 10.40 (s) (NH, 1H).

¹H NMR of **LCI** (CDCl₃) δ 2.34 (s) (CH₃, 3H), 6.40 (s) (NH, 1H) 7.10 (d) (Ar-H, *J* = 9Hz, 2H), 7.30 (d) (Ar-H, *J* = 9Hz, 2H,), 7.33 (s) (NH, 1H), 8.33 (s) (NH, 1H), 8.79 (s) (NH, 1H); ¹³C NMR of **LCI** (DMSO-d₆) δ 21 (CH₃), 127, 130, 131, 134, 137, 140, 145, 172 (C=S).



Scheme 1. Synthetic pathway of ligands, LH (5a) and LCl (5b)

2.4. Synthesis of cobalt complexes (LH-Co and LCl-Co)

The two metal complexes **LH-Co** and **LCI-Co** have been synthesized by slow adding of a 0.001 mol of cobalt acetate tetrahydrate (0.249 g of $Co(CH_3COO)_2.4H_2O$) dissolved in hot methanol to hot methanolic solution containing 0.292 g or 0.326 g of ligand **LH** or **LCI**, respectively (0.001mol and 20 ml). The formed mixtures have been subjected to heat with reflux for 2 h at 65 °C during which colored products were separated out. Using vacuum filtration to separate the colored precipitates from the hot solutions, then methanol & ether were used to wash the precipitate and finally dried under vacuum.

3. Results and discussions

3.1. Stoichiometry and nature of the complexes

Molecular formulae of the synthesized ligands and their metal complexes along with their empirical formulae, molecular weights, colors, melting points, molar conductance values and analytical results are depicted in Table 1. Analysis of the synthesized organic ligands (LH &LCl) and their divalent cobalt complexes (LH-Co and LCl-Co) by means of elemental analysis tool showed that the structures of the synthesized compounds are in good agreement with the predicted molecular formulae represented in Table 1. The results supported the formation of the cobalt chelates in the molar ratio 1:1 (M:L).

Measurement of the molar conductance from 10^{-3} M solution of the measured complexes in DMF supported their non-electrolytic type ($\Lambda = 14.6 \& -18.2 \ \Omega^{-1} \text{cm}^2 \text{ mol}^{-1}$ for **LH-Co** and **LCI-Co**, respectively) [31,32]. The compounds were found to the highly stable in air. They are easily soluble in most polar organic solvent but not soluble in non polar solvents.

Comp.	Molecular formula	Color	$(\Lambda_{m})^{[a]}$	m. p.	Microanalysis, Calc. (Found) %				
anda	(Empirical formulas)	(Mol Wt)		(yield)					
coue	(Empirical for mulae)				С%	Н%	N%	M% ^[c]	
LH	$C_{11}H_{12}N_6S_2$	Orange		224 ^[b]	45.19	4.14	28.74		
		(292.38)		(89%)	(45.23)	(4.18)	(28.62)		
LH-Co	[(LH)Co(OAc)]0.5H ₂ O	Deep reddish	14.6	>300	37.32	3.61	20.09	14.09	
	$C_{13}H_{15}N_6O_{2.5}S_2Co$	brown		(64 %)	(37.18)	(3.89)	(20.21)	(14.32)	
		(418.36)							
LCl	$C_{11}H_{11}N_6S_2Cl$	Orange		180 ^[b]	40.42	3.39	25.71		
		326.83		(92%)	(40.51)	(3.25)	(25.86)		
LCl-Co	[(LCl)Co(OAc)(H ₂ O) ₂]	Deep reddish	18.2	>300	32.54	3.57	17.51	12.28	
	$C_{13}H_{17}N_6O_4S_2ClCo$	brown (479.83)		(84 %)	(32.47)	(3.48)	(17.49)	(11.87)	

Table 1. Micro-analysis and physical characteristic of the synthesized compounds

^a Molar conductivity of 10^{-3} M DMF solution Ω^{-1} cm² mol⁻. ^b decomposition temperature.

