

# Ni(II) Butylmethylthiocarbamate: Physico-Chemical Properties, X-Ray Crystallography, DFT and Anti-Corrosion Screening in Different Acids

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In industrial sectors, pickling and acid cleaning are mutual processes where acid solutions, such as hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), are used to eliminate the corrosion products yielded on metal surfaces; thus, improving the performance of the machineries. However, the usage of the acid could lead to another metal deterioration. Dithiocarbamate inhibitor is defined as an organic compound that has good corrosion inhibition properties that can work as an inhibitor in an acid environment. Dithiocarbamate (DTC) assists by reducing acid reactivity which prohibits metal dissolution in the acid. In this study, the Ni(II) *N*-butylmethylthiocarbamate (Ni[BuMedtc]<sub>2</sub>) complex was synthesised by using an in-situ method and characterised by elemental analyser, attenuated total reflection Fourier transform infrared (ATR-FTIR), ultraviolet-visible (UV-Vis) spectroscopy and X-ray crystallographic study, and the chemical properties of the Ni[BuMedtc]<sub>2</sub> complex was successfully calculated by the Discrete Fourier Transform (DFT) approach. The experimental results which were obtained through the weight-loss analysis method in two different acids – 1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> – indicated that the inhibition efficiency increased as the inhibitor concentration increased. The outcome showed that the Ni[BuMedtc]<sub>2</sub> performed better as an inhibitor in 1 M HCl as compared to in 1 M H<sub>2</sub>SO<sub>4</sub> to protect the metal exterior because H<sub>2</sub>SO<sub>4</sub> is more corrosive due to the excessive presence of H<sup>+</sup>.

**Keywords:** corrosion inhibitor; concentration; dithiocarbamate

## I. INTRODUCTION

Corrosion is a condition where a metal undergoes deterioration and loses its critical possessions due to chemical, electrochemical and other reactions of the exposed surface. Extreme corrosion occurs especially during the cleaning process when corrosive acids are used. Increasing economic loss due to metal corrosion is a major concern in the industrial sector. A convenient approach to address the problem of metal corrosion is by the application of organic corrosion inhibitors. Furthermore, to use organic corrosion inhibitors is the most effective and economical

method among all anticorrosive ways (Qiang *et al.*, 201). Corrosion inhibitor plays an important role in handling industrial metal corruptions. It can prevent metal dissolution and reduce acid consumption (Soltani *et al.*, 2016). As reported, various types of organic compounds act as corrosion inhibitors and contain multiple bonds in their structures that mainly contain nitrogen (N), sulfur (S) or oxygen (O) atoms (Hong-bo *et al.*, 2002, Hebbar *et al.*, 2014). High electron density on the heteroatoms, such as N, O, and S, has a high tendency to resist corrosion due to the

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strong tendency of N and S to share electrons with metal to form ring chelates (Liu *et al.*, 2019). Figure 1 shows the general structure of DTC. In recent years, DTC complex is widely applied in various areas, such as manufacturing, agricultural and biological activities (Kanchi *et al.*, 2014; Szolar, 2007). DTC is known as a versatile ligand due to its ability to form complexes with almost all elements and stabilise a variety of oxidation states of transition metals (Kamaludin *et al.*, 2013; Nabipour *et al.*, 2010). Dithiocarbamates are characterised with the partial double bond character of C-N and C-S of thioureide moiety (Andrew & Ajibade 2018). In this study, the synthesis and characterisation of Ni[BuMedtc]<sub>2</sub> complex was investigated to evaluate the complex's potency as a corrosion inhibitor, whereas the chemical properties of the Ni[BuMedtc]<sub>2</sub> complex calculated by DFT method was evaluated.

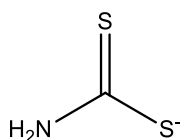


Figure 1. The structure of DTC

## II. MATERIALS AND METHODS

### A. Material and Physical Measurement

The chemicals used were purchased from Sigma Aldrich and used without purification. The melting point was determined in capillary tube by using a melting point apparatus, namely the SMP10 Stuart model. Elemental analysis of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) of the Ni[BuMedtc]<sub>2</sub> complex was carried out with Elemental Fison EA 1108 CHNS-O analyser. The FTIR-ATR spectra were recorded on ATR plate disc by using Perkin Elmer model GX spectrophotometer in the range of 4000-650 cm<sup>-1</sup> at room temperature. The electronic spectra were measured by PG instrument T80/T80+ spectrophotometer in the region of 200-600 nm by using DMSO as a solvent. Gravimetric analysis was done by using a Lindberg/Blue furnace with temperatures that ranged from room temperature to 600°C. Molar conductivity value was

measured at room temperature by using SI Analytic Lab 970 conductivity meter at the concentration of 2 x 10<sup>-3</sup> M with DMF as a solvent. X-ray crystallography study was executed on a Bruker Apex II CCD diffractometer at 0 K. The structure and bonding properties of the Ni[BuMedtc]<sub>2</sub> complex were studied by using DFT calculations.

