International Journal of Engineering & Technology, 7 (4.42) (2018) 102-106

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Characterization and Anti-Corrosion Study on Different Substituents of Ni(Ii) Dithiocarbamate Complexes

S. R. Mohd Zambri, N. S. Habdul Latif, N. N. Mohd Zulkamal Punnia, S. A. I. Sheikh Mohd Ghazali and N. N. Dzulkifli*

Faculty of Applied Science, Universiti Teknologi MARA, Kuala Pilah, Negeri Sembilan, Malaysia
**Corresponding author E-mail: nurnadia@ns.uitm.edu.my*

Abstract

Dithiocarbamate is a ligand that can act as a corrosion inhibitor due to the presence of sulphur and nitrogen atoms. Ni(II) *N*-methylcyclohexyl dithiocarbamate, Ni[MeCycHexdtc]$_2$ and Ni(II) *N*-ethylcyclohexyldithiocarbamate, Ni[EtCycHexdtc]$_2$ complexes were synthesized through direct synthetic method at room temperature and characterized using the Elemental Analyzer (CHNS), Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR), Ultraviolet-Visible (UV-Vis), Nuclear Magnetic Resonance (NMR), molar conductivity, and gravimetric analysis. The Ni[MeCycHexdtc]$_2$ complex had indicated a square planar geometry, but it was not the case for the Ni[EtCycHexdtc]$_2$ complex which showed a tetrahedral geometry. The efficiency of the synthesized inhibitors was studied in different concentrations; 0.001 M, 0.01 M, and 0.1 M (1 M HCl and 1 M H_2SO_4) at room temperature.

Keywords: *concentration; corrosion in hibitor; dithiocarbamate; mild steel; acid.*

1. Introduction

Schiff bases or imines are carbonyl group compounds of an aldehyde or a ketone which has been replaced by an imine or azomethine group [1]. It is represented by the general formula $R_1R_2C{=}NR_3$, where R can be a substituent. Metal dithiocarbamate complexes are widely studied due to their metal binding property and chelates which play a crucial part in the biological, agricultural, and industrial fields [2]. Dithiocarbamates are sulphur-nitrogen containing ligands that exhibit a rich and varied coordination chemistry. They also provide a wide range of transition and main group metal complexes [3]. Dithiocarbamate is a versatile class of monoanionic 1,1-dithio ligand which forms stable complexes with transition and non-transition metal ions and shows a variety of coordination modes [4]. The possession of two donor sulphur atoms in the ligand greatly influences the chelating properties of dithiocarbamate [5]. It has been proven that Ni(II) dithiocarbamate complexes display stimulating variations in reaction to soft Lewis bases like phosphines and hard nitrogenous bases [6]. There are different coordination modes for dithiocarbamate complexes including bidentate, anisodentate and monodentate. The synthesis structure of Ni(II) dithiocarbamate complexes lies on the bidentate mode due to the coordination of the Ni atom to four sulphur atoms of ligands.

Mild steel is used in trials for corrosion analysis. Mild steel is one of the essential engineering tools due to its low cost and excellent mechanical property which cause it to be broadly used as a construction material in many industries. As mild steel may be brutally attacked by acid solutions used in various industries, inhibited acid solutions are frequently used in place in order to reduce corrosion due to voluntary or involuntary attack by the acid on metals [7]. Here, a study on the anti-corrosion screening of metal dithiocarbamate complexes will be conducted to evaluate the effectiveness of anti-corrosion agents in an acidic medium to prevent severe corrosion, especially for metals used in industries. The hypothesis of anti-corrosion screening emphasizes that as the inhibitor concentration increases, the inhibition efficiency on mild steel also increases.

The objectives of the study are focused on synthesizing Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$ complexes and characterizing these complexes using the Ultraviolet-Visible (UV-Vis), Elemental Analyzer (carbon, hydrogen, nitrogen and sulphur), Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR), molar conductivity, and gravimetric analysis.

2. Results and Discussion

2.1. Physical Measurements

The physical characteristics of the synthesized inhibitors, Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$ are shown in Table 1. There are differences in terms of colour, gravimetric analysis, melting point, molar conductivity and elemental analysis (CHNS). Gravimetric analysis was conducted to investigate the metal percentage of the synthesized inhibitors. The analysis was carried out with temperatures ranging from room temperature to 600 °C. Molar conductivity was conducted at 1 x 10^{-3} M. Both complexes were neutral complexes as the molar conductivity for both using 25 mL of DMSO solvent were in the range of non-electrolyte complexes. The percentages of carbon, nitrogen, hydrogen, and sulphur were determined using an elemental analyser for both Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$. The proposed structures for the synthesized inhibitors, Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$ are tabulated in Table 2.

