SYNTHESIS, CHARACTERISATION AND CORROSION INHIBITION SCREENING OF Co(II) DITHIOCARBAMATE COMPLEXES IN HCl AND H$_2$SO$_4$

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Abstract

Most industries use acids during cleaning processes where they may cause severe corrosion attacks on metal surfaces. This study utilised a corrosion inhibitor to reduce the corrosion rate. Cobalt(II) *N*-methylcyclohexylamine dithiocarbamate, Co[MeCycHexdtc]$_2$ and cobalt(II) *N*-ethylcyclohexylamine dithiocarbamate, Co[EtCycHexdtc]$_2$ were synthesised by using the in-situ method with a molar ratio of 2:2:1 (carbon disulphide:amine:metal salt) in cold ethanolic solution and characterised by using the Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) and Ultraviolet-Visible (UV-Vis) spectroscopies. In the FTIR-ATR analysis, the presence of dithiocarbamate moiety was proven by the data shown with the presence of a new specific stretching bands, thioureide band, $\upsilon(C\text{\textperiodcentered}\text{\textperiodcentered}N)$ which is found in the range of 1478–1481 cm^{-1} and $\upsilon(C\text{\textperiodcentered}\text{\textperiodcentered}S)$ in 1010-1012 cm^{-1} of the spectra in both Co(II) complexes. For UV-Vis analysis, the Co(II) complexes showed two transitions, $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, which indicated that the coordination between metal ions and dithiocarbamates ligands has successfully formed. The presence of peaks above 400 nm confirmed the *d-d* transition of Co(II) complexes. Furthermore, mild steel corrosion inhibition screening was studied using two corrosive media (1 M HCl and 1 M H$_2$SO$_4$) with and without varied inhibitor concentrations. As the inhibitor concentration increased, the efficiency of the corrosion inhibitor also increased at a constant temperature.

Keywords: acid; corrosion inhibitor; dithiocarbamate; mild steel

Introduction

Corrosion is a natural process that occurs when an electrochemical reaction develops between a metal surface and its surroundings, causing the surface to deteriorate (Raja *et al*., 2016). Metal corrosion is a process in which the surrounding medium caused a metal to lose its basic properties (Li *et al*., 2019). Metal corrosion happens due to acids such as hydrochloric acid and sulfuric acid used in most manufacturing activities for example, in acid cleaning, acid pickling, industrial acid treatment, acid de-scaling and oil well acidising (Bahrami *et al*., 2010). Due to these corrosion problems to offshore structures, many industries especially the vital oil and gas production industry face a serious threat from the looming financial cost of corrosion. Corrosion can be avoided and controlled in many ways such as, by selecting corrosion resistant materials, ensuring optimal structural designs, and providing cathodic protection. One other effective corrosion protection method is the use of inhibitors onto the metals as it can reduce the rate of corrosion (Dariva and Gallo, 2014). According to a study by Chigondo and Chigondo (2016), the majority of previous corrosion inhibitors are inorganic inhibitors that contain phosphate, chromate, and other heavy metals, and their toxic nature has prompted researchers to seek out alternatives. Regulations restrict its usage due to its toxicity which poses a hazard to aquatic life in the

marine ecosystem. Because of its corrosion resistance, cobalt is an innocuous element with a broad array of applications in the metallurgical industry.

Dithiocarbamates are known to act as corrosion inhibitors for metals as the compounds are generally, adsorbed on the metal surface to form a protective thin film and effectively blocking the active corrosion sites. Dithiocarbamate is a compound that is most commonly used in the biological, industrial, agricultural and chemical applications. Dithiocarbamate can produce a variety of coordination modes when it binds with a metal for example, isobidentate, anisobidentate, monodentate, and bidentate by the resonance between two strong binding sites within the structure which are two sulphur atoms in the presence of the anionic CS_2^- moiety (Sivasekar *et al.*, 2015; Adeyemi and Onwudiwe, 2018). This has been supported by Odularu and Ajibade (2019), who added that dithiocarbamates are versatile ligands due to their possession of two donor sulphur atoms in the ligands that enabled them to chelate with various types of metals.