### B. Synthesis of Ni[BuMedtc]<sub>2</sub> Complex

Ni[BuMedtc]<sub>2</sub> complex was synthesised by using in-situ method at 277 K in ethanol. 2 mmol carbon disulfide (CS<sub>2</sub>) was added into 3 mmol *N*-butylmethylamine and stirred for 1 h. Next, 1 mmol Ni(II) nitrate solution was added dropwise into the mixture and continued with another 1 h of stirring to obtain a green precipitate. The precipitate was then filtered and washed by using ethanol and dried in a desiccator. The recrystallisation of the product was done in the mixture of ethanol and chloroform with a ratio of 1:3.

### C. Recrystallisation and X-ray Crystallography Study

Recrystallisation process was carried out by dissolving the complex in ethanol (EtOH) and chloroform (1:3 v/v). The crystallographic study was collected by the detector diffractometer (Mo K $\alpha$  = 0.71076 Å) on a crystal with a size range of 3.046 <  $\theta$  < 25.095.

### D. Weight Loss Measurements

Mild steel specimens of (2 x 3.5) cm<sup>2</sup> in dimensions were polished by using an emery paper and washed with distilled water, followed with acetone and then dried at room temperature. The specimens were weighed before and after the immersion in 10 mL of 1M HCl and H<sub>2</sub>SO<sub>4</sub> for 24 h in the absence and presence of various concentrations of the inhibitor at 40 °C. The percentage inhibition efficiency was calculated by:

$$\% \eta_w = \frac{W_1 W_2}{s t} \times 100$$

Where, W<sub>1</sub> and W<sub>2</sub> are the weight loss in the absence and presence of the inhibitor, respectively, s is the surface area of the mild steel and t is the time taken.

### E. Computational Method

The crystal was optimised in the solution phase using a continuum solvent model (CPCM) based on density functional theory (DFT) at the B3LYP/LANL2DZ level before it was further used to calculate chemical reactivity properties (Latif *et al.*, 2018).

## III. RESULTS AND DISCUSSION

### A. Physical Properties of Ni[BuMedtc]<sub>2</sub> Complex

The Ni[BuMedtc]<sub>2</sub> complex was prepared by using in-situ technique with the ratio of 2:2:1 (CS<sub>2</sub>: amine: Ni(II) salt). The yield of the synthesised complex was high, which was 75% for Ni[BuMedtc]<sub>2</sub>. The general reaction scheme of the

Ni[BuMedtc]<sub>2</sub> complex preparation is shown in Figure 2. The colour of the complex was observed as dark green for Ni[BuMedtc]<sub>2</sub> and was stable at an open atmosphere as well as soluble in dimethylsulfoxide (DMSO), ethanol (EtOH), methanol (MeOH) and tetrahydrofuran (THF), but partially soluble in water (H<sub>2</sub>O). The melting point for the Ni[BuMedtc]<sub>2</sub> complex was higher than 300°C, which occurred due to the formation of covalent bonds in the metal complexes. Meanwhile, the molar conductivity for Ni[BuMedtc]<sub>2</sub> revealed that the complex was a non-electrolyte since the value appeared in the range of 0-30 S cm<sup>2</sup> mol<sup>-1</sup>. The CHNS elemental analysis data showed congruence between the experimental and theoretical values based on the suggested general structures. Table 1 shows the physical properties of Ni[BuMedtc]<sub>2</sub>.

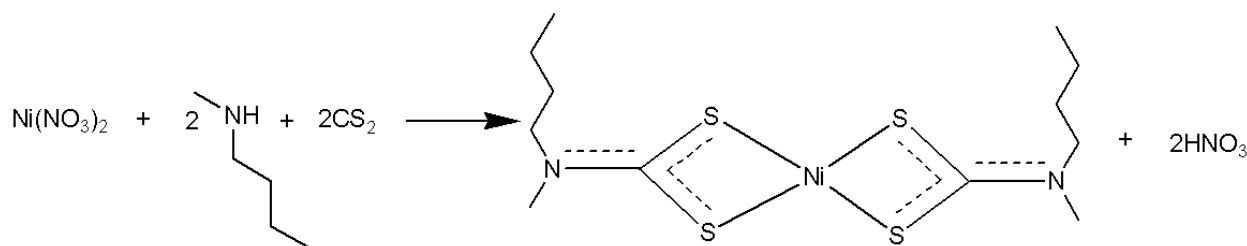


Figure 2. The general reaction scheme of the Ni[BuMedtc]<sub>2</sub> complex

Table 1. Physical characteristics of synthesised inhibitor

Complex	Colour	Yield (%)	MP	MC (S cm <sup>2</sup> mol <sup>-1</sup> )	Elemental analysis (calculated)			
					C	H	N	S
Ni[BuMedtc] <sub>2</sub>	Dark green	75	> 300	2.0	37.60 (37.20)	6.30 (6.44)	7.30 (7.68)	33.46 (33.15)

