

Synthesis, Characterization and Anti-Corrosion Studies Of A Pentadentate Ligand and Its Copper (II) Complexes

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ABSTRACT: A pentadentate ligand was synthesized using 4-tertiarybutyl-2,6-bis(chloromethyl) phenol and nicotinic hydrazide. It was characterized by UV-Visible, FT-IR, ¹H-NMR, ¹³C-NMR and mass spectroscopic techniques. The above ligand was coordinated with copper(II) precursors to form corresponding copper (II) complexes. The complexes were characterized by UV-Visible spectra, FT-IR spectra and Conductivity measurements. The anticorrosion activity of the ligand and their complexes were studied.

Keywords: 4-tertiarybutyl-2,6-bis(chloromethyl) phenol, Nicotinic hydrazide, Pentadentate ligand, Copper (II) complexes, anticorrosion activity.

I. INTRODUCTION

Many metals having various uses in Industrial and Domestic applications. Most of the metals are susceptible to corrosion which leads to destruction or degradation of the metal surface and ultimately reduction of life of the material. So, it is necessary to prevent corrosion [1]. Even though there are many traditional ways of prevention of corrosion, the high toxicity of chromate, phosphate and arsenic compounds leads to various environmental and health problems. So, it is necessary to reduce the use of these which make us to look for the development of other inhibitors [2]. The use of corrosion inhibitor is one of the well known methods to prevent corrosion because only a small quantity of the inhibiting compound is needed when compared to other inhibitors. The inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective hydrophobic thin film on the metallic surface. As a result, the rates of the anodic and/or cathodic corrosion reactions are retarded [3]. The efficiency of these corrosion inhibitors is related to the presence of polar functional groups with S, O or N atoms in the molecule, heterocyclic compounds and pi electrons. The inhibitor that contains oxygen, nitrogen or sulfur is adsorbed on the metallic surface blocking the active corrosion sites [4-6]. Here we have synthesized some copper(II) complexes using a ligand derived from Nicotinic hydrazide and copper(II) precursors.

II. EXPERIMENTAL

2.1. Materials And Methods

All the chemicals and solvents were purchased from SD-fine chemicals. FT-IR spectra were obtained in Shimadzu IR-Affinity-I spectrometer and sample pellets were prepared using KBr. UV-Visible spectra were recorded using Systronics spectrophotometer operating in the range of 200-800 nm. ¹H NMR and ¹³C NMR spectrum of ligand was recorded from Bruker 400 MHz spectrometer. Conductance of Ligand and complexes were recorded using Elico conductometer. Cyclic Voltammetry was done in HCH Instruments.

2.2. Synthesis Of Ligand

4-tertiarybutyl-2,6-bis(chloromethyl)phenol was treated with Nicotinic hydrazide in ethanol in 1:2 ratio[7-8]. A yellow solid was obtained, filtered and re-crystallized in ethanol.

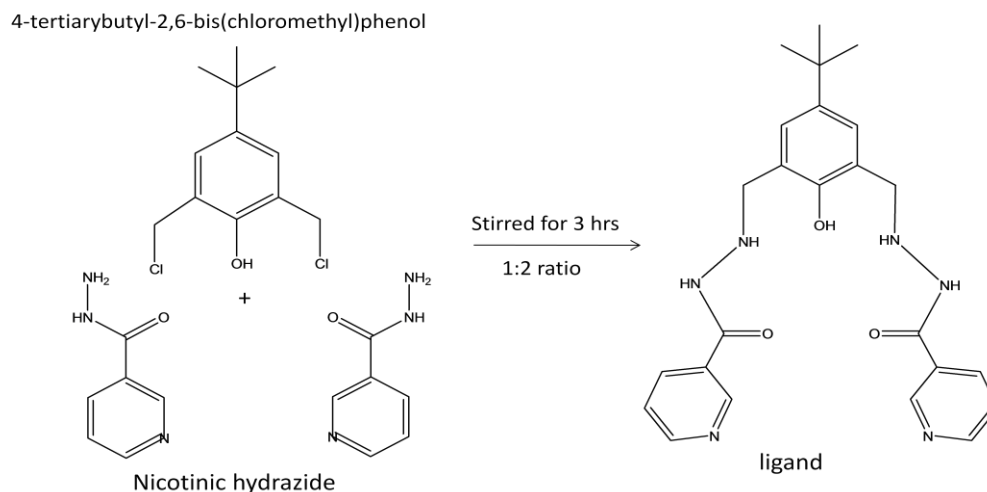


Fig2: Synthesis of ligand

2.3. Synthesis of copper precursors

Phthalic acid was dissolved in hot water and sodium hydroxide was added and stirred in a magnetic stirrer. A solution of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in water was slowly added to the above mixture in 1:2 ratio [9-11]. A light blue solid obtained, filtered and washed with water.

