

[Zn(TAC)]Cl COMPLEX POTENTIAL AS CORROSION INHIBITORS: SYNTHESIZATION AND CHARACTERIZATION

Siti Aisyah Musa, Nur Nadia Dzulkifli

School of Chemistry and Environment, Faculty of Applied Sciences

University of Technology MARA, Negeri Sembilan Branch, Kuala Pilah Campus, 72000 Kuala Pilah, Negeri Sembilan, Malaysia

*Corresponding author: nurnadia@ns.uitm.edu.my

Abstract

Corrosion of metal is a severe issue in any industry which is considered to involve many costs. The use of acid solution during cleaning to get rid of rust in industries may contribute to metal corrosion. Since corrosion impact is causing worries, especially in many industries, the application of a corrosion inhibitor is required to reduce the rapid deterioration reaction of a metal surface that is exposed to corrosion 'boosters' like oxygen gas and water. A corrosion inhibitor, which is [Zn(TAC)]Cl, was produced from the reaction between thiacetazone (TAC) with ZnCl₂ in an acetonitrile solvent with ratio 1:1 (ligand:metal). The elemental analysis (C, H, N, and S), FT-IR, UV-Visible, melting point, gravimetric analysis, and molar conductivity were used to characterize the synthesized complex. Based on infrared spectra and electronic transitions, the shifting of a complex from the ligand *indicates* that the ligand is coordinated to the metal ion through carbonyl O, azomethine N, and thiolate S; thus, producing a tridentate complex. Melting point for the complex was higher than ligand. [Zn(TAC)]Cl was gained after being confirmed by 1:1 electrolyte behavior and elemental analysis calculations. A metal oxide, ZnO, was formed with the calculated percentage of Zn(II) ion, 13.66 % after combustion through the gravimetric analysis. [Zn(TAC)]Cl portrayed better inhibitory action against corrosion of mild steel *as* compared to the ligand in both acidic media, H₂SO₄ and HCl. A higher concentration of inhibitor gave a higher percentage of corrosion inhibition efficiency.

Keywords: Thiacetazone (TAC), Zn(II), Schiff base, corrosion, inhibitor.

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Introduction

Schiff base was first reported in 1864 with the first preparation of imines. Da Silva et al. (2011) proved the versatility of Schiff base through its widely use in biological activity and industrial purposes. Thiosemicarbazone is one of the Schiff bases with a general formula of NH₂-C(S)NH-N=R, as shown in Figure 1.

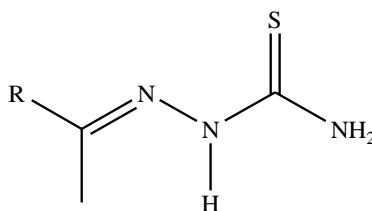


Figure 1. General structure of thiosemicarbazone

Thiosemicarbazone acts as a ligand and coordinates the central metal ion to form complexes. Corrosion is a worldwide industrial problem that affects natural and industrial environments. Nearly all aqueous environments can promote corrosion, which occurs under numerous complex conditions, especially in oil and gas production, processing, and pipeline systems (Popoola et al.,

2013). Besides, HCl and H₂SO₄ are the most difficult common acids to handle in respect to corrosion and material constructions (Ajeel et al., 2012). Khaled et al. (2010) found that thiosemicarbazones are effective inhibitors for mild steel corrosion in 1.0 M HCl solution. This was proven by the increasing inhibitor concentration that can raise the values of both inhibition efficiency and polarization resistance. This is also supported by Bisceglie et al. (2015) who stated that the inhibition efficiency tends to increase as HCl concentration decreases.

Experimental

I. Physical measurement

The melting point was measured by using a melting point apparatus (model SMP10 Stuart) and taken in an open capillary tube. The molar conductivity values were measured with DMF at room temperature by using an SI Analytic Lab 970 conductivity meter at 2×10^{-3} M concentration. The elemental analysis of synthesized compounds was performed by using CHNS/O Model Fision EA 1180 and Thermo Finnigan Flash EA 1112 Series. Meanwhile, the infrared spectra were recorded on a Fourier Transform-Infrared Attenuated Total Reflectance (FTIR-ATR) Perkin Elmer Spectrophotometer. The electronic absorption spectra were recorded on a PG Instrument T80/T80+ spectrophotometer by using 1 cm quartz cuvette with sample concentrations of 1×10^{-5} M in the 200–600 nm region, aided by DMSO as a solvent.

II. Synthesis Zn(II) Complex

The TAC (5 mmol) was dissolved in 20 mL acetonitrile. Then, ZnCl₂ (5 mmol) was dissolved in 10 mL acetonitrile and added dropwise to the ligand solution. The reaction mixture was refluxed for 3 h at 70°C. The formed precipitate was filtered, washed with methanol and left to dry over anhydrous silica gel.