\* ( ) = calculated value

\*MP = melting point

\*MC = Molar conductivity

### B. IR Spectra

The contrast of vital stretching bands that were obtained from FTIR-ATR spectrophotometer for CS<sub>2</sub>, N-butylethylamine and Ni[BuMedtc]<sub>2</sub> are shown in Figure 3 and listed in Table 2. The Ni[BuMedtc]<sub>2</sub> complex showed an appearance of a strong absorption band at 1518 cm<sup>-1</sup>, which indicated the presence of ν(C=N) band, whereas CS<sub>2</sub> and N-butylethylamine did not contain the absorption. This band is known as a thioureide band which is shown by the partial double bond character that occurred due to the

delocalisation of electron density within the DTC moiety. The ν(C=N) band was a derivative of ν(C-N) band in which only N-butylethylamine that had the absorption recorded at 1498 cm<sup>-1</sup>. The shifting in the thioureide value to a higher wavenumber compared with its raw materials was due to the mesomeric drift of π electron density from the dithiocarbamate ligand moiety towards the Ni that increased in carbon-nitrogen double bond character (Sathiyaraj *et al.*, 2018). The outcome was consistent with a

higher character of double bond between the carbon and nitrogen atom (Antonio *et al.*, 2020). The absorption of  $\nu(\text{C}=\text{S})$  band shown in  $\text{CS}_2$  was at  $1541\text{ cm}^{-1}$ . Meanwhile, a medium stretching band that was detected in the region of  $967\text{ cm}^{-1}$  for the  $\text{Ni}[\text{BuMedtc}]_2$  complex indicated the presence of  $\nu(\text{C}\equiv\text{S})$  band. The  $\nu(\text{C}-\text{S})$  band which appeared around  $967\text{ cm}^{-1}$  directed a symmetrically bidentate coordination of the  $-\text{CS}_2$  group to the Ni metal (Bobinihi *et al.*, 2018). The coordination of ligand to the metal centre was verified, whereby the stretching band shifted to a lower wavenumber due to the reduction of the carbon-sulfur double bond character to partial double bond character. The

absorption of  $\nu(\text{C}\equiv\text{S})$  band of the  $\text{Ni}[\text{BuMedtc}]_2$  complex showed a greater character of single bond between the carbon and sulfur atoms in the  $\text{CS}_2$  group upon complexation. By calculating the number of the splitting of this band, the chelating character of the dithiocarbamate ligand in the complex can be identified (Awang *et al.*, 2010). Based on the results obtained, the  $\text{Ni}[\text{BuMedtc}]_2$  complex possessed a bidentate manner of DTC ligand since there was only a single band present within the region. The absence of  $\nu(\text{N}-\text{H})$  band in the  $\text{Ni}[\text{BuMedtc}]_2$  complex proved that the deprotonation of  $2^\circ$  amines and also proved that coordination occurred between DTC and metal ion.