In this study, the corrosion of mild steel was observed due to the presence of acids and inhibitors. The corrosion inhibition efficiency of Co(II) complexes were determined by the immersion of mild steel in the absence and presence of different concentrations of inhibitors by using the weight loss method in an acidic environment. Hence, this study aims to synthesis, characterise by using Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) and Ultraviolet-Visible (UV-Vis) spectroscopies, and screen the corrosion inhibition of Cobalt(II) *N*-methylcyclohexyl dithiocarbamate, Co[MeCycHexdtc]$_2$ and Cobalt(II) *N*-ethylcyclohexyl dithiocarbamate, Co[EtCycHexdtc]$_2$ complexes on mild steels.

Methods

Instrumentations

The molar conductivity values were measured with DMSO solvent at room temperature by using SI Analytic Lab 970 conductivity meter at the concentration of 1×10^{-3} M and the percentage of the metal in the Co(II) complexes were determined by gravimetric analysis using the furnace Model Lindberg/Blue. An apparatus of melting point model SMP10 Stuart was used to detect the melting point of the synthesised Co(II) complexes whereby an open capillary tube was used to obtain the melting point. Besides, other characterisations were carried out such as FTIR-ATR and UV-Vis Spectroscopies. FTIR-ATR was used to determine the presence of functional groups in the synthesised Co(II) complexes where the infrared spectra of the compounds were verified within the spectra range of $4000 – 400$ cm^{-1} for mid-IR at room temperature using the Perkin Elmer model GX spectrophotometer. The electronic spectra, on the other hand, were measured by a spectrophotometer (T80/80+, PG Instruments) in the region of $200 – 600$ cm^{-1} with dimethyl sulfoxide (DMSO) as a solvent.

Chemical Synthesis

Co[MeCycHexdtc]$_2$: *N*-methylcyclohexylamine, carbon disulphide and cobalt(II) nitrate was mixed in an ethanolic solution with a molar ratio of 2:2:1, respectively. Next, 6 mmol of *N*-methylcyclohexylamine was dissolved in ethanol and the solution was stirred for 30 minutes in 25 mL conical flask at 0°C. Then, a cold ethanolic solution of carbon disulphide was added to the solution. Multiple drops of cold ammonia were added into the mixture while the pH of the solution was maintained at a range of 6-7 and then continuously stirred for 30 minutes. A cold ethanolic solution of cobalt (II) nitrate was added dropwise to the dithiocarbamate solution after 30 minutes while stirring. The precipitate was filtered and washed with methanol and dried in a desiccator for 24 hours. The same method was repeated by replacing with *N*-ethylcyclohexylamine to synthesis Co[EtCycHexdtc]$_2$ complex.

Corrosion Inhibition Study

Preparation of acids and different concentrations of inhibitor

1 M of 37% HCl and 1 M H$_2$SO$_4$ were prepared using $M_1V_1 = M_2V_2$. The inhibitor was prepared with varying concentrations of 0.1, 0.01 and 0.001 M.

Weight Loss Analysis

For weight loss analysis, four pieces of 1.5 cm x 4 cm mild steel were used to determine the efficiency of corrosion by weight loss technique. The mild steels were polished by using emery paper and washed with distilled water and acetone and dried at room temperature. Then, the mild steels were immersed in 1 M HCl with and without inhibitor at room temperature for 24 hours at different inhibitor concentrations of 0.1 M, 0.01 M and 0.001 M. Thereafter, the mild steels were rinsed by using distilled water and then dried. The weight of the mild steels was recorded before and after the 24 hours immersion and compared to determine the weight loss that reflected the rate of corrosion. The steps were repeated three times to get an average value and repeated again with different acid, 1 M H_2SO_4 with the same varying concentrations accorded to the HCl.