^ccalculated from TG thermograms

3.2. EI-Mass spectroscopy

The mass spectra of the organic ligands LH & LCl and their complexes LH-Co & LCl-Co were interpreted in order to ensure the composition and pureness of such compounds. Figure 1 & 2 illustrate the mass spectra with some characteristic fragments of LH and its cobalt complexes LCl-Co while the mass spectra of LCl and its cobalt complex LCl-Co are interpreted in Figs S1 and S2. Mass spectra of LH, LCl, LH-Co and LCl-Co gives the molecular ion peak at 293, 327, 419 and 480, respectively, corresponding to M⁺+1 for LH and LH-Co and the molecular weight of and LCl and LCl-Co (theoretical molecular weights are 292.39, 326.83, 418.36 and 479.83 for LH, LCl, LH-Co and LCl-Co, respectively) confirming the formation of the compounds as proposed in Table 1 and Scheme 1.



Figure 1. The EI-mass spectra with fragmentation pattern for ligand LH



Figure 2. The EI-mass spectra with fragmentation pattern for complex LH-Co

3.3.¹H and ¹³C NMR spectra

Our target multi-dentate ligands **LH** and **LCI** were prepared *via* condensation reaction in acidic medium from 5-acetyl-1,3,4-thiadiazole derivatives, **3**, and thiosemicarbazide, **4**, as sketched in Scheme 1. The data extracted from ¹H NMR of the two ligands (Fig. 1) proved their structures. ¹H NMR spectra of the two ligands **LH** and **LCI** showed the presence of singlet signal for CH₃ protons at 2.30 and 2.34 ppm, respectievely. Also,

they have four singlet signals at δ 7.62-8.14 (m, 6H, Ar-H and NH), 8.15, 8.40, 10.40 and one in the aromatic region (for **LH**) and at δ 6.40, 7.33, 8.33 and 8.79 ppm (for **LCI**). The apperance of four different NH signals indicated the existance of H-bond between one proton of NH₂ and N=C groups which leds to the nonequevelant two protons of the amino group of thiosemicarbazone moiety [20]. Also, ¹³C NMR of the synthesized ligand **LCI** appeared all the nine characteristic signals for the non-equivalent carbon atoms (Figure 3).



Figure 3. ¹H NMR (a) and ¹³C NMR (b) spectra of ligand LCl

3.4. FT-IR spectra

Identification of the coordination sites in the organic ligand that participate in bond formation with the central ion can easily achieved by accurate comparison of FT-IR spectra of the ligand with that of metal chelates. Coordinated function groups peaks, usually, undergo alteration either in their positions and/or their intensities. Some other peaks disappear after complexation. The most important infrared bands showed by the organic ligands and their cobalt chelates are represented in Table 2.

The spectra of the two ligands **LH** and **LCl** exhibited two bands at 3398 & 3264 cm⁻¹ for **LH** and at 3411& 3222 cm⁻¹ for **LCl** that assigned to asymmetric and symmetric vibrations of NH₂ groups while The bands appearing at 3152 and 3139 cm⁻¹ was assigned to v(NH) of the imino group [33]. These vibrations occurred, in the spectra

of complexes, almost at the same place indicating that these bands remained uncoordinated in the metal complexes. Some of these bands underwent shift in their position to higher or lower wavenumbers in spectra of metal complexes as a result of their involvement in H-bonding [34].

The absorption band characteristic of the v(SH) of thioimide group that frequently appears in the range 2500–2700 cm⁻¹ is missing in the spectrum of LCl ligand which proves that this ligand is present in the thione form in the solid state and the possibility of thioamide-thioimidoltautomerism (H–N–C=S, N=C–SH) is not possible [35]. Such band appeared in the spectrum of L-H at 2630 cm⁻¹ as a sharp signal showing that this complex exists in the thiole form in the solid state.

The three bands appearing at in the spectrum of **LH** at 1605, 1288 & 889 cm⁻¹ and appearing at in the spectrum of **LCl** at 1595, 1299 & 734 cm⁻¹ assigned to v(C=N), v(C=S) and δ (C=S),respectively. In the spectra of complexes **LH-Co** and **LCl-Co**, such bands have shifted to higher or lower wavenumbers confirming the attachment of azomethine nitrogen and thiolate sulfur to the metal center. The participation in the coordination to the metal center [35]. The participation nitrogen atom in coordination to Co center is further supported by the existence of non-ligand bands at 455 and 461 cm⁻¹ in the spectra of **LH-Co** and **LCl-Co**, respectively, which assignable to v(N-M). The two bands appearing in the spectrum of **LH-Co** at 1564 and 1308 cm⁻¹, and in the spectrum of **LCl-Co** at 1545 and 1342 cm⁻¹ assignable to v_{asy} and v_{sym} of the acetate group, respectively. The difference between the two bands was calculated to be 256 and 203 cm⁻¹ for **LH-Co** and **LCl-Co**, respectively, supporting the monodentate nature of the acetato group [26].