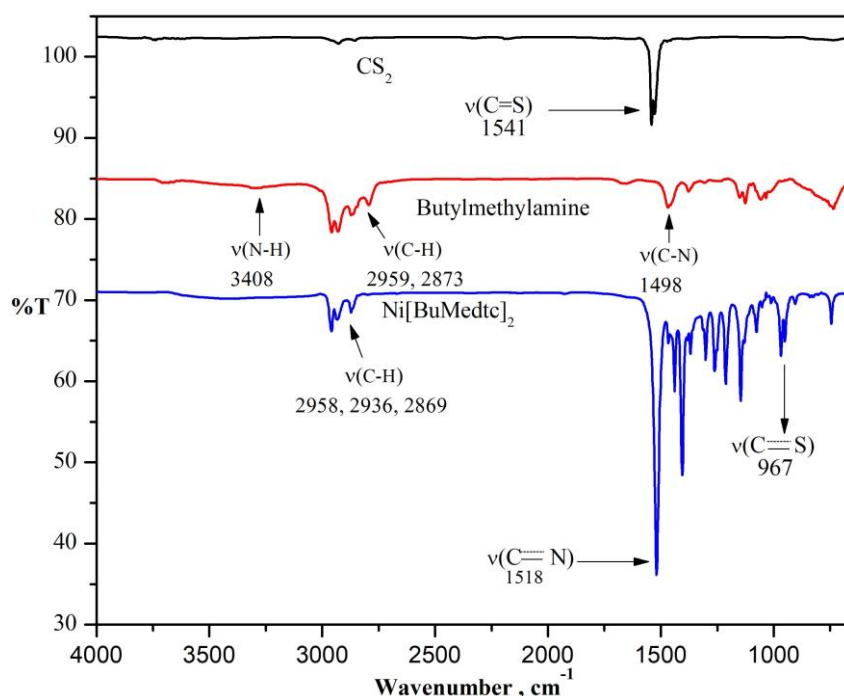


Figure 3. IR spectra of  $\text{CS}_2$ ,  $N$ -butylethylamine and  $\text{Ni}[\text{BuMedtc}]_2$

Table 2. IR spectra data for  $\text{CS}_2$ ,  $N$ -butylethylamine and  $\text{Ni}[\text{BuMedtc}]_2$

Compound	Wavenumber, $\text{cm}^{-1}$					
	$\nu(\text{C}-\text{H})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}=\text{S})$	$\nu(\text{C}\equiv\text{S})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}\equiv\text{N})$
Carbon disulphide, $\text{CS}_2$	-	-	1541	-	-	-
$N$ -butylethylamine	2959,2873	3408	-	-	1498	-
$\text{Ni}[\text{BuMedtc}]_2$	2958, 2936,2869	-	-	967	-	1518

### C. Electronic Spectra

The structure of Ni[BuMedtc]<sub>2</sub> complex can be confirmed by comparing the electronic spectra between the raw materials and the complex as shown in Figure 4. Onwudiwe *et al.* (2016) reported that intra-ligand bands between 205 nm and 280 nm were identified as n-σ\* transition (Onwudiwe *et al.*, 2016). The Ni[BuMedtc]<sub>2</sub> did not show the n-σ\* transition while the CS<sub>2</sub> and *N*-butylethylamine displayed the transition at 235 nm and 241 nm, respectively. The Ni[BuMedtc]<sub>2</sub> spectrum exhibited three distinctive absorption peaks at 325 nm, 380 nm and >400 nm. CS<sub>2</sub> did not contain any transition of π-π\*, but for *N*-

butylethylamine, the transition appeared at 318 nm. The peak appeared at 325 nm for Ni[BuMedtc]<sub>2</sub>, attributed to the π-π\* that moved upward with lower absorbance and had the probability to overlap with n-π\* transition. CS<sub>2</sub> and *N*-butylethylamine did not possess any *d-d* transition. In Ni[BuMedtc]<sub>2</sub> complex, the *d-d* transition was observed as a weak or small absorption peak at above 400 nm because the transition was categorised as a Laporte Forbidden transition. The electronic spectrum of the complex portrayed a weak absorption peak due to *d-d* transition representing a four-coordinated DTC ligand around the Ni(II) ion.

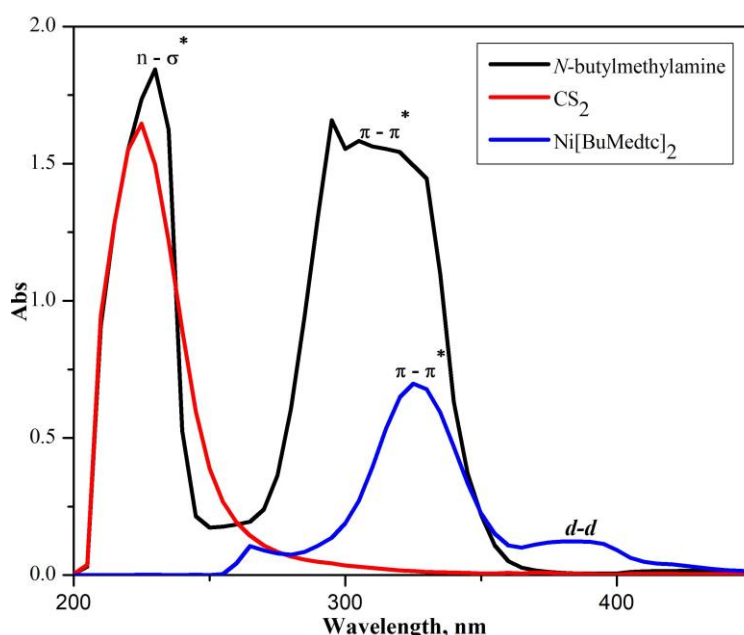


Figure 4. Electronic spectrum of  $1.0 \times 10^{-5}$  M of CS<sub>2</sub>, *N*-butylethylamine and Ni[BuMedtc]<sub>2</sub>