Result and Discussion

Physical Measurements

The dithiocarbamate ligand is an intermediate product of the complete synthesis process of Co(II) complexes. The in-situ method was used to synthesis Co[MeCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ complexes. These complexes were synthesised by the reaction of the mixture of amine derivatives, carbon disulphide (CS_2), and cobalt(II) nitrate, Co(NO$_3$)$_2$ with a molar ratio of 2:2:1, respectively, in a cold condition. Both the cobalt(II) complexes obtained green colour precipitates. Table 1 shows the melting point and percentage yield obtained from the synthesised Co(II) complexes. The synthesis schemes of Co(II) complexes are shown in Figure 1 and Figure 2.

Table 1. Physical properties of Co(II) complexes

Compound	Color	Melting point (°C)	Yield (%)	% Metal
Co[MeCycHexdtc]$_2$	Green	341.3 – 342.2	80.68	15. 90 (14.18)
Co[EtCycHexdtc]$_2$	Green	339.7 − 340.9	83.97	14.75 (13.29)
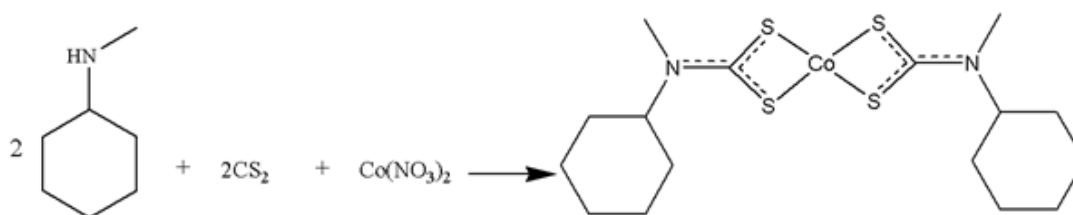
Figure 1. The synthesis scheme of Co[MeCycHexdtc]$_2$
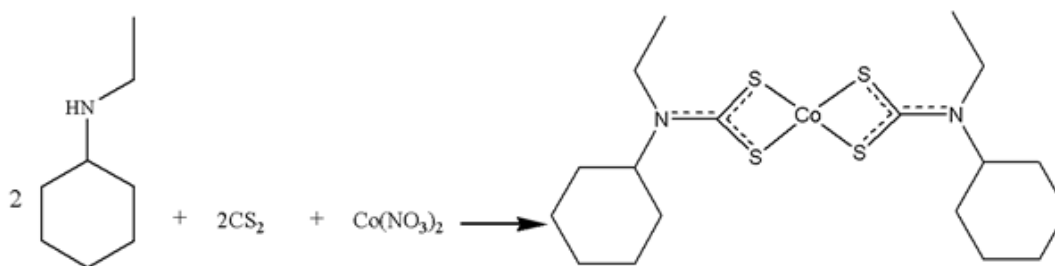
Figure 2. The synthesis scheme of Co[EtCycHexdtc]$_2$

Gravimetric Analysis

Gravimetric analysis can determine the mass of the metal in percentage in the Co(II) complexes by using muffle furnace at room temperature until 500°C. The percentage of Co(II) complexes were obtained at 15.90% and 14.75% for both Co[MeCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$, respectively, by using the calculation as shown:

$$\text{Gravimetric factor (GF)} = \frac{\text{Molecular weight of analyte}}{\text{Molecular weight of precipitate}} \times \frac{a}{b}$$

$$\text{Weight of analyte} = \text{Weight of precipitate left x GF}$$

$$\% \text{ of analyte} = \frac{\text{Weight of analyte}}{\text{Weight of precipitate}} \times 100\%$$

Molar Conductivity

The molar conductivity of the Co(II) complexes was observed in 1×10^{-3} M of DMSO as a solvent in the range of $0 – 30$ Scm^{2}mol^{-1} [15 Scm^{2}mol^{-1}] and revealed a non-electrolyte nature. This non-electrolyte behaviour was proven by Keles et al. (2015) where the central metal did not bond with any of the counter ion.

Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR)

The FTIR-ATR in the range $4000 – 650$ cm^{-1} was used to determine the spectra data that corresponded to four important functional groups of Co(II) complexes, υ(C$\cdots$S), υ(C$\cdots$N), υ(C-N), and υ(C$=$S) which provided useful information on the coordination behaviour of ligand to metal ion (Khan et al., 2018). The data obtained was compared between the bands of both Co(II) complexes and raw materials. A sharp band observed at 1541 cm^{-1} attributed to the stretching band of υ(C$=$S) from CS$_2$ while when the dithiocarbamate was coordinated to the metal ion, the band of υ(C$\cdots$S) was shifted to a lower wavenumber 1011 cm^{-1} and 1012 cm^{-1} for both Co[MetCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ complexes, respectively. This decrease in wavenumber was due to the reduction of carbon-sulphur double bond character to partial double bond character. Latif et al. (2018) stated that the band which was observed at 1000 ± 70 cm^{-1} region proved a bidentate character while monodentate character was splitting at the same band in the same region. Additionally, the thioureide band of υ(C$\cdots$N) was observed at 1478 cm^{-1} for Co[EtCycHexdtc]$_2$ and 1481 cm^{-1} for Co[MeCycHexdtc]$_2$ where it shifted to a higher wavelength from 1449 cm^{-1} in amine derivatives. The partial double bond character of υ(C$\cdots$N) indicated the coordination of ligand with metal ions. However, according to Khan et al. (2018), the absorption band of υ(M$-$S) was observed within the range 423-431 cm^{-1}. This bonding proved the coordination of metal ions with the dithiocarbamate ligands through S atom. The IR spectra data for Co(II) complexes are shown in Table 2.

Table 2. FTIR-ATR spectra data for the raw materials and Co(II) complexes

Compound	Wavenumber, cm^{-1}					
	υ(C−H)	υ(N−H)	υ(C=S)	υ(C$\overset{..}{=}$S)	υ(C−N)	υ(C$\overset{..}{=}$N)
Carbon disulphide, CS$_2$	-	-	1541	-	-	-
N-methylcyclohexylamine	2926 2852 2789	3281	-	-	1449	-
N-ethylcyclohexylamine	2927 2853	3281	-	-	1449	-
Co[MetCycHexdtc]$_2$	2933 2853	-	-	1011	-	1481
Co[EtCycHexdtc]$_2$	2953 2857	-	-	1012	-	1478

Ultraviolet-Visible (UV-Vis)

The UV-Vis spectroscopy was operated by using DMSO as a solvent and the electronic spectra of Co(II) complexes were observed and recorded. In order to prove the formation of the Co(II) complexes, the electronic spectra were compared with CS$_2$. Table 3 shows the electronic spectra data for the Co(II) complexes and CS$_2$.

The absorption peaks of Co[MeCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ complexes were observed at 280 nm and 275 nm, respectively, which corresponded to the intraligand π-π* transitions of N-C=S and S-C=S, and have been supported by Nqombolo and Ajibade (2016). When the metal reacted with the ligand and formed the Co(II) complexes, bathochromic shift in the Co(II) complexes were observed. Both of the Co(II) complexes shifted to a higher wavelength where it was observed from 264 nm in CS$_2$ to 280 nm and 275 nm in the Co(II) complexes, respectively. This shifting was due to the coordinating effect of the dithiocarbamate ligands to the metal ion in both Co(II) complexes. However, the transitions at 330 nm [Co[MeCycHexdtc]$_2$] and 325 nm [Co[EtCycHexdtc]$_2$] were observed and indicated as n-π* transition. Rani *et al*. (2012) stated the transition of n-π* was in the system of N-C-S which attributed to lone pair electron transition in N and S atoms.

The observed peaks for both Co(II) complexes showed the *d-d* transition at more than 400 nm, which was due to the excitation of electron in the *d* orbital of the metal ion. Moreover, most transition metal complexes were coloured which could also be considered as the indicator of the coordination of ligand in the Co(II) complexes. The characteristics of the colour of the Co(II) complexes could be determined by the electron transfer in *d-d* transition (Al-Obaidy *et al*., 2020). Besides, the electronic spectra of *d-d* transition appeared at more than 400 nm which proved that dithiocarbamate ligand was successfully coordinated to Co(II) ion.