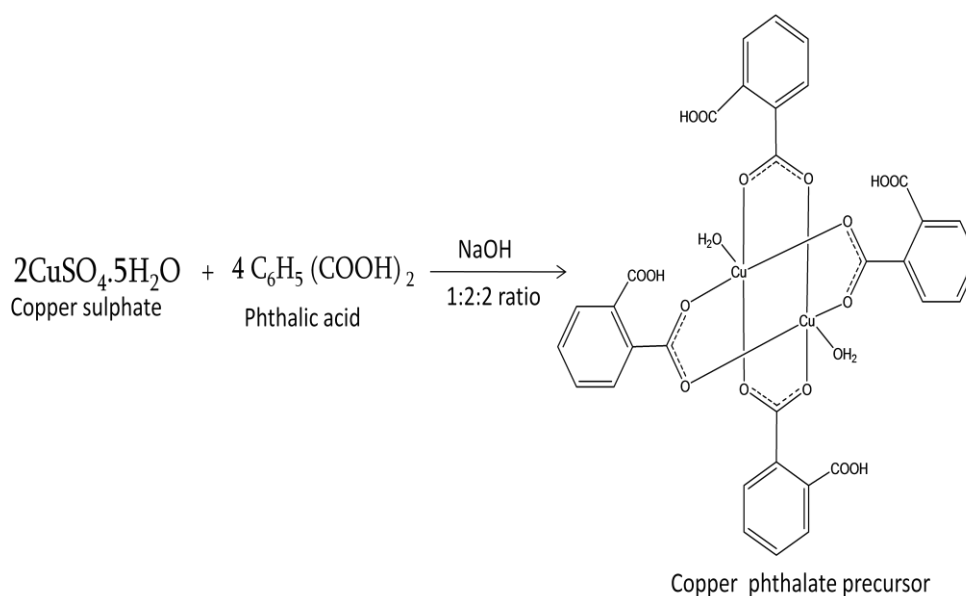


Fig3: Synthesis of copper precursor

Similarly other precursors were prepared using different substituted Benzoic acids.

2.4. Synthesis of copper complexes

The above ligand was dissolved in ethanol. Sodium hydroxide was added and stirred for few minutes. A solution of copper precursors in ethanol was slowly added and sodium perchlorate was added in 1:1:1:2 and continued stirring for 5 hours [12-14]. A dark green solid was obtained and filtered.