III. Corrosion Inhibition Study

An acidic solution of 1 M of 37 % HCl and 1 M of 95 % H₂SO₄ was prepared by using a dilution method. The concentrations of inhibitors were 0.1, 0.01, and 0.001 M, respectively, and were prepared by diluting with the prepared 1 M of HCl and H₂SO₄. Determination of mild steel weight loss was tested in triplicate at 40 °C for 24 h and the average mass was calculated.

Results and Discussion

The elemental analysis for C, H, N and S revealed that the calculated and experimental data were in good agreement. Element percentages are shown in Table 1. [Zn(TAC)]Cl precipitate was obtained after condensation between ligand and ZnCl₂ in ACN. Product formed for gravimetric analysis was a metal oxide, which was ZnO. Calculated percentage of Zn(II) ion in the complex was 13.66 %. The [Zn(TAC)]Cl molar conductivity was in the 65-90 Scm²mol⁻¹ range, indicating 1:1 behavior electrolyte with the formula [Zn(TAC)]Cl. Figure 2 shows the proposed structure of the complex.

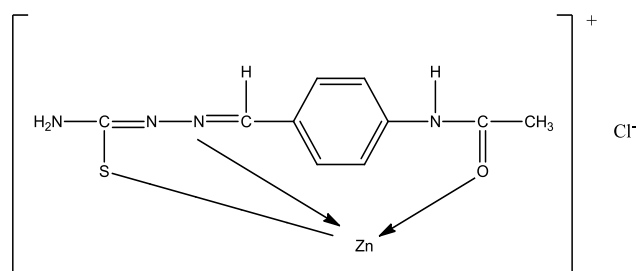


Figure 2. Proposed structure of [Zn(TAC)]Cl
Table 1. Physicochemical Analysis

Compound	Melting point (°C)	Yield (%)	Elemental Composition (%)			
			C	H	N	S
TAC	229-231	-	50.85 (50.74)	5.08 (5.15)	23.73 (25.55)	13.56 (11.30)
[Zn(TAC)]Cl	240-242	86.34	35.82 (37.29)	3.28 (4.30)	16.72 (18.13)	9.55 (7.39)

I. Infrared Spectroscopy

Based on Figure 3 and Figure 4, the stretching band of $\nu(\text{C}=\text{N})$ in the TAC, shifted to higher wavenumber as compared to [Zn(TAC)]Cl spectrum which contributed an evidence on azomethine N involvement in the coordination (Chandra et al., 2013; Zemedede et al., 2014). The $\nu(\text{C}=\text{O})$ was also shifted towards higher wavenumbers; thus, proved the carbonyl O coordination to the metal ion (Muralisankar et al., 2016). The stretching band of $\nu(\text{C}=\text{S})$ in the ligand shifted to a lower wavenumber in the complex, indicating that the thiolate sulfur atom was involved in the complexation (Refat et al., 2013; Okoronkwo et al., 2013); thus, it may be concluded that the ligand behaved as a tridentate chelating agent, coordinating through azomethine N, carbonyl O, and thiolate sulfur.