Table 3. The UV-Vis spectra data of carbon disulphide and Co(II) complexes

Compound	Wavelength, λ_{max} (nm)	Electronic transition
Carbon disulphide, CS$_2$	264	π-π*
Co[MetCycHexdtc]$_2$	280	π-π*
	330	n-π*
	>400	*d-d*
Co[EtCycHexdtc]$_2$	275	π-π*
	325	n-π*
	>400	*d-d*

Corrosion Inhibition Study
Dithiocarbamate can act as a corrosion inhibitor which is known to lessen the corrosion rate on mild steel surfaces when it is added in small quantities to the corroding system. One of the techniques that can be used to determine the competency of Co(II) complexes as corrosion inhibitors is the weight loss method. The weight loss method was conducted in triplicates and the data (corrosion rate, surface coverage and inhibitor efficiency) for the various acid solutions that either did not contain any inhibitors or had different concentrations of inhibitor were calculated by using the equation indicated below:

$$C_R = \frac{W_a - W_b}{At}$$

$$\theta = 1 - \frac{W_i}{W_o}$$

$$\eta_W (\%) = \left(1 - \frac{W_i}{W_o}\right) \times 100\%$$

In the equation above, where W_b and W_a are the specimen weight before and after immersion in the inhibitor solution, w_o and w_i are the values of weight loss of metal in uninhibited and inhibited solutions, respectively, A is the total area of the metal specimen (cm^2), t is the exposure time (h), C_R is the corrosion rate and η_w is the inhibitor efficiency. These two different inhibitors were compared on its corrosion inhibition competencies in different acids. The data showed Co[MetCycHexdtc]$_2$ has a higher corrosion inhibition competency compared to Co[EtCycHexdtc]$_2$ in both acid solutions. The increase in the molecular weight of the complex reduced the corrosion inhibition competency because of deficit in the linearity of the structure and the arrangement of the complex structure will be distorted to adsorb on the mild steel surface (Okafor *et al.,* 2004).

Two different acids, which were hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) were used for this study. Both acids were tested with different concentrations of inhibitors to determine the effects and competencies of inhibitors toward the corrosion inhibition on mild steel surfaces. Figure 3 and Figure 4 show the data of the competency of corrosion inhibition of Co(II) complexes in both 1M HCl and 1M H_2SO_4 of acid solutions with different inhibitor concentrations of 0.001 M, 0.01 M and 0.1 M. According to the graph, the inhibitor competency increases when the concentration of inhibitor increased thus, the corrosion rate on the mild steel decreased. This was proven by Li *et al.* (2019) where the corrosion competency increased when the concentration of inhibitor was increased due to the molecules of corrosion inhibitor that formed a barrier film between the metal and the corrosive solution thus protecting the metals. Besides, the efficiency of corrosion inhibitor increased due to the presence of polar atom groups such as heteroatoms and π–electron systems in the structure of Co(II) complexes (Sehmi *et al.*, 2020).

