

Synthesis and study of complexes of tetradentate Schiff base and bridging ligand of thiocyanate with transition metals of Ni and Co

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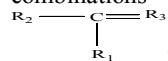
Abstract: In this study, Schiff base ligand was provided using the materials 2 and 3 - diaminopyridine and Salicylaldehyde in absolute ethanol solvent with reflux method. Then, at first stage, the complexes of transition metals of Nickel (Cr) and Cobalt (Co) with ligand supplied, were studied with along thiocyanate synthesized and cyclic voltammeter (CV). Thiocyanate anion was demonstrated due to the presence of a sharp peak in the range of 2000cm⁻¹ and displacements in the infrared spectrum compared to the ligand spectrum indicated kourdinating of oxygen and nitrogen to the central metal. Electron spectra in the complexes with axial ligand due to the nature of giving electron, central ligand reduce or increase the intensity of transitions which is confirmed in complex formation. Cyclic voltammeter (CV) also allowed that we can obtain other information of the electron character of the complexes besides the electron spectrum and evaluate the possibility of using them as a catalyst in oxidation - reduction reactions.

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INTRODUCTION

Schiff base ligands are defined by the combinations that contain azomethine groups



in their structure. These combinations are obtained by means of a kind one amines concentration with a one carbonyl group contained molecule. Schiff base ligands can make stable complexes with many metal ions. These combinations have many applications. Some applications of Schiff bases are in paint and plastic, industry agriculture, biochemistry, liquid crystal provision and physiology [1]. The other application of these compounds is in sensors and analytic studies [2,3]. In order to be able to increase choosing and sensibility of the new industrial methods in analytic systems, Schiff base are used as analytic indicators [4]. Ismet kaya and associates (2008) reported that a new schiff base polymer has made as a compound (PHMPMDAP) by spectroscopy, elemental analysis and thermal analysis. This azomethine polymer, easily complexes with transitions elements Co(II), Zn(II), Fe(II), Cu(II) and Pb(II). By using the study of IR, UV-Vis phenol oxygen and safety nitrogen indicated that ligand has a configuration. Data Thermogravimetric analysis (TGA) indicates that polymer has as stability as monomer. Obtained polymer structure by using FT-IR, UV-Vis, ¹³CNMR, ¹HNMR has reinforced and detection has performed by TGA, SEC and solubility tests. Also, electrical conductivities of PHMPMDAP and polymer-

metal complexes are measured by four probe technique [5].

MATERIALS AND METHODS

Ligand synthesis (2,3-diaminopyridine and salicylaldehyde)

In a 250 ml ballon we solved 1 mol 2,3-diaminopyridine (1 mmol and 0.109 g) in 30 ml absolute ethanol and refluxed it for half an hour. Then we added 2 mol salicylaldehyde (2 mmol and 0.2 cc) and refluxed it for 3 to 4 hours on a magnetic mixer and we continued refluxion until refluxion sediment formed. When a dark brown sediment formed we filtrated the sediment. To make sure that the sample is pure, we did TLC test during the experiment. First, we solved a little amount of the sample in ethanol and with a capillary tube we put the sample on TLC paper and we put it in hexane and ethyl acetate (1:1) solvent. Blemish went up in the solvent. Because it has capillary feature and it is made sure of sample purity by seeing just one blemish in the tank. Also sample electrical conduction in ethanol solvent with 10⁻³ M concentration was measured and it was 0.11 s/cm in 16 °C figure (1).

The synthesized combination has the following formula:

Chemical formula: C₁₉H₁₅N₃O₂
Molecular weight: 317.33 g. mol⁻¹

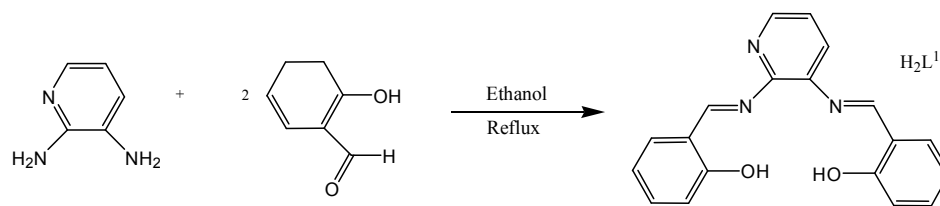


Figure 1. Ligand 2,3-diaminopyridine and salicylaldehyde synthesis

Synthesis of complex of cobalt (II) chloride with the Schiff base ligand 2 and 3- diaminopyridine and phyridine karbaldehyde with thiocyanate axial ligand. Within ballon 250 ml, we solved ligand supplied (1 mmol) in 30 ml absolute ethanol and refluxed for half an hour. Then, we added salt of cobalt (II) chloride (1 mmol and 0.237gr) in the same ratio of stoichiometric and refluxed on a magnetic stirrer for an hour. Finally, we added the thiocyanate salt in the same ratio of stoichiometric (6 mmol and 0.582gr) to the reaction mixture, as axial ligand, and reflux was continued for another 3 hours. To ensure the purity of the sample, we did TLC test during the research. Melting point of sample was approximately obtained 348 °C. Electrical conductivity of Complex was measured with the concentration of 10⁻³ M and its content was obtained 1.47 cm/sμ in 16°C.