### D. X-ray Crystallographic Study

From the recrystallisation result, it was proven that Ni[BuMedtc]<sub>2</sub> yielded a single crystal structure. Figure 5 shows the ORTEP plot for Ni[BuMedtc]<sub>2</sub>. Figure 5 reveals that the Ni[BuMedtc]<sub>2</sub> complex was a four-coordinated compound in which Ni(II) ion was coordinated to the DTC ligand through thiolate S ion in a bidentate fashion. Ni[BuMedtc]<sub>2</sub> adopted a trigonal system with a space group of R-3 and unit cell; where  $a = 25.544(10)$  Å,  $b = 25.544(10)$  Å,  $c = 7.018(5)$  Å, and  $Z = 9$  (Table 3). Figure 5 shows the 3D structure of Ni[BuMedtc]<sub>2</sub>. From Table 4, the bond length of C-S (1.7144 Å) was between the range of C-S single bond

(1.732(3) Å) and C=S double-bond (1.663(3) Å) (Keter *et al.*, 2014). This proved that there was a presence of partial double-bond character in Ni[BuMedtc]<sub>2</sub>. Meanwhile, the bond length of C-N (1.3113 Å) was shorter as compared to the normal bond length (1.45 Å), which showed the partial double-bond character in this complex. The values of these bond lengths were designated for both C-S and N-C bonds, and alteration of dithiocarbamate with thioureide tautomers in the solid state (El-Sayed *et al.*, 2019). Both bond lengths were in excellent agreement with the  $\nu(\text{C-N})$  and  $\nu(\text{C-S})$  stretching bands, as observed in the IR spectra. Ni(II) dithiocarbamate complexes can be found in two types of

geometries, which are tetrahedral and square planar (Beyramabadi *et al.*, 2012). The X-ray Crystallography structure of Ni[BuMedtc]<sub>2</sub> showed that it adopted a distorted tetrahedral geometry since two four-membered coordinated rings (S(1)-Ni(1)-S(2) = 79.17° and S(1)-Ni(1)-S(2) = 79.17° were perpendicular to each other. Meanwhile, the distortion of Ni atom of 100.83° was slightly different from the ideal tetrahedral geometry, which was 109.5° and proved that Ni[BuMedtc]<sub>2</sub> belonged to distorted tetrahedral geometry. Table 5 shows the bond angle (°) of Ni[BuMedtc]<sub>2</sub>.

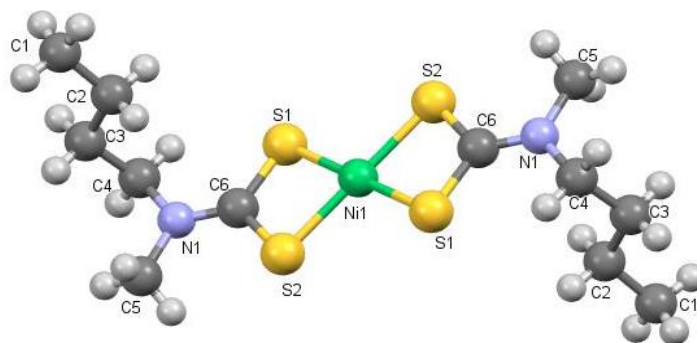


Figure 5. ORTEP plot of Ni[BuMedtc]<sub>2</sub> at the 50% probability level with the atom numbering scheme

Table 3. Crystallographic study of Ni[BuMedtc]<sub>2</sub>

	<b>Ni[BuMedtc]<sub>2</sub></b>
Empirical formula	C <sub>12</sub> H <sub>24</sub> N <sub>2</sub> NiS <sub>4</sub>
Formula weight (g/mol)	383.30
Crystal system	Trigonal
Space group	R-3
<i>a</i> (Å)	25.544 (10)
<i>b</i> (Å)	25.544 (10)
<i>c</i> (Å)	7.018 (5)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	120
<i>V</i> (Å <sup>3</sup> )	3965 (13)
Mo K (Å)	0.71076
<i>Z</i>	9
D/ Mgm <sup>-3</sup>	1.445 (5)
F (ooo)	1818
Color	Green
Temperature	293(2)
Theta range (°)	3.046-25.095
Goodness of fit on F <sup>2</sup>	1.064
<i>R</i> indices (all data)	0.0650