The data tabulated in Table 4 and 5 indicated that after a 24 hours immersion of the mild steels with the various concentrations of inhibitors and acid solutions, the inhibitor competency was higher when immersed with HCl compared to H_2SO_4. This showed that H_2SO_4 was a stronger acid solution than HCl due to its greater rate of corrosion on the mild steel surface in H_2SO_4 compared to HCl. This is because, while reacting with the metal surface, H_2SO_4 releases two protons compared to HCl and this presence of double H^+ in H_2SO_4 makes the acid more corrosive than HCl (Loto, 2018; Latif *et al*., 2018).
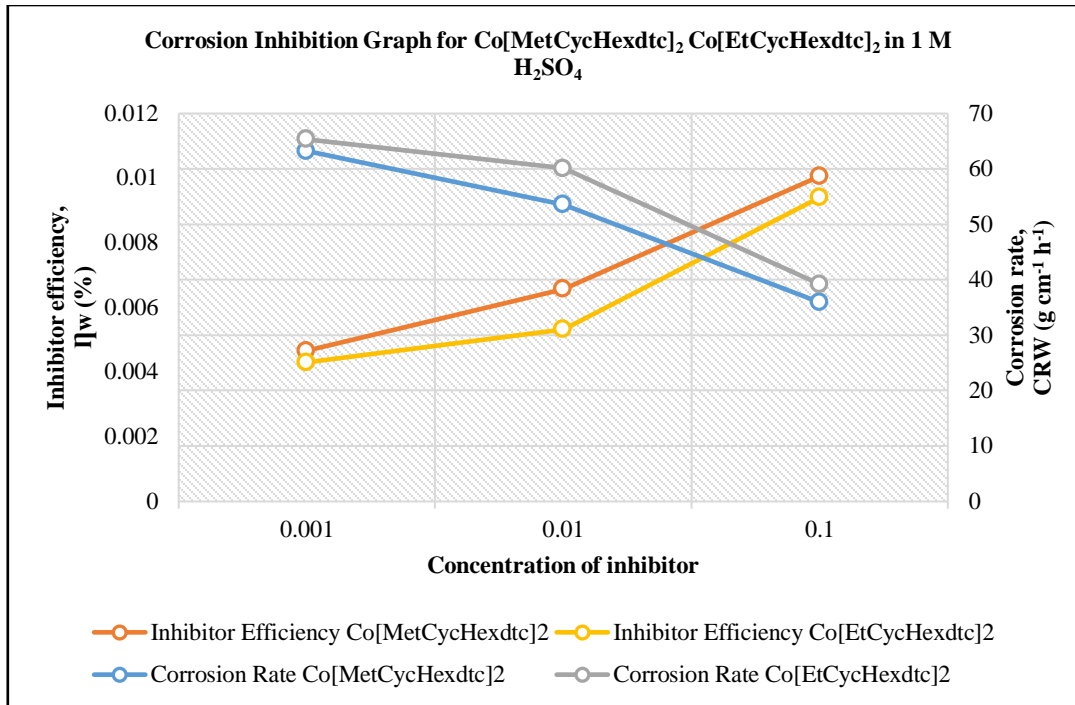
Figure 3. Inhibitor efficiencies of Co[MetCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ in 1 M H$_2$SO$_4$.
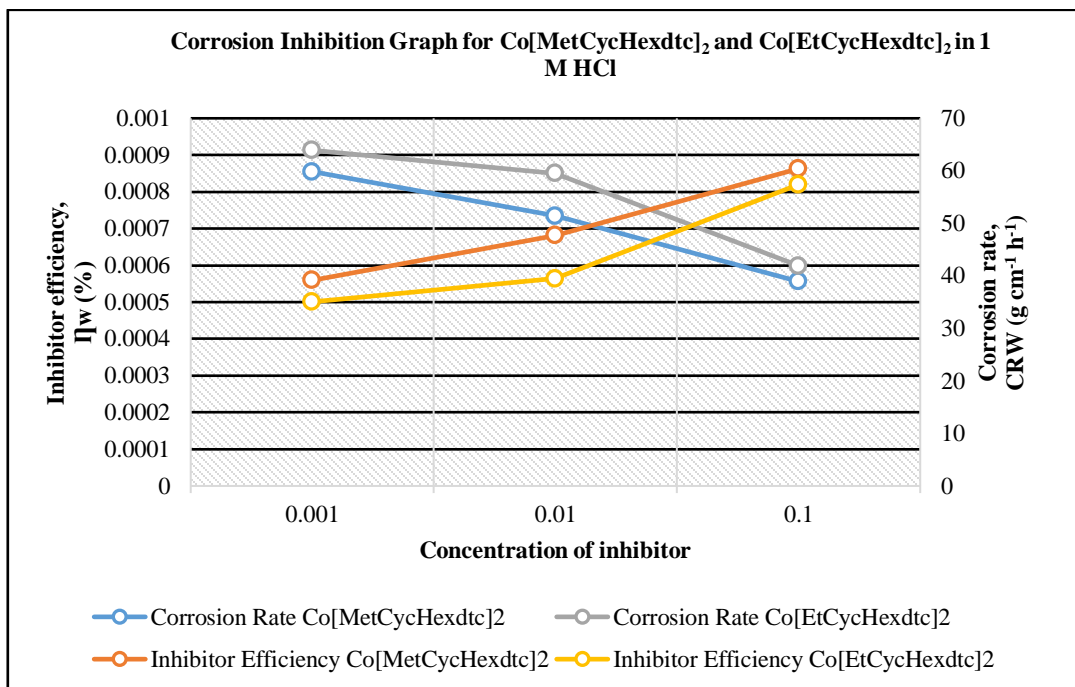