Table 2. Assignments of diagnostic important bands in IR spectra for the compounds under study.

Journal Pre-proof										
Compound	vNH ₂ ,vNH	vC-H sp ³	vC=N	vN-N	δΝΗ	vCS,	vM-N			
LH	3398, 3264, 3152	2932	1605	1074	1489	1288, 889	-			
LH-Co	3430,3279, 3156	2940	1564	1021	1498	1308, 845	455			
LCl	3411, 3222,3139	2975	1595	1197	1495	1299, 734	-			
LCI-Co	3429, 3231, 3183	2930	1601	1088	1486	1317, 725	461			

3.5. Thermogravimetric analysis

Thermal analysis is a helpful tool that is applied to assign the thermal behavior and stability of metal chelates as well as understanding their coordination behavior through introducing exemplary information about their thermal characteristics, intermediates, and final products of their decomposition steps [23]. It is also very helpful to assign the nature and amount of H_2O and/or other solvent content and as well as the coordinated anionic groups. Based on these facts, the synthesized metal chelates, **LH-Co** & **LCI-Co**, were subjected to TG/DTG analysis. Detailed thermo-analytical results for the two complexes **LH-Co** & **LCI-Co** are depicted in Table 3 and interpreted in Fig. 4.

Careful study of the complexes thermograms showed that complexes LH-Co & LCl-Co decomposed within five successive steps within the temperature range 28-800 °C. The first step appeared at 28-93 and 28-156 °C for LH-Co & LCl-Co and assigned to the loss of lattice and coordinated water molecules, respectively. Within the second stage that appeared at 93-229 and 156-220 °C, partial decomposition of the organic ligands occurred with the loss of CH₃ +NH for LH-Co and CH₃ +Cl⁻ for LCl-Co. The coordinated acetate anion got lost within the third step which appeared at 229-323 and 220-325 °C for LH-Co & LCl-Co, respectively. The last two stages in both complexes assigned to the degradation of the organic ligands that appeared within the ranges 323-500 and 500-800 °C for LH-Co and 25-493 and 493-594 °C for LCl-Co leading to the formation of CoS as final decomposition product from which the percent of the metal content has been calculated.



Figure 4.TG/DTG curves of the two complexes LH-Co & LCl-Co

Table 3. The decomposition stages, tempera	ature ranges, theoretical, found weight lo	SS
and DTG temperature of cobalt complexes.		

Complex no.	Temp.	DTG	Mass loss %		Assignment
(Mol. Wt.)	range (°C)	temp	Calc.	Exp.	
	28-93	48	2.15	1.70	-Loss of half lattice H ₂ O molecule.
LH-Co	93-229	205	7.17	7.50	- Loss of oneCH ₃ + NH groups.
[(LH)Co(OAc)]0.5H ₂ O	229-323	282	14.11	13.65	- Loss of one coordinated CH ₃ COO ⁻
(418.36)					group.
	323-500	459	36.02	33.41	- Loss of C ₃ HN ₃ S moiety.
	500-800	553	9.30	9.90	-Further decomposition of ligand leaving
					CoS+4C.
			14.32	14.09	-% of metal content.
LCI-Co	28-156	77	7.5	7.82	-Loss of two coordinated H ₂ O molecules.
$[(LCl)Co(OAc)(H_2O)_2]$	156-220	199	10.52	9.92	- Loss of one Cl ion + CH_3 group.
(479.83)	220-325	265	17.93	18.08	- Loss of one coordinated CH ₃ COO ⁻
					group+ C=N group.
	325-493	440	28.17	28.38	- Loss of C ₇ H ₅ NS moiety.
	493-594	560	11.46	11.42	-Further decomposition of ligand leaving
					CoS.
			12.28	11.87	-% of metal content.