Table 1: Physical characteristics of synthesized inhibitors

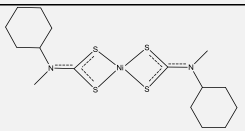
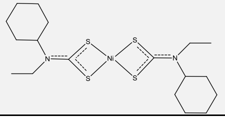
Complexes	Color	% yield	% metal	MP	MC (µS/cm)	Elemental analysis (calculated)			
						C	H	N	S
Ni[MeCycHexdtc]$_2$	Dark green	80.1	12.8 (13.5)	> 300	2.0	44.16 (44.16)	6.62 (6.43)	6.47 (6.43)	29.91 (29.48)
Ni[EtCycHexdtc]$_2$	Pale green	83.2	12.25 (12.67)	> 300	1.8	46.67 (46.68)	7.14 (6.90)	5.55 (6.05)	27.31 (27.7)

*( ) = calculated value.

*MP = melting point.

*MC = molar conductivity.

Table 2: Proposed structures of synthesized inhibitors

Name	Structures
Ni[MeCycHexdtc]$_2$	
Ni[EtCycHexdtc]$_2$	

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

Table 3 shows the selected FTIR-ATR stretching bands for the starting materials and complexes. The FTIR-ATR spectra were recorded at a range of 650 to 4000 cm^{-1}. The dithiocarbamate had three main regions where the v(C-N) of the NCS region ranged from 1580-1450 cm^{-1}, v(C-S) of S-C=S was around 1060-940 cm^{-1} and M-S arose at the range of 420-250 cm^{-1} [8]. The stretching band of v(C-N) was 1449 cm^{-1} for both *N*-MeCycHex and *N*-EtCycHex. The $v(C\overset{\cdots}{-}N)$ that appeared at 1470-1500 cm^{-1} was assigned as a thioureide band [9]. A sharp and narrow stretching band from the complexes showed the peaks of $v(C\overset{\cdots}{-}N)$ at 1497 cm^{-1} (Ni[MeCycHexdtc]$_2$) and 1485 cm^{-1} (Ni[EtCycHexdtc]$_2$) due to its partial double bond character. The band appeared at a greater wavenumber due to the delocalisation of electrons towards the centre metal after being coordinated with the dithiocarbamate ligands [8]. The region of v(C=S) of CS$_2$ was shown at the peak of 1541 cm^{-1}, while for Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$, the bands of $v(C\overset{\cdots}{-}S)$ were at 1008 cm^{-1} and 1006 cm^{-1}, respectively. This condition proved the structure of Ni(II) complexes in which the stretching band shifted to a lower wavenumber due to the decrease of the carbon-sulphur double bond character to a partial double bond character. The decline of wavenumber at about 100 cm^{-1} verified the fact that the dithiocarbamate ligand had bonded to the metal ion through the S atom [10].
The stretching band of v(N-H) disappeared at both complexes after the hydrogen from the amine was deprotonated by ammonia as tabulated in Table 3. The infrared absorption spectra of the metal dithiocarbamate complexes were verified to be a vital element in the analysis of the coordination mode of the monodentate or bidentate of the dithiocarbamate ligands. The v(C-S) band detected at 1012 cm^{-1} was designated as a bidentate chelating mode of the ligand towards the metal cation [11]. In general, the presence of only one band in the 1000 ± 70 cm^{-1} region is attributed to its bidentate character. Meanwhile, the splitting of the same band in the same region is attributed to its monodentate character [12]. The bidentate character of Ni complexes was also reported with the observation of a single peak in that region: 1008 cm^{-1} (Ni[MeCycHexdtc]$_2$) and 1004 cm^{-1} (Ni[EtCycHexdtc]$_2$).