Table 4. Bond length (Å) of Ni[BuMedtc]<sub>2</sub>

Type of bond	Bond length (Å)	Type of bond	Bond length (Å)
Ni(1) - S(1)	2.1952	C(1) - H(1A)	0.96
S(1) - C(6)	1.7118	C(2) - H(2B)	0.97
N(1) - C(6)	1.3113	C(4) - H(4B)	0.97
Ni(1) - S(2)	2.2016	C(1) - H(1B)	0.96
S(2) - C(6)	1.7144	C(3) - H(3A)	0.97
C(1) - C(2)	1.4931	C(5) - H(5A)	0.96
Ni(1) - S(1)a	2.1952	C(1) - H(1C)	0.96
N(1) - C(4)	1.4600	C(3) - H(3B)	0.97
C(2) - C(3)	1.4792	C(5) - H(5B)	0.96
Ni(1) - S(2)a	2.2016	C(2) - H(2A)	0.97
N(1) - C(5)	1.4635	C(4) - H(4A)	0.97
C(3) - C(4)	1.4993	C(5) - H(5C)	0.96

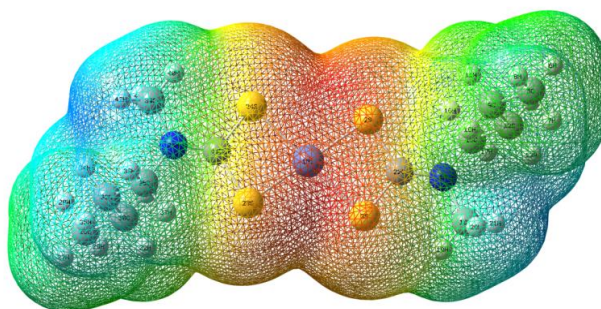
Table 5. Bond angle (°) of Ni[BuMedtc]<sub>2</sub>

Type of bond	Bond angle (°)	Type of bonding	Bond angle (°)
S(1) - Ni(1) - S(2)	79.17	Ni(1) - S(2) - C(6)	85.20
S(2) - Ni(1) - S(1)a	100.83	C(5) - N(1) - C(6)	120.58
Ni(1) - S(1) - C(6)	85.46	N(1) - C(4) - C(3)	113.47
C(4) - N(1) - C(6)	122.61	S(2) - C(6) - N(1)	124.50
C(2) - C(3) - C(4)	112.99	S(1) - Ni(1) - S(2)a	100.83
S(1) - C(6) - N(1)	125.78	S(1)a - Ni(1) - S(2)a	79.17
S(1) - Ni(1) - S(1)a	180.00	C(4) - N(1) - C(5)	116.77
S(2) - Ni(1) - S(2)a	180.00	C(1) - C(2) - C(3)	114.53
S(1) - C(6) - S(2)	109.71		

### E. Molecular Electrostatic Potential

Molecular electrostatic potential (MEP) is commonly used to display the reactivity region of a compound. The MEP mapping of the Ni[BuMedtc]<sub>2</sub> complex in Figure 6 shows the appearance of four regions, which were red, yellow, green and blue. The red region at the centre of the

compound showed that it contained the highest electron density. This region was categorised as an electrophilic attack region. This effect came from the four electronegative sulfur atoms bonded to the Ni atom to form the Ni[BuMedtc]<sub>2</sub> complex.

Figure 6. The molecular electrostatic potential (MEP) of the Ni[BuMedtc]<sub>2</sub>



### F. Chemical Reactivity Properties

Table 6 shows the energy value of the chemical reactivity of the Ni[BuMedtc]<sub>2</sub>. It can be seen that the formation energy of the Ni[BuMedtc]<sub>2</sub> was in negative value (-21511.99 eV), showing that the complex was thermodynamically stable. The inertness and stability were also related to the ionisation energy and affinity electron of the compound. In this study, the Ni[BuMedtc]<sub>2</sub> showed that its ionisation energy and electron affinity were 5.95 and 1.94 eV, respectively. The calculated result indicated that it aligned with the weight loss data which found that the Ni[BuMedtc]<sub>2</sub> was less effective as a corrosion inhibitor due to its stability (Parveen *et al.*, 2016). The calculated data also aligned with the Weight Loss data which showed that the Ni[BuMedtc]<sub>2</sub> complex contributed to a significant ability to be a corrosion inhibitor to the mild steel.

Table 6. The calculated reactivity properties of Ni[BuMedtc]<sub>2</sub>

	Value (eV)
Formation Energy	-21511.99
Ionisation Energy	5.95
Electron affinity	1.94

### G. Weight Loss Method

By using the weight loss method, the inhibition efficiency (%) ( $\eta_w$ ) and corrosion rate ( $C_{RW}$ ) of Ni[BuMedtc]<sub>2</sub> were calculated by using the formula equation below:

$$\Delta W = W_1 - W_2 \quad (1)$$

$$C_{RW} = \frac{\Delta W}{S \times t} \quad (2)$$

$$\theta = \frac{C_{RW}^0 - C_{RW}}{C_{RW}^0} \quad (3)$$

$$\eta_w = \frac{C_{RW}^0 - C_{RW}}{C_{RW}^0} \times 100\% \quad (4)$$

Where:

$W_1$  = The initial weight of mild steel before immersion (g).