3.6.UV-Vis spectra and magnetic moment measurements

Electronic spectral analysis is considered the main tool that is applied to assign the type of geometrical structure exhibited by the metal center in metal complexes. It is also very useful to assign the type of electronic transitions exhibited by different functions groups in both organic and inorganic compounds.

The UV-Vis spectra of the two ligands LH & LCl and their complexes were measured in the solid state using nujol mull technique. The free ligands exhibited two bands at 248 & 294 nm for LH and at 241 & 284 cm⁻¹ for LCl that assigned to assigned to $\pi \rightarrow \pi^*$ transitions of aromatic benzene ring and azomethine groups, respectively. The band that appeared at 357 and 335 nm in the spectra of LH and LCl, respectively, assigned to $n\rightarrow\pi^*$ transition of azomethine groups. In the spectra of cobalt complexes, LH-Co and LCL-Co, such bands have shifted to longer wavelengths (appeared at 251, 306 and 360 nm in the spectrum of LH-Co and at 252, 300 and 346 nm in the spectrum of LCl-Co) as a consequence of coordination of the azometnie nitrogen to the metal center [36, 37].

LH-Co complex exhibited also one broad band centered at 668 nm due to ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$ transition characteristic for tetrahedral geometry [38]. Another broad band centered at about 536 nm due to spin-orbital coupling. The tertrahedral geometry of **LH-Co** has been further supported by calculating the μ_{eff} value which found to be 4.08 B.M evidencing tetrahedral geometry [38].

The electronic spectrum of **LCI-Co** complex exhibited two bands at 559 and 683 cm⁻¹ assignable to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(p)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ transitions, respectively, supporting octahedral configuration [39,40]. Such complex exhibited μ_{eff} of 4.65 B.M which is characteristic of high-spin octahedral complexes.

Based on the previous results the structures of the two complexes **LH-Co** and **LCI-Co** can be illustrated as following (Scheme 2).



Scheme 2. Structures of the two complexes LH-Co and LCl-Co

- **3.7.** Investigation of the corrosion inhibition of the prepared ligands and complexes
- 3.7.1. Weight-loss measurements

The experiments of weight-loss (WL) were carried out on cylindrical carbon steel rods with areas closed to 12 cm^2 and were prepared for these measurements as reported earlier [2,3]. The inhibition efficiencies (% IE) of the investigated inhibitors were calculated from the values of corrosion rate (CR) of carbon steel (determined in mpy) using the following equation [41]:

% IE =
$$\theta \ge 100 = \left[1 - \frac{CR_{inh}}{CR}\right] \ge 100$$
 (1)

Where, the values of corrosion rate are expressed as CR and CR_{inh} in the obscurity and existence of inhibitor, respectively.

WL measurements of carbon steel in 1.0 M HCl were performed in the absence and existence of different concentrations of the synthesized ligands (**LH**, **LCl**) and their complexes (**LH-Co**, **LCl-Co**) in the concentration ranging from 100 to 900 ppm at 25 °C. For briefly, curves of weight-loss (WL) versus time obtained for the ligand **LH** and its cobalt complex (**LH-Co**) are illustrated in Fig. 5. % IE and values of CR of carbon steel of all investigated compounds are also estimated and tabulated in Table 4. The collected data from Table 4 revealed that CR values reduced with increasing inhibitor concentration. Therefore, the new synthesized derivatives can be considered as effective corrosion inhibitors for carbon steel in HCl (1.0 M). Careful examination of the results (tabulated in Table 4 and clarified in Fig. 6 (a & b) showed that at the same inhibitors concentration, the inhibition capacities are little enhanced in the order: **LH** > **LCl** > **LH**-**Co** > **LCl-Co** indicating that the possible steric effects and electronic density of donor atoms of the test compound are considered as the main reason in the adsorption operation.



Figure 5. Weight-loss (WL) versus immersion time of carbon steel corrosion in 1.0 M HCl solution in the absence and presence of different concentrations of ligand **LH** (a) and its complex **LH-Co** (b) at 25 $^{\circ}$ C.