Table 3: Selected FTIR-ATR absorption for starting materials and metal complexes, cm^{-1}

Compound	Wavenumber, cm^{-1}					
	v(C-H)	v(N-H)	v(C=S)	$v(C\overset{\cdots}{-}S)$	v(C-N)	$v(C\overset{\cdots}{-}N)$
Carbon disulphide, CS$_2$	-	-	1541	-	-	-
N-MeCycHex	2926, 2852, 2789	3281	-	-	1449	-
N-EtCycHex	2927, 2853	3281	-	-	1449	-
Ni[MeCycHexdtc]$_2$	2935	-	-	1008	-	1497
Ni[EtCycHexdtc]$_2$	2940	-	-	1006	-	1484

2.3. Ultraviolet-Visible (UV-Vis)

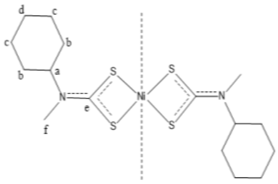
The electronic spectra showed the transitions that appeared in both complexes at the range of 200-500 nm. At region 320 nm (n-π* transition), the absorption peak showed a sulphur atom character due to its non-bonding electron. However, it tended to disappear, indicating a bidentate linkage between the ligand with a metal ion. This might be due to the bonding between carbon and sulphur which formed a double bonding to partial bonding. The π-π* transition in the complexes at 260 nm showed $(S\overset{\cdots}{-}C\overset{\cdots}{-}S)$ and $(S\overset{\cdots}{-}C\overset{\cdots}{-}N)$ chromophores which were not observed in the complexes. The absorption peak of amine to complexes shifted to a higher wavelength. There was a new absorption peak, thus showing that the *d-d* transition existed in both complexes and proving that the complexes were successfully formed.

2.4. Nuclear Magnetic Resonance (NMR)

A complete list of ^{1}H NMR and ^{13}C NMR data of the synthesized inhibitor, Ni[MeCycHexdtc]$_2$, is summarised in Table 4. The ^{1}H NMR statistics provide the formation of synthesized inhibitors as specified by the presence and integration of C-H protons of the dithiocarbamate groups [13]. The ^{1}H NMR spectrum of Ni[MeCycHexdtc]$_2$ displayed a singlet at 3.01 ppm corresponding to the methyl proton (-CH$_3$). The CH$_3$ proton attached to the nitrogen still appeared upfield due to its proton integration corresponding to the three which were better shielded [14]. The Ni[MeCycHexdtc]$_2$ complex was recognised as a square planar complex due to the diamagnetic characteristic of its nickel(II) atom. This was proven by the outcome from ^{1}H NMR where the cyclo compound (-CH$_2$) was found from regions 1.05 ppm to 1.79 ppm, while the hydrogen at –CH in the cyclo compound was found from regions 4.17 ppm to 4.23 ppm. The presence of the nitrogen atom caused the hydrogen that was attached to the carbon to be de-shielded to downfield. The nitrogen atom was attracted towards the carbon atom due to its electron-drawing effect, thus reducing the electron density of the proton that was attached to the carbon [15].

The ^{13}C NMR spectrum of Ni[MeCycHexdtc]$_2$ was also consistent with its structure. There were very intense peaks at the 3.32 ppm region which proved the existence of the DMSO solvent in ^{13}C NMR. Moreover, in ^{13}C NMR, there were only six peaks, which means that the amount of carbon in the Ni[MeCycHexdtc]$_2$ complex was symmetrical. The ^{13}C chemical shifts of thioureide carbon atoms were correlated to the π bonding in the NCS_2^-. The chemical shift at the 203.94 ppm region showed the thioureide carbon ($–CS_2$) characteristic. The downfield signal of thioureide carbons was due to the mesomeric shift of electron density from dithiocarbamate moiety towards the metal centre [16]. Whereas, the methyl carbon ($-CH_2$) in $Ni[MeCycHexdtc]_2$ was de-shielded due to the bonding with nitrogen from the thioureide π system, and the signal was observed at 58.83 ppm. Meanwhile, the $Ni[EtCycHexdtc]_2$ complex showed no peak from each carbon which proved its paramagnetic and tetrahedral complex. Therefore, it was impossible to show any peak due to the high spin of the complex.