$W_2$  = The final weight of mild steel after immersion (g).

$\Delta W$  = The weight loss (g).

$S$  = The surface area of the mild steel (cm).

$T$  = Time of immersion (h).

$C_{RW}$  = The corrosion rate in the presence of inhibitor (g cm<sup>-2</sup> h<sup>-1</sup>).

$C_{RW}^0$  = The corrosion rate in the absence of inhibitor (g cm<sup>-2</sup> h<sup>-1</sup>).

$\eta_w$  = The percentage of inhibitor efficiency (%).

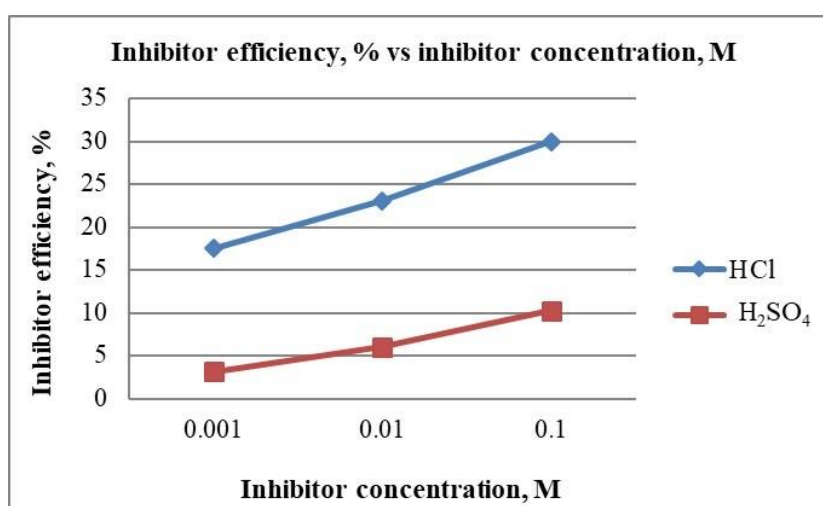
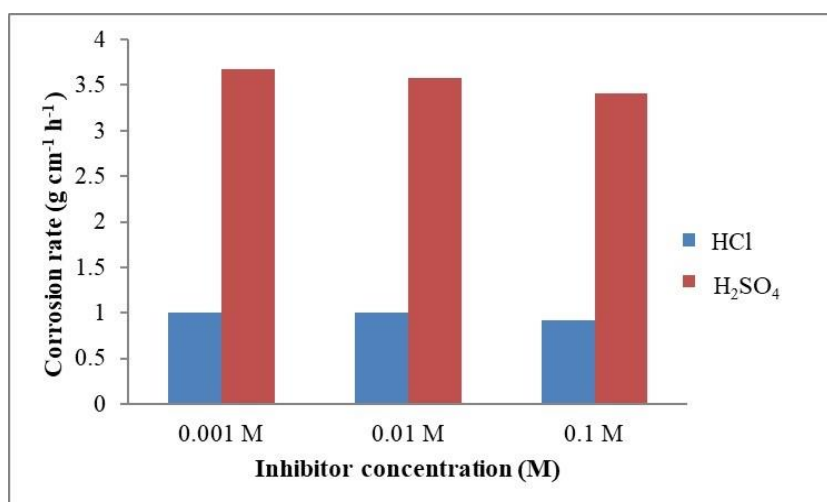
The weight loss of mild steel in two types of acids, which were HCl and H<sub>2</sub>SO<sub>4</sub>, was measured and tabulated in Table 7. It was done to identify the ability of the complex as a corrosion inhibitor. From Table 7, it is displayed that the corrosion rate ( $C_{RW}$ ) of mild steel decreased as the concentration of inhibitor increased. Meanwhile, the inhibitor efficiency ( $\eta_w$  (%)) increased as the concentration of inhibitor increased. This occurred due to the presence of lone pairs of nitrogen and sulfur atoms in the complex which allowed it to be adsorbed on the metal surface more easily and forming an insoluble stable form on the surface of mild steel which would then reduce the corrosion attack (Noor Khadijah *et. al.*, 2014; Shetty & Shetty 2008). From Figure 7, it can be observed that the complex was able to act as a corrosion inhibitor in different concentrations and types of acid. This was because the complex contained sulfur and nitrogen atoms. The organic compound that had two atoms, which were sulfur and nitrogen, was known as an acid inhibitor. It can be concluded that the inhibitor efficiency increased as the inhibitor concentration increased. In addition, it showed that Ni[BuMedtc]<sub>2</sub> can act as an inhibitor better in 1 M HCl than in 1M H<sub>2</sub>SO<sub>4</sub>. Figure 8 shows the graph of corrosion rate versus inhibitor concentrations of 1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> in Ni[BuMedtc]<sub>2</sub>. The graph shows that as the inhibitor concentration was increased, the corrosion rate was gradually decreased and that the corrosion rate in H<sub>2</sub>SO<sub>4</sub> was greater than in HCl. The corrosion rate in 1 M H<sub>2</sub>SO<sub>4</sub> was higher due to the presence of high concentrations of H<sup>+</sup> in H<sub>2</sub>SO<sub>4</sub> which made it more corrosive as compared to HCl (Samina *et al.*, 2011). H<sub>2</sub>SO<sub>4</sub> is an effective protonating agent. It can entirely dissociate to form two H<sup>+</sup> ions and enhance the corrosion rate. H<sub>2</sub>SO<sub>4</sub> is highly corrosive as emphasised by its highly exothermic (heat generating) reaction with water (Hagen & Jarnberg, 2019). Electrons from the mild steel can react with hydrogen ions in H<sub>2</sub>SO<sub>4</sub> acid solutions to form a metal sulfate and produce hydrogen gas which is then adsorbed on