Figure 6. Variation of inhibition efficiencies with the concentrations of the synthesized ligands and their complexes: (a) **LH & LH-Co**, (b) **LCl & LCl-Co**, for the corrosion of carbon steel corrosion in 1.0 M HCl solution at 25 °C.

3.7.2. Potentiodynamic polarization (PP) measurements

In both EIS and PP techniques, we calculated the percentage of IE of the test inhibitors as published earlier [2,3]. The PP measurements for carbon steel in solution of HCl (1.0 M) in the presence and absence of various concentrations of the thiadiazole-compounds are carried out (only PP curves obtained for the ligand **LCl** and its cobalt complex (**LCl-Co**) as representative examples are only presented here in Fig. 7) and all parameters related to corrosion are evaluated and are tabulated also in Table 4. The extracted results showed that the addition of fixed concentrations of thiadiazole compounds to the blank solution turned both the cathodic and anodic branches of curves of the polarization towards lower current density values, indicating the delay of the anodic and cathodic reactions, thereby inhibiting iron corrosion. Since, the inhibitor exhibited anodic and cathodic inhibition effects with slightly shift in E_{corr} value to more anodic potentials, it could be deduced that such new thiadiazole derivatives perform as mixed-type inhibitors [41-43]. Enhancement of % IE values were found with increasing concentrations of inhibitors and the extent of inhibition efficiencies of the compounds, at the same concentration, followed the order:

LH > LCl > LH-Co > LCl-Co, in consistent with the results obtained from WL measurements.

Table 4. Corrosion parameters of carbon steel corrosion in 1.0 M HCl solution and the values of % IE of the synthesized compounds obtained from the three employed techniques (WL, PP and EIS) at $25 \,^{\circ}$ C.

Inh.	Concn	WL		РР					EIS	
	(ppm)	CR	% IE	-E _{corr} (mV(SCE)	β _a (mV/dec.)	-β _c (mV/dec.)	i _{corr} (μA/cm ²)	% IE	R _{ct}	% IE
	0	241		448	96	74	610		55	
	100	81	66	441	127	85	220	64	152	64
	200	57	76	435	128	88	140	77	240	77
LH	300	38	84	431	133	94	92	85	345	84
	400	24	90	427	127	87	67	89	458	88
	500	17	93	421	135	95	49	92	688	92
	100	87	64	445	136	93	214	65	145	62
	200	60	75	441	138	99	159	74	220	75
LCl	300	36	85	435	121	102	92	85	344	84
	400	27	89	418	142	106	61	90	459	88
	500	21	91	406	124	110	43	93	610	91
	100	92	62	442	124	83	226	63	157	65
	200	65	73	441	130	79	171	72	195	72
LH-Co	300	41	83	434	128	93	110	82	344	84
	400	28	88	421	137	92	79	87	458	88
	500	24	90	417	141	104	61	90	610	91
	100	89	63	446	139	89	219	64	146	62
	200	68	72	437	137	98	165	73	212	74
LCl-Co	300	38	84	431	143	97	116	81	324	83
	400	31	87	443	147	86	92	85	502	89
	500	27	89	424	131	88	79	87	557	90



Figure 7. Potentiodynamic polarization curves of carbon steel corrosion in 1.0 M HCl solution in the absence and presence of different concentrations of: (a) ligand **LCl**, and (b) its complex **LCl-Co** at 25 $^{\circ}$ C.