Table 4: ^1H NMR and ^{13}C NMR of $Ni[MeCycHexdtc]_2$

Complex	Signal position (δ ppm)	Compound	Structure
^1H NMR	1.05-1.79 (m)	$-CH_2$ (cyclo)	
	3.01 (s)	-CH3	
	4.17-4.23 (m)	-CH (cyclo)	
^{13}C NMR	24.93-25.33 (s)	-CH2 (c and b)	
	29.03 (s)	-CH2 (d)	
	31.89 (s)	-CH2 (d)	
	58.83 (s)	-NCH (a)	
	203.94 (s)	-CS2 (e)	

2.5. Corrosion Inhibition Study

The effect of the addition of synthesized inhibitors at different concentrations on the corrosion of mild steel in 1 M HCl and 1 M H_2SO_4 solution was studied using the weight loss method at room temperature after 24 hours of immersion [17]. Different concentrations of synthesized inhibitors were also studied in acidic mediums of 0.001 M, 0.01 M, and 0.1 M. The corrosion rate (C_{RW}) and inhibition efficiency (η_w) in the absence and presence of various concentrations of inhibitors are presented in Tables 5 and 6. The initial and final weight of mild steel in the acid immersion was compared to examine the C_{RW} and η_w of the synthesized inhibitors. Figures 1 and 2 show that different concentrations of inhibitors had influenced the inhibitor efficiency in 1 M HCl and 1 M H_2SO_4. The calculated values of η_w of the synthesized inhibitors indicated that η_w increased with increases in inhibitor concentration, with a maximum η_w of 26.0 % and 16.4 % in 1 M HCl for $Ni[MeCycHexdtc]_2$ and $Ni[EtCycHexdtc]_2$, respectively. Meanwhile, in 1 M H_2SO_4, there was a maximum η_w of 45.0 % and 51.6 % respectively using the 0.1 M inhibitor concentration.

The corrosion inhibition of $Ni[MeCycHexdtc]_2$ and $Ni[EtCycHexdtc]_2$ in 1 M HCl and 1 M H_2SO_4 can be explained in terms of adsorption of its molecules on the surface of the mild steel [17]. This enhancement is due to the carbon and oxygen atoms of the adsorbed compound which supported the absorption of the Schiff base onto the surface of the mild steel to slow down corrosion [18]. Figure 3 shows that in 1 M HCl, $Ni[MeCycHexdtc]_2$ is more efficient than $Ni[EtCycHexdtc]_2$. The corrosion activity in H_2SO_4 is higher than HCl because of the presence of high concentrations of H^+ in H_2SO_4 which makes it more corrosive compared to HCl [19]. H_2SO_4 is highly corrosive as emphasized by its highly exothermic (heat generating) reaction with water [20]. The formulas for corrosion rate, C_{RW} and inhibitor efficiency, η_w are shown below:

$$\Delta W = w_1 - w_2 \tag{1}$$

$$C_{RW} = \frac{\Delta W}{s \times t} \tag{2}$$

$$\Theta = \frac{C^0_{RW} - C_{RW}}{C^0_{RW}} \tag{3}$$

$$\eta_W = \frac{C^0_{RW} - C_{RW}}{C^0_{RW}} \times 100\% \tag{4}$$

Where:

W_1 = The initial weight of mild steel before immersion (g).
W_2 = The final weight of mild steel after immersion (g).
ΔW = The weight loss (g).
S = Surface area of the mild steel (cm).
T = Time of immersion (h).
C_{RW} = The corrosion rate in the presence of inhibitor (g cm^{-2} h^{-1}).
$C°_{RW}$ = The corrosion rate in the absence of inhibitor (g cm^{-2} h^{-1}).
η_w = The percentage of inhibitor efficiency (%).

Table 5: Corrosion inhibitor data using 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	0.134	9.31×10^{-4}	-
$Ni[MeCycHexdtc]_2$	0.1	0.098	6.81×10^{-4}	26.9
	0.01	0.114	7.92×10^{-4}	14.9
	0.001	0.115	1.04×10^{-4}	14.2
$Ni[EtCycHexdtc]_2$	0.1	0.112	7.78×10^{-4}	16.4
	0.01	0.114	7.92×10^{-4}	14.9
	0.001	0.116	8.056×10^{-4}	13.5

Table 6: Corrosion inhibitor data using 1 M H_2SO_4

Inhibitor	Concentration (M)	Weight loss, ΔW (g)	Corrosion rate, C_{RW} (g cm^{-1} h^{-1})	Inhibitor efficiency, η_w (%)
Blank	1	0.741	5.146×10^{-3}	-
$Ni[MeCycHexdtc]_2$	0.1	0.407	2.83×10^{-3}	45.0
	0.01	0.501	3.48×10^{-3}	32.4
	0.001	0.502	3.49×10^{-3}	32.2
$Ni[EtCycHexdtc]_2$	0.1	0.358	2.49×10^{-3}	51.6
	0.01	0.468	3.25×10^{-3}	36.8
	0.001	0.658	4.569×10^{-3}	11.2