Synthesis of complex of nickel (II) chloride with the Schiff base ligand 2 and 3- diaminopyridine and phyridine karbaldehyde with thiocyanate axial ligand. We solved ligand supplied (1 mmol) in 30 ml absolute ethanol within ballon 250 ml, and refluxed for half an hour. Then, we added salt of nickel (II) chloride (1 mmol and 0.237gr) in the same ratio of stoichiometric and refluxed on a magnetic stirrer for an hour. Finally, we added the thiocyanate salt in the same ratio of stoichiometric (6 mmol and 0.582gr) to the reaction mixture, as axial ligand, and reflux was continued for

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RESULTS AND DISCUSSION

Spectrum UV/Vis combination of cobalt (II) plus ligand along with thiocyanate:

In this complex, an absorption band was seen in the range of 200-280 nm, which was concerned to the Aromatic $\pi \rightarrow \pi^*$ transitions, and a long peak was appeared in the range of 280 – 400 nm which was corresponding to the $\pi \rightarrow \pi^*$ transitions of C=N bond, and also a Peak was observed in the range of 400-500 nm which was concerned to the transition of the n $\rightarrow \pi^*$ and also the transitions d-d of complex appeared in the range of 500-800 nm. The presence of thiocyanate axial ligand had greatly influenced the transfers, which were confirmed in the formation of this complex.

The comparison of electron spectrum with the ligand spectrum of this compound showed Koorinating of the central metal to two atoms of nitrogen and phenolic oxygen, which transfers in this combination were displaced to the red wavelength area.

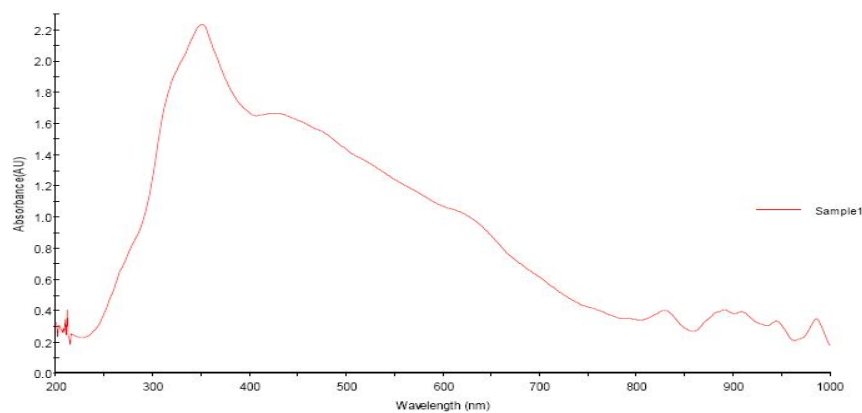


Figure 2. Spectrum UV / Vis combination of cobalt (II) plus ligand along with thiocyanate

Spectrum UV / Vis combination of nickel (II) plus ligand along with thiocyanate

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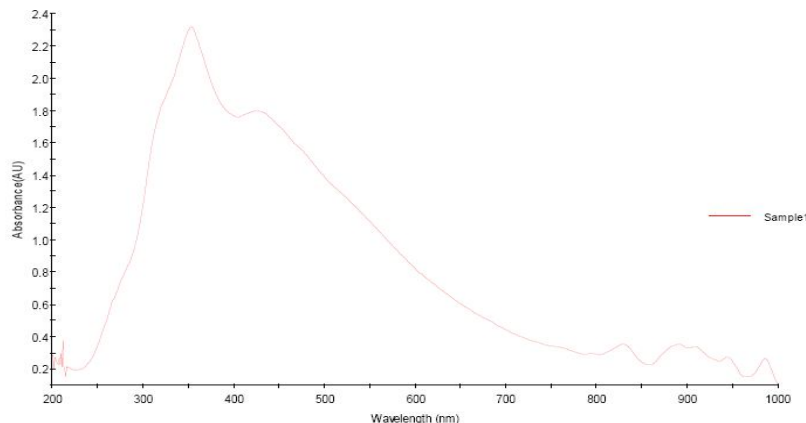


Figure 3. Spectrum UV / Vis combination of nickel (II) plus ligand along with thiocyanate

Spectrum UV / Vis combination of cobalt (II) plus ligand along with thiocyanate:

Cyclic Voltamogram of complex synthesized with speed of 0.1 vs^{-1} and in the range of 0.8 to -2 V were investigated in DMSO solution. In comparing ligand chart with complex obtained in the upper range of the chart, namely in the oxidation part, a peak was observed in the range of -0.1 to 0.21 V and also was seen a broad and short peak in the range of -0.5 to -0.65, which was shifted relative to the ligand peak. At the bottom of the chart, namely in reduction part, two peaks were respectively seen in areas of -0.34 to 0.25 v and -1.22 to

-1.5, which was displaced in the range of reduction than the ligand peak.

With comparison of oxidation and reduction peaks obtained in this chart, we concluded that both peaks appeared in the oxidation region were observed in the reduction region. Therefore, its electrochemical behavior indicated the state of being reversible, and broad oxidation peak was due to the ligand and metal, which appeared in close location. Displacements which had taken place in both oxidation and reduction region, were confirmed the formation of the desired compound and prepared complex with electro active thiocyanate.