3.7.3. Electrochemical impedance spectroscopy (EIS) measurements

The adsorption phenomena and the mechanisms in corrosion researches are explained by using the commonly EIS technique. Nyquist plots of carbon steel corrosion in 1.0 M HCl solution in the absence and presence of several concentrations of thiadiazole-compounds are plotted but only Nyquist plots for the ligands LH and LCl are illustrated in Figure 6. The values of R_{ct} and % IE are also listed in Table 4. Figure 8 illustrated that, for all examined compounds, the impedance spectra in absence and existence of inhibitors exhibit single depressed capacitive loops, which reveals that the adsorption of the examined inhibitors occurs by simple surface coverage and such compounds behave as primary interface inhibitors, and the corrosion of carbon steel was mainly controlled by the process of charge transfer and double layer behavior. Furthermore, it can be noticed that the general shape of the capacitive loops is similar in the absence or presence of the inhibitors with different concentrations suggesting that there is no change in the mechanism of the corrosion process [44]. The obtained impedance spectra were analyzed by fitting the experimental data to a simple equivalent circuit model, illustrated in Fig. 9, which includes a double layer capacitance (C_{dl}) and a charge transfer resistance (R_{ct}) , and the two elements are in series with a solution resistance (R_s) . The diameter of the capacitive semicircle of carbon steel in the corrosive medium (solution of 1.0 M HCl) was lower than that of the inhibited solutions. Hence, the carbon steel electrode/HCl system show higher impedance in the presence of inhibitors. This behaviour demonstrates that the corrosion resistance of carbon steel in the presence of the examined inhibitors occurs as a result of a decrease in the rate of carbon steel corrosion, and this attitude enhanced with increasing inhibitor concentration. Also, increasing value of $R_{\rm ct}$ with increasing the inhibitor concentrations indicates that the examined compounds act as inhibitors via adsorption at the carbon steel electrode/HCl solution interface leading to a decrease in their electrical capacities as they displace water molecules and other ions originally adsorbed on the metal surface [45]. Also, the increase of the value of R_{ct} with inhibitor concentrations implies that the number of the inhibitor molecules which adsorbed on the surface of carbon steel increase resulting in the construction of protective films on the electrode surface, and hence, become barriers to hinder the mass

and charge transfer, leading to increase the inhibition efficiencies. These results confirm that the investigated compounds act as efficient inhibitors for the corrosion of carbon steel in 1.0 M HCl solution. From the acquired outcomes of the three employed techniques, it can be observed that the results of the inhibition efficiencies of the inhibitors obtained from the three techniques are in good agreement with each others.



Figure 8. Nyquist plots for the corrosion of carbon steel corrosion in 1.0 M HCl solution in the absence and presence of different concentrations of the ligands: (a) **LH**, and (b) **LCl** at 25 $^{\circ}$ C.



Figure 9. The equivalent circuit model used to fit the experimental results.

3.6.4. Surface examinations

Scanning electron microscopy (SEM) micrographs of carbon steel samples in a free 1.0 M HCl (corrosive solution) and with 500 ppm of the examined compounds are illustrated in Figure 10(a–f). Figure 10a and b manifest the pure carbon steel surface before and after immersion in the corrosive solution for 12 h, respectively. Figure 10b shows the very elevated roughness of carbon steel surface which became strongly

damaged along with the appearance of several cracks and pits which ascribed to the aggressiveness of the examined acid medium. Figure 9 (c–f) shows SEM micrographs of carbon steel surface after treatment with 500 ppm of the synthesized compounds: LH, LCl, LH-Co and LCl-Co, respectively, supplemented to the corrosive solution. The micrographs indicate that, the surfaces of carbon steel samples suffered remarked changes from the previous case where both the elevated roughness and the strong damage shown in the steel surface was disappeared and the surface was largely covered with the inhibitor molecules on the whole surface. This can be attributed to the strong adsorption of the inhibitors on carbon steel surface, causing a decrease in the contact between carbon steel surface and the corrosive solution resulting in a good corrosion inhibition and protection of the steel surface [44].



Figure 10. SEM micrographs of carbon steel surface: (a) before immersion in the corrosive solution (1.0 M HCl), (b) after 12 h immersion in 1.0 M HCl, as well as (c), (d), (e) and (f) after 12 h immersion in the corrosive media containing 500 ppm of the synthesized compounds: LH, LCl, LH-Co and LCl-Co, respectively, at 25°C.

1.1.1. Adsorption considerations

An inhibition property was shown for thiadiazole ligands and their cobalt complexes *via* their adsorption on the metal surface as well as some alternative adsorption isotherms such as Langmuir, Frumkin, Freundlich, Temkin, etc. have been widely utilized to investigate the mode of adsorption of the tested inhibitor molecules and then their corrosion inhibition mechanism. In the present study, Langmuir adsorption isotherm, which is a relation between the values of fractional surface coverage (C_{inh}/θ) for the investigated inhibitors against inhibitor concentration (C_{inh}), was fitted and is shown in Fig. 11. The values of correlation coefficient for the investigated compounds were near to 1, which reveals that the inhibitor adsorption on the surface of carbon steel is well fitted to the Langmuir adsorption isotherm [46,47], which is represented by the bellow equation [48]:

(2)

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

Where K_{ads} is the equilibrium constant of adsorption.