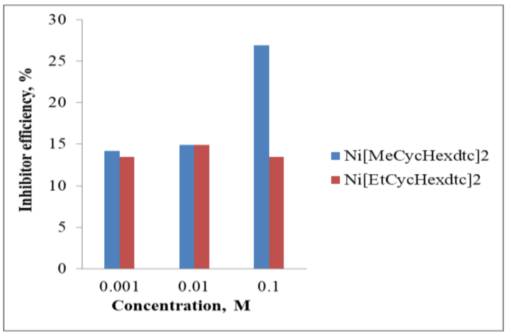


Fig. 1: Graph of concentration of inhibitors, M versus inhibitor efficiency, % in 1 M HCl

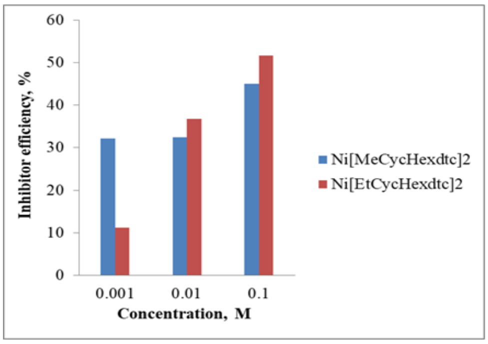


Fig. 2: Graph of inhibitor concentration, M versus inhibitor efficiency, % in 1 M H_2SO_4

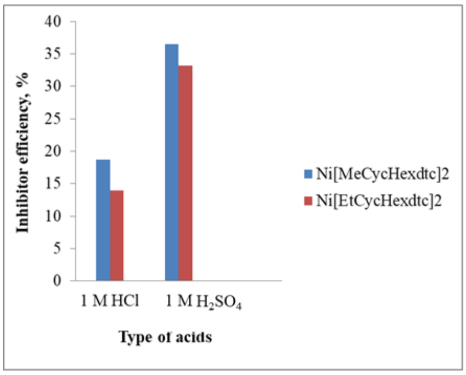


Fig. 3: Comparison graph of acid type versus inhibitor efficiency between 1 M HCl and 1 M H_2SO_4

3. Experimental

3.1. General Methods

The infrared spectra were determined using the mid-infrared Fourier Transform Infrared- Attenuated Total Reflectance (FTIR-ATR) Perkin Elmer model GX Spectrophotometer at a range of 4000-600 cm^{-1}. The electronic absorption spectra were studied using the Ultraviolet-Visible (UV-Vis) PG instrument T80/T80+ spectrophotometer at a range of 200-800 nm with methanol as a solvent. ^1H and ^{13}NMR spectra were dignified by the JEOL JNM-ECP 400 MHz Nuclear Magnetic Resonance (NMR) spectroscopy. The elemental analyser model Flash EA110 was used to determine the percentages of carbon, nitrogen, hydrogen, and sulphur in the complexes. The percentage of metal was acquired using the SI analytic Lab 970 Conductivity meter at a concentration of 1 x 10^{-3} M and using DMSO as a solvent.

3.2 Chemical synthesis

1) Synthesis of Ni(II) complexes

The ratios for amine, carbon disulphide (CS_2), and salt were 2:2:1, respectively. 2 mmol of carbon disulphide was added into 2 mmol of an ethanolic solution of *N*-methylcyclohexylamine (*N*-MeCycHex) in a 250 mL conical flask, and the mixture was stirred at room temperature for 30 minutes. Following that, 5 drops of ammonia were added to the mixture and the stirring was continued for 30 minutes. Then, 1 mmol of an ethanolic solution of nickel (II) nitrate was added to the mixture under continuous stirring for 2 hours in order to ensure the complete synthesis of the complex which allows for the formation of precipitate. The precipitate was collected by filtration and rinsed with hexane. Then, it was dried in a desiccator. The product was then recrystallized to obtain a pure compound and was characterized using the Fourier Transform Infrared- Attenuated Total Reflectance (FTIR-ATR) spectroscopy, Ultraviolet-Visible (UV-Vis) spectrophotometer, CHNS Analyser, and Nuclear Magnetic Resonance (NMR) spectrophotometer. The product was also analysed for its molar conductivity, gravimetric analysis, and corrosion inhibition. The same procedure was repeated for the synthesis of Ni[EtCycHexdtc]$_2$ using another amine, *N*-ethylcyclohexylamine (*N*-EtCycHex).