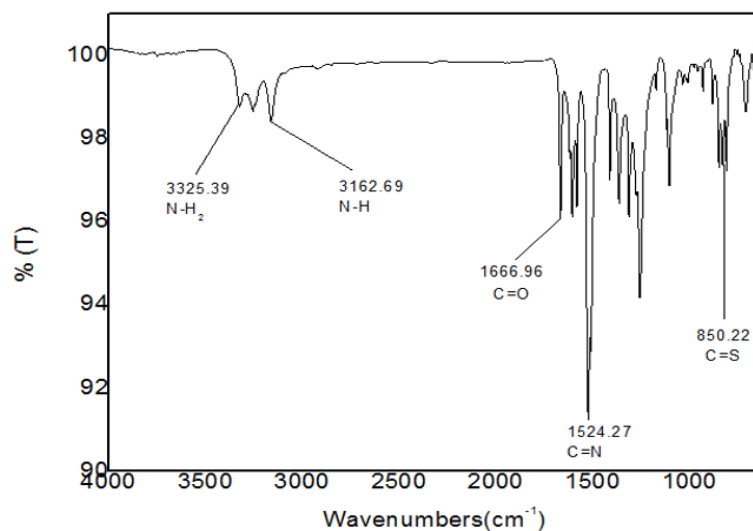


Figure 3. Infrared spectra of TAC

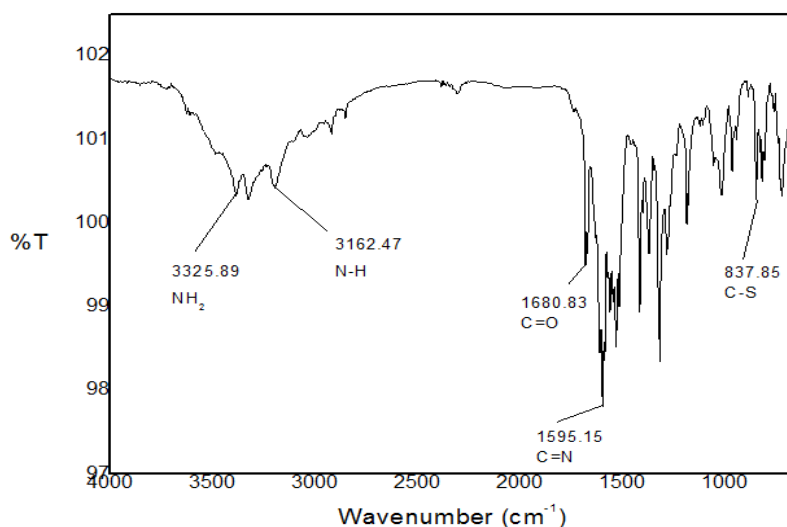


Figure 4. Infrared spectra of [Zn(TAC)]Cl

II. UV-Visible Spectroscopy

Based on Table 2, there are two electronic transitions that exist in the ligand spectra and [Zn(TAC)]Cl, which were $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ intraligand transitions. The absorption peak for $n\text{-}\pi^*$ transition in the [Zn(TAC)]Cl mainly involved C=N and C=S, which appeared at 325nm, showing a hypsochromic shift to a shorter wavelength as compared to the ligand absorption peak. Besides, the $\pi\text{-}\pi^*$ transition due to the C=C aromatic ring, portrayed bathochromic shift to a longer wavelength upon complexation. The shift in the complex to a shorter or longer wavelength provided confirmatory of the ligand coordination to the metallic ions (Refat et al., 2013).

Table 2. Electronic Transitions Data for TAC and [Zn(TAC)]Cl

Compounds	Transitions	$\lambda_{\text{max}}(\text{nm})$	Molar absorptivity, $\epsilon (\text{M}^{-1}\text{cm}^{-1})$
TAC	$n\rightarrow\pi^*$	330	80400
	$\pi\rightarrow\pi^*$	215	39800
[Zn(TAC)]Cl	$n\rightarrow\pi^*$	325	2064
	$\pi\rightarrow\pi^*$	225, 205	1473, 2066

III. Corrosion Inhibition Study

Figure 5 and Figure 6 show the relation between inhibition efficiency and inhibitor concentration in both acids. [Zn(TAC)]Cl was more efficient to inhibit the corrosion as compared to the ligand. This indicated that when the inhibitor concentration increased, more molecules were adsorbed onto the metal surface, promoting a wider surface coverage (Goulart et al., 2013; Abbasov et al., 2013). The corrosion inhibition efficiency percentage was higher in H_2SO_4 as compared to HCl at the same concentration. A few reports pointed out the synergistic effect of halide ions on mild steel corrosion in an acidic solution. Ajeel et al. (2012) stated that the corrosiveness in HCl was due to the effect of chloride ions (Cl^-) that had a more aggressive effect and was responsible for pitting on the metal surface than the sulfate ion.

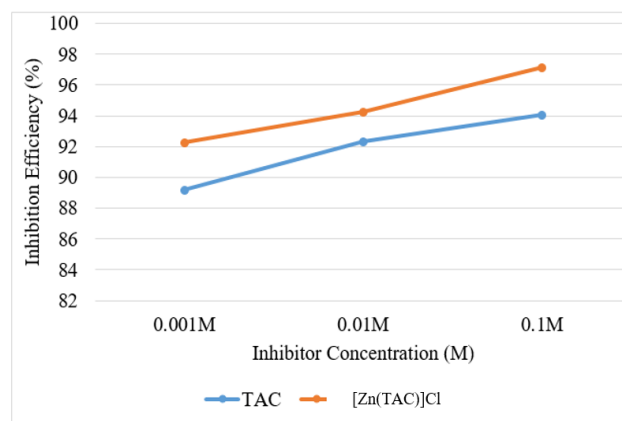


Figure 5. Inhibition Efficiency versus Inhibitor Concentration in H₂SO₄

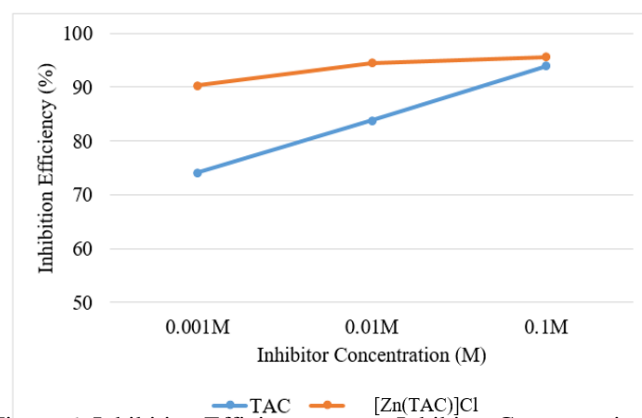


Figure 6. Inhibition Efficiency versus Inhibitor Concentration in HCl

Conclusion

[Zn(TAC)]Cl was successfully synthesized by using condensation method. The proposed structure of the complex was supported by elemental analysis, molar conductivity, gravimetric analysis, FT-IR, and UV-Vis. The ligand behaved as a tridentate chelating agent. [Zn(TAC)]Cl showed better inhibition action against corrosion as compared to the ligand in both acids.

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