Figure 11. Langmuir adsorption isotherms for the synthesized ligands and their complexes: (a) **LH, LH-Co** and (b) **LCl, LCl-Co** adsorbed on the carbon steel surface in 1.0 M HCl solution at 25 °C.

On comparison between the efficiency of the examined inhibitors (synthesized ligands and their cobalt complexes) in the present investigation and the previous reports of employment of metal ion complexes as corrosion inhibitors, e.g. Adam et. al. [43], who studied the inhibition performance of three anionic oxide-vanadium Schiff base Nsalicylidene amino acid complexes on the corrosion of carbon steel in HCl solution. They found that the synthesized complexes protect carbon steel form corrosion, yielding maximum inhibition efficiency up to 94.7% in the presence of 1.0 mM inhibitor and all complexes act as mixed-type inhibitors. Also, Abdel-Gaber, et. al. [47] studied the corrosion inhibition of Schiff base (N,N'-bis-(salicylaldehyde)-1, 3-diaminopropane) and its cobalt complex on the corrosion of steel in acidic medium. Their outcomes showed that PDP measurement showed 73.41% inhibition efficiency in the presence of 35 mol/L. However, EIS measurement displayed 84.3% and 83.2% inhibition efficiencies at the same concentration and temperature. Abd El-Lateef, et. al. [44] synthesized four of metal ion complexes of salicylidene anthranilate sodium salt ligand and studied their inhibition action on the corrosion of carbon steel in 1.0 M HCl by various techniques. The results obtained from PDP and EIS techniques displayed that, the examined ligand and their Mcomplexes act as effective and mixed-type inhibitors and the maximum inhibition efficiency was about 95%. Also, the adsorption of such compounds on carbon steel surface could be exemplified by Langmuir isotherm.

4. CONCLUSION

Two derivatives of 1,3,4-thiadiazolethiosemicarbazone, which synthesized by the condensation reaction of 2,3-disubstituted-5-acetyl-1,3,4-thiadiazolederivatives with thiosemicarbazide in acidic medium, have been used as chelating agent for the synthesis of divalent cobalt complexes. The structures and purity of both ligands and their complexes have been identified applying different analytical and spectral tools. Analytical data indicated that the complexes have been formed in the molar ratio 1:1 (L:M) having the formulae [(LH)Co(OAc)]0.5H₂O and [(LCl)Co(OAc)(H₂O)₂]; where LH and LCl are 1,3,4-thiadiazolethiosemicarbazone ligands. When comparing the

results of infrared IR-spectra of ligands with those for metal complexes, we found that ligands acted as monobasic tridentate connecting to the metal ion center through nitrogen atoms of azomethine group & thiadiazole ring and deprotonated SH group. UV-Vis spectra and magnetic moment data showed that the complexes have have tetrahedral and octahedral geometry. The synthesized ligands and their complexes were also investigated as inhibitors for the corrosion of carbon steel in HCl (1.0 M) at 25 °C using various techniques as weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscopy. The results extracted from these experimental results revealed that the inhibition efficiencies of the tested derivatives was found to depend on their concentrations and structures. The inhibition efficiencies of the synthesized compounds increased also with raising temperature. At the same inhibitors concentration, the inhibition efficiencies are slightly increased in the order: LH > LCl > LH-Co > LCl-Co. The results derived from all applied techniques are harmonious with each other.

Conflict of Interest

The authors declare no conflict of interest

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Highlights

- The divalent cobalt complexes of the two novel 1,3,4thiadiazolethiosemicarbazone have been synthesized.
- The structure of the two complexes have been proved to have tetrahedral and octahedral geometry from their spectral data.
- The synthesized ligands and their complexes were investigated as inhibitors for the corrosion of carbon steel in HCl.
- The obtained results revealed that the inhibition efficiencies of the tested derivatives were found to depend on their concentrations and structures and were increased with raising temperature.

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All authors participated in the experimental work, analysis the data, writing and revised the article

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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