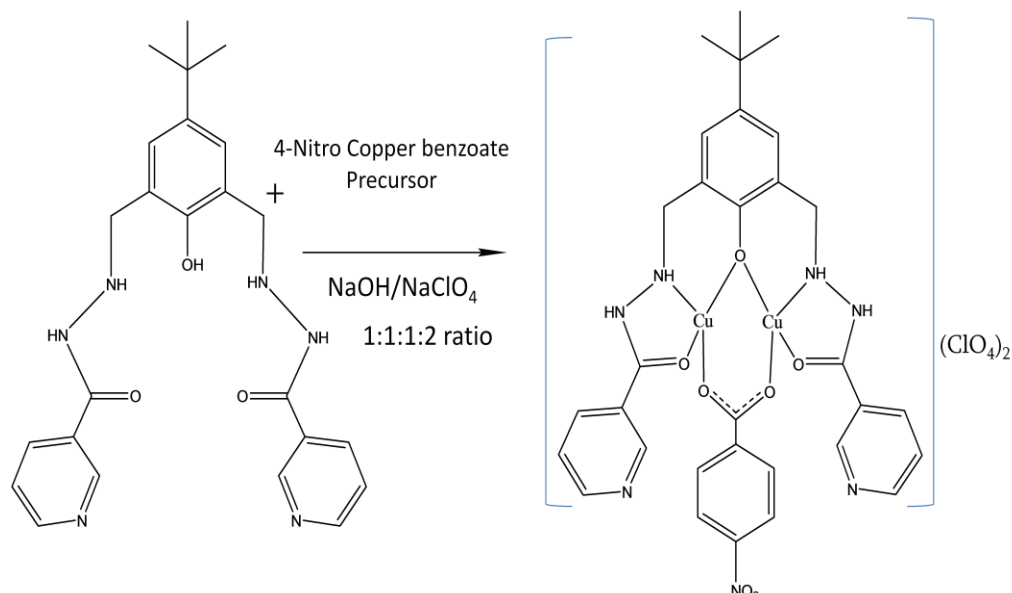


Figure 4: Synthesis of copper complex (C5P1)

Similarly 4- Methyl Copper benzoate (C5P2), 4-Amino Copper benzoate (C5P3) were synthesized.

III. RESULTS AND DISCUSSION

The above ligand was characterized by UV-Visible, FT-IR, ¹H-NMR, ¹³C-NMR spectral studies. The UV-Visible spectrum of the ligand shows $\pi - \pi^*$ transition at 291 nm of benzene, $\pi - \pi^*$ transition of carbonyl at 339 nm and $n - \pi^*$ transition at 387 nm. The FT-IR Spectrum shows NH stretching at 3247 cm⁻¹, aromatic CH stretching at 2958 cm⁻¹, C=O stretching at 1651 cm⁻¹, CO stretching at 1207 cm⁻¹. The ¹H NMR spectrum shows aromatic protons adjacent to nitrogen at 9.006, aromatic protons away from nitrogen at 7.804, methylene proton at 4.575. ¹³C NMR spectrum shows hydroxyl carbon at 147.3, tertiarybutyl carbon at 31.34, carbonyl carbon at 164.42, aromatic carbon adjacent to nitrogen at 150.27 and aromatic protons away from nitrogen at 121.91. The mass spectrum shows peaks at m/e values 448, 269, 161 etc., shows the presence of molecular ion peak and fragmented ion peaks [15-16].

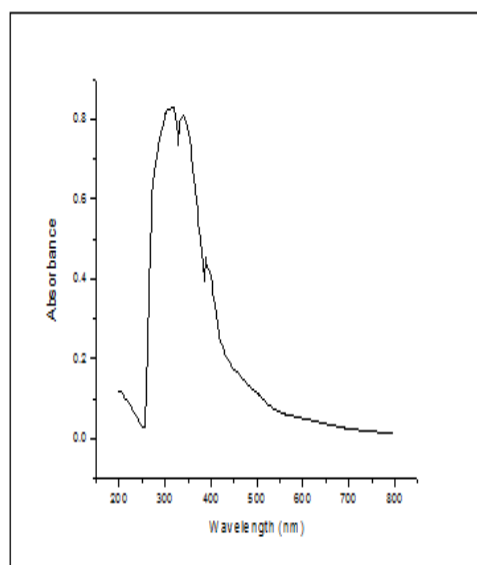


Figure 5: UV-Visible spectrum of Ligand

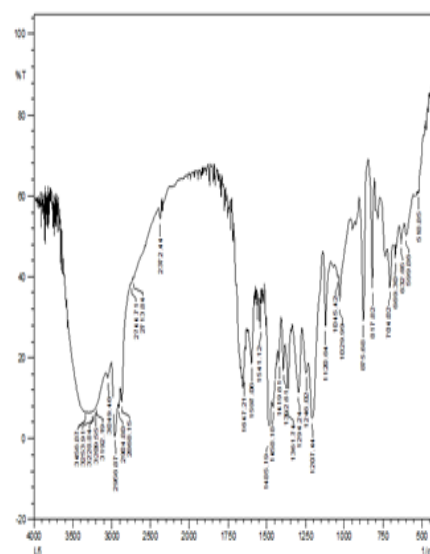


Figure 6: FT-IR spectrum of Ligand

S. No.	Sample Code	λ max value (nm)			
		$\pi - \pi^*$ transition of Benzene	$\pi - \pi^*$ transition C=O	$n - \pi^*$ transition	d-d transition
1	L	291	329	387	-
2	C5P1	296	358	399	591
3	C5P2	298	346	401	567
4	C5P3	300	348	401	584