1) Gravimetric Analysis

0.03 g sample was weighed in a crucible and distilled water was added to hydrate the sample. 9 M of H_2SO_4 was added drop by drop into the sample afterward. The sample was then burnt in a muffle furnace starting from room temperature up to 600 °C. Next, the sample was cooled at room temperature and reweighed. The procedure was repeated until a constant mass was obtained.

2) Molar conductivity

The value of molar conductivity was measured using a DMSO solvent at room temperature at the concentration of 1 x 10^{-3} M. The sample was diluted in 25 mL of DMSO solvent. A probe was inserted into the solution to read the molar conductivity value in µS/cm.

3.3 Corrosion Inhibition Study

1) Preparation of acid and inhibitor solutions

For the corrosion inhibition study, 1 M HCl and 1 M H_2SO_4 were prepared using the formula $M_1V_1 = M_2V_2$. The HCl and H2SO4 were chosen as acid mediums for the anti-corrosion screening to compare the effectiveness of the inhibitor on the corrosion of mild steel under different acidic environments. Different inhibitor concentrations were set; 0.001 M, 0.01 M, 0.1 M, and 1 M.

2) Weight loss technique

Mild steel was selected to be tested in the weight loss analysis. The mild steel was cut into a 2 cm x 3.5 cm rectangular sheet, scraped using emery paper and then rinsed with distilled water, followed by acetone. It was then dried at room temperature. The initial weight of the mild steel was taken using an analytical balance. The mild steel was immersed in 10 mL of 1 M HCl with and without the inhibitor and left immersed for 24 hours at a temperature of 40 °C. Then, the mild steel was rinsed with distilled water, dried at room temperature and reweighed to define the weight loss occurred. The test was repeated for different concentrations of inhibitors; 0.001 M, 0.01 M, and 0.1 M. The whole procedure was also repeated for the 1 M $H_2SO_{4.}$

4. Conclusion

The chemical structure of the synthesized inhibitors, Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$ can be confirmed using the elemental analyzer (CHNS), FTIR-ATR, UV-Vis, NMR, gravimetric analysis and molar conductivity. Additionally, the synthesized inhibitors both showed distinctive bidentate characteristics as supported by the characterization of the complexes. The inhibition performance of Ni[MeCycHexdtc]$_2$ and Ni[EtCycHexdtc]$_2$ on mild steel was investigated using the weight loss method. As a result, it was shown that inhibition efficiency increases with increases in inhibitor concentration. The corrosion rate occurring in 1M H_2SO_4 on the mild steel was superior to 1 M HCl due to its high concentration of H^+.

Acknowledgements

We are grateful to all with whom we had the pleasure to work with during this study. First and foremost, we would like to express our gratitude to the Faculty of Applied Sciences, Universiti Teknologi MARA Kuala Pilah, Negeri Sembilan, Malaysia (UiTM) for providing the facilities and financial support. Our deepest gratitude also goes to the Head of Programme of B. Sc. (Hons.) Chemistry of UiTM Kuala Pilah.

References

[1] Silva D L, Modolo L V, Alves R B, De R M A, Martins C V B, De F A. (2011). J. Adv. Res. 2(1), 2011, 1-8, https://doi.org/10.1016/j.jare.2010.05.004

[2] Sathiyaraj E, Selvaganapathi P, Thirumaran S, and Ciattini S. Synthesis, spectral, structural and computational studies on NiS_4 and NiS_2NP chromophores: Anagostic and C–H···π (chelate) interactions in [Ni(dtc)(PPh_3)(NCS)] (dtc = *N*-(2-phenylethyl)-*N*-(4-methoxybenzyl)dithiocarbamate and *N*-(2-phenylethyl)-*N*-(4-chlorobenzyl)dithiocarbamate). J. Mol. Struct., 2016, 1119: 385–395

[3] Awang N, Kamaludin N F, Baba I, Chan K M, Rajab N F, and Hamid A. Synthesis, Characterization and Antitumor Activity of New Organotin (IV) Methoxyethyldithiocarbamate Complexes. Orient. J. Chem., 2016, 32(1): 101–107