Figure 4. Inhibitor efficiencies of Co[MetCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ in 1 M HCl.

Table 4. Data of corrosion inhibition screening in different concentration of Co(II) complexes in 1 M HCl

Inhibitor	Concentration (M)	Weight Loss, ΔW (g)	Corrosion rate, C_{RW} (g cm^{-1} h^{-1})	Inhibitor efficiency, η_w (%)
Blank	1	0.2023	1.40×10^{-3}	-
Co[MetCycHexdtc]$_2$	0.1	0.0801	5.56×10^{-4}	60.41
	0.01	0.1058	7.35×10^{-4}	47.70
	0.001	0.1231	8.55×10^{-4}	39.15
Co[EtCycHexdtc]$_2$	0.1	0.0862	5.99×10^{-4}	57.39
	0.01	0.1224	8.50×10^{-4}	39.50
	0.001	0.1314	9.13×10^{-4}	35.05

Table 5. Data of corrosion inhibition screening in different concentration of Co(II) complexes inhibitor in 1M H$_2$SO$_4$

Inhibitor	Concentration (M)	Weight Loss, ΔW (g)	Corrosion rate, C_{RW} (g cm^{-1} h^{-1})	Inhibitor efficiency, η_w (%)
Blank	1	2.1449	1.49×10^{-2}	-
Co[MetCycHexdtc]$_2$	0.1	0.8865	6.16×10^{-3}	58.67
	0.01	1.3229	9.18×10^{-3}	38.32
	0.001	1.5615	10.84×10^{-3}	27.20
Co[EtCycHexdtc]$_2$	0.1	0.9684	6.72×10^{-3}	54.85
	0.01	1.4784	1.03×10^{-2}	31.07
	0.001	1.6065	1.12×10^{-2}	25.10

Conclusion

In conclusion, both Co(II) complexes, Co[MeCycHexdtc]$_2$ and Co[EtCycHexdtc]$_2$ were successfully synthesised with in-situ method with a molar ratio of 2:2:1 (carbon disulphide:amine derivatives:metal salt) under cold condition. The Co(II) complexes were characterised by using FTIR-ATR, UV-Vis, molar conductivity, and gravimetric analysis to prove the coordination and functional groups of the compounds in the complexes. The FTIR-ATR data showed the presence of a strong stretching band of $\upsilon(C\dot{=}N)$ and a new thioureide band of $\upsilon(C\dot{=}S)$ in both Co(II) complexes. Thus, the infrared spectra data for both Co(II) complexes confirmed as a bidentate dithiocarbamate ligand behavior as its dithiocarbamate ligand and its symmetrical chelation to the metal ion through both of the sulphur atoms. In UV-Vis analysis, the shifting of the transition of π-π^* to the higher wavelength from raw material to the Co(II) complexes indicated the coordinating effect of the dithiocarbamate ligands to the metal ion in both Co(II) complexes. Based on the results obtained from the corrosion inhibition study, it can be conclusively said that the higher the concentration of the inhibitor, the greater is the corrosion inhibitor competency. Finally, after comparing HCl and H$_2$SO$_4$, it was proved that H$_2$SO$_4$ is a stronger acid compared to HCl due to its higher rate of corrosion. This is because, H$_2$SO$_4$ has two protons compared to HCl that only has one.

Acknowledgement

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