the mild steel surface. The sulfate ions that are integral to sulfuric acid environments because it can scrub off the zinc sulfurous acid do not participate directly in the corrosion sulfate film which shields the mild steel from acidic attack. attack. Hydrogen gas can be a problem with mild steel in This reaction leads to the corrosion of mild steel.

 Table 7. Corrosion inhibition data of the Ni[BuMedtc]<sub>2</sub> complex in 1 M HCl and H<sub>2</sub>SO<sub>4</sub>

Acid solution	Complexes	Concentration (M)	Weight loss, ΔW (g)	Corrosion rate, C <sub>rw</sub> (g cm <sup>-1</sup> h <sup>-1</sup> )	Inhibitor efficiency, η <sub>w</sub> (%)
HCl	Blank	1	0.1630	1.306 x 10 <sup>-3</sup>	-
	Ni[BuMedtc] <sub>2</sub>	0.1	0.1142	9.151 x 10 <sup>-4</sup>	29.94
		0.01	0.1254	1.004 x 10 <sup>-3</sup>	23.07
		0.001	0.1345	1.077 x 10 <sup>-3</sup>	17.48
H <sub>2</sub> SO <sub>4</sub>	Blank	1	0.474	3.798 x 10 <sup>-3</sup>	-
	Ni[BuMedtc] <sub>2</sub>	0.1	0.426	3.413 x 10 <sup>-3</sup>	10.26
		0.01	0.445	3.576 x 10 <sup>-3</sup>	6.05
		0.001	0.459	3.678 x 10 <sup>-3</sup>	3.16


 Figure 7. Inhibitor efficiency versus inhibitor concentration in 1M HCl and 1M H<sub>2</sub>SO<sub>4</sub>

 Figure 8. Inhibitor concentration versus corrosion rate in Ni[BuMedtc]<sub>2</sub>

#### IV. CONCLUSION

As a conclusion, Ni[BuMedtc]<sub>2</sub> was successfully synthesised by in-situ method and characterised by using FTIR-ATR, UV-Vis, elemental analysis and X-ray single diffraction. The crystal structure of Ni[BuMedtc]<sub>2</sub> complex adopted a distorted tetrahedral geometry which was the structure of the synthesised Ni[BuMedtc]<sub>2</sub> complex and revealed that the coordination made in the complex was S, S-bidentate coordination. The IR spectra were fully parallel with the X-ray single-crystal diffraction. The chemical properties, such as the energy of complex formation, ionisation energy and electron affinity of the Ni[BuMedtc]<sub>2</sub> complex, were successfully calculated by using DFT approach. The theoretical data was aligned to the experimental data, proving that the Ni[BuMedtc]<sub>2</sub> complex effectively acted as a corrosion inhibitor in this study. The complex demonstrated a promising anti-corrosion activity since the corrosion rate decreased as the inhibitor concentration increased. Finally,

Ni[BuMedtc]<sub>2</sub> is a good corrosion inhibitor in 1 M HCl but not 1 M H<sub>2</sub>SO<sub>4</sub> because H<sub>2</sub>SO<sub>4</sub> is a more corrosive acid due to the excessive presence of H<sup>+</sup>.

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