Table – 1

2.6. FT-IR spectra of the complexes

The band at 3247 cm^{-1} in ligand is shifted to lower frequency shows the coordination of metal to the ligand. Similarly, the C=O stretching frequency of free ligand at 1652 cm^{-1} shows the decrease in stretching frequency upon complexation. Two new bands around 450 cm^{-1} and 520 cm^{-1} corresponds to M-O and M-N stretching frequencies respectively [18].

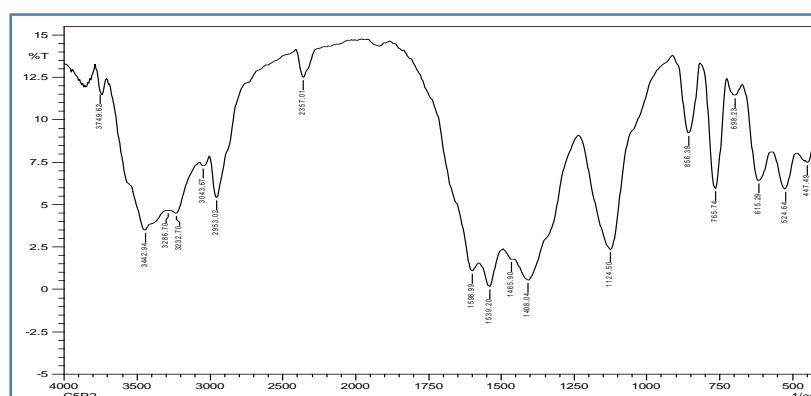


Figure 11: FT-IR spectrum of complex C5P2

S. No	Sample Code	Type Stretching Vibration in cm^{-1}					
		NH	Ar-CH	C=O	ClO_4^-	M-N	M-O
1	L	3247	2958	1651	-	-	-
2	C5P1	3228	2958	1641	1122	511	468
3	C5P2	3239	2960	1624	1118	524	447
4	C5P3	3243	2939	1589	1112	530	457

Table-2

2.7. Conductance measurements

The molar conductance of the complexes were recorded in Dimethylformamide (DMF). The molar conductance values shows that complexes are 1:2 electrolytes in nature.

Sl. No.	Sample Code	Molar Conductance ($\text{Mho cm}^2\text{ mol}^{-1}$)
1	C5P1	124
2	C5P2	137
3	C5P3	131

Table-3

2.8. Cyclic Voltammetry

The Cyclic Voltammetric data reveals that all the complexes exhibit a one electron transfer and the complexes are quasi reversible [19]. The electron movement is sluggish.

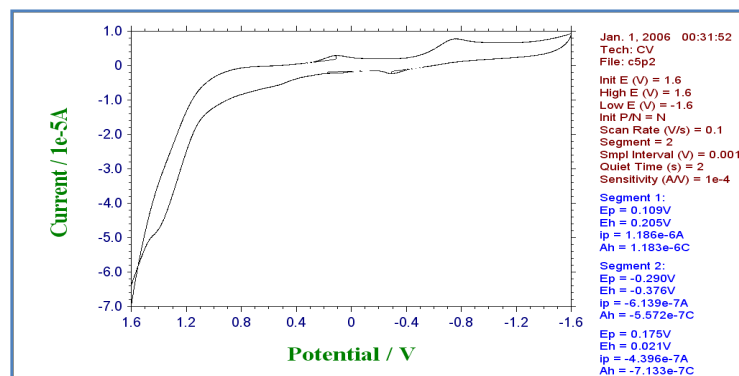


Fig: 12 - Cyclic Voltammetry of complex C5P2

Sl. No.	Sample Code	IPa ^{e-6}	IPc ^{e-6}	IPa/IPc
1	C5P1	2.501	4.669	0.535
		4.499	5.669	0.794
2	C5P2	1.808	2.100	0.861
		3.564	5.872	0.607
3	C5P3	1.716	2.007	0.855
		1.675	2.582	0.649

Table-4

IV. CORROSION INHIBITION

Copper has moderate resistant towards atmosphere and some chemicals but in aggressive media it is susceptible to corrosion. Incorporation of organic compound with copper helps to improve its action as corrosion inhibitor [20].

4.1. Weight loss measurement method:

Corrosion inhibition effects studied by weight loss measurement technique. In this method a string of Mild Steel is cut into small piece and weighed (Wu). It is placed in a beaker containing 20 ml of 0.1N HNO₃ for 48 hours. After 48 hours, the string is washed, dried and weighed (Wi). The loss in weight is calculated. Similarly a string of Mild Steel taken and placed in a beaker containing 20 ml of 0.1N HNO₃ and 25 mg of Ligand and complexes. The weight before and after 48 hours is noted. From the loss of weight Inhibition Efficiency (Ef) in percentage is calculated as follows.

4.2. Inhibitor efficiency (I.E)

The inhibitor efficiency could be measured by the follow equation:

$$E_f = \frac{W_u - W_i}{W_u} \times 100$$

Wu

where,

Ef is inhibitor efficiency (percentage),

Wi is corrosion rate of metal with inhibitor and

Wo is corrosion rate of metal without inhibitor.

SL NO	CODE	INITIAL WT	FINAL WT	LOSS IN WT	% OF WT LOSS	IE %
1	MS	0.141	0.092	0.049	34.8	0.0
2	L3	0.137	0.112	0.025	18.2	49.0
3	C5P1	0.138	0.129	0.009	6.5	81.6
4	C5P2	0.149	0.136	0.013	8.7	73.5
5	C5P3	0.147	0.129	0.018	12.2	63.3

Table-5

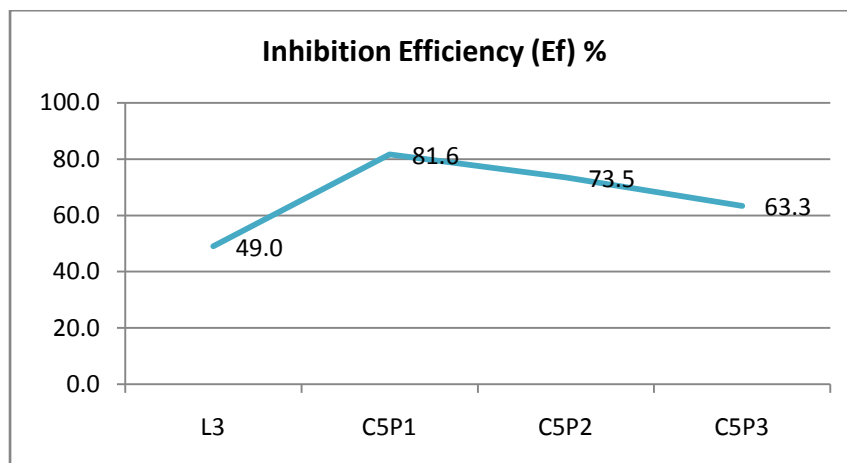


Fig: 13 – Corrosion Inhibition effect of Ligand and Complexes

From the above results, the corrosion of Mild Steel is reduced considerably by incorporation of the Ligand and its Complexes. The organic inhibitors containing oxygen, nitrogen is well adsorbed on the metallic surface blocking the active corrosion sites and as a result the Ligand and its Copper Complexes showed a good corrosion inhibitor activity against Mild Steel.

V. CONCLUSION

A multi-dentate ligand was synthesized using 4-tertiarybutyl-2,6-bis - (chloromethyl) phenol and Nicotinic hydrazide . It was characterized by UV-Visible, FT-IR, ¹H-NMR, ¹³C-NMR spectral studies and Mass spectroscopy. The above ligand was coordinated with various copper precursors to form corresponding copper complexes. The complexes were characterized by UV-Visible spectra, FT-IR spectra and Conductivity measurements. The molar conductance values show that all the complexes are found to be 1:2 electrolyte. The Ligand and its Copper(II) complexes showed a good corrosion inhibitor activity against Mild Steel.

ACKNOWLEDGEMENT

Our sincere thanks to Thiruvalluvar University, Muthurangam Government Arts College and VIT and other Institutions for helping us.

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