[4] Dar S H, Thirumaran S, and Selvanayagam S. Synthesis, spectral and X-ray structural studies on Hg(II) dithiocarbamate complexes: A new precursor for HgS nanoparticles. Polyhedron., 2015, 96:16–24

[5] Kamaludin N F, Awang N, Baba I, Hamid A, and Meng C K. Synthesis, characterization and crystal structure of organotin(IV) *N*-butyl-*N*-phenyldithiocarbamate compounds and their cytotoxicity in human leukemia cell lines. Pak. J. Biol. Sci., 2013, 16(1): 12–21

[6] Arul B, Peuronen A, and Lahtinen M. Synthesis and structural studies on Ni (II) dithiocarbamates : Exploring intramolecular Ni Á Á Á H – C interactions. Polyhedron., 2017, 123:453–461

[7] Ansari K R, and Quraishi M A. (2014). Bis-Schiff bases of isatin as new and environmentally benign corrosion inhibitor for mild steel. J. Ind. Eng. Chem., 2014, 20(5):2819–2829

[8] Ajibade P A, and Ejelonu B C. Group 12 dithocarbamate complexes: Synthesis, spectral studies and their use as precursors for metal sulfides nanoparticles and nano composites. Spectrochim. Acta A. Mol. Biomol. Spectrosc., 2013, 113:408-414

[9] Abdul Mutalib A F, Baba I., Farina Y, and Samsudin M W. Synthesis and characterization of diphenyltin(IV) dithiocarbamate compounds. Anal. Sci., 2011, 15(1):106-112

[10] Onwudiwe D C, and Ajibade P A. Schiff base and non-Schiff base macrocyclic ligands and complexes incorporating the pyridine moiety-The first 50 years. Coord. Chem. Rev., 2010, 280:203-253

[11] Tamilvanan S, Gurumoorthy G, Thirumaran S, and Ciattini S. Synthesis, characterization, cytotoxicity and antimicrobial studies on Bi(III) dithiocarbamate complexes containing furfuryl group and their use for the preparation of Bi_2O_3 nanoparticles. Polyhedron., 2017, 121:70–79

[12] Hidayah N, Zainal Z, and Silong S. Synthesis of zinc sulphide nanoparticles from thermal decomposition of zinc *N*-ethyl cyclohexyl dithiocarbamate complex. Mater. Chem. Phys., 2016, 173:33–41

[13] Al-jaroudi S S, Altaf M, Seliman A A, Yadav S, Arjmand F, Alhoshani A, … and Isab A A. Synthesis, characterization, in vitro cytotoxicity and DNA interaction study of phosphanegold (I) complexes with dithiocarbamate ligands. Inorg. Chim. Acta., 2017, 464:37–48

[14] Sivasekar S, Ramalingam K, Rizzoli C, and Alexander N. Synthesis, structural, Continuous Shape Measure and bond valence sum characterization of bismuth(III) complexes of substituted dithiocarbamates and their solvothermal decomposition. Inorg. Chim. Acta., 2014, 419:82–88

[15] Pavia D L, Lampman G M, Kriz G S, and Vyvyan J R. Introduction to spectroscopy. Cengage Technology Edition, 2015, pp15-43.

[16] Sonia A S, and Bhaskaran R. Tris dithiocarbamate of Co(III) complexes: Synthesis, characterization, thermal decomposition studies and experimental and theoretical studies on their crystal structures. J. Mol. Struct., 2017, 1134:416–425

[17] Zarrouk A, Zarrok H, Ramli Y, Bouachrine M, Hammouti B, Sahibed-dine A, and Bentiss F. Inhibitive properties, adsorption and theoretical study of 3,7-dimethyl-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one as efficient corrosion inhibitor for carbon steel in hydrochloric acid solution. J. Mol. Liq., 2016, 222:239–252

[18] Elemike E E, Onwudiwe D C, Nwankwo H U, and Hosten E C. Synthesis, crystal structure, electrochemical and anti-corrosion studies of Schiff base derived from o-toluidine and o-chlorobenzaldehyde. J. Mol. Struct., 2017, 1136:253–262

[19] Samina M, Karim A, and Venkatachalam A. Corrosion study of iron and copper metals and brass alloy in different medium. E-J. Chem., 2011, 8:344-349

[20] Hagen M, Van Der, and Järnberg J. Sulphuric, hydrochloric, nitric and phosphoric acids (Vol. 43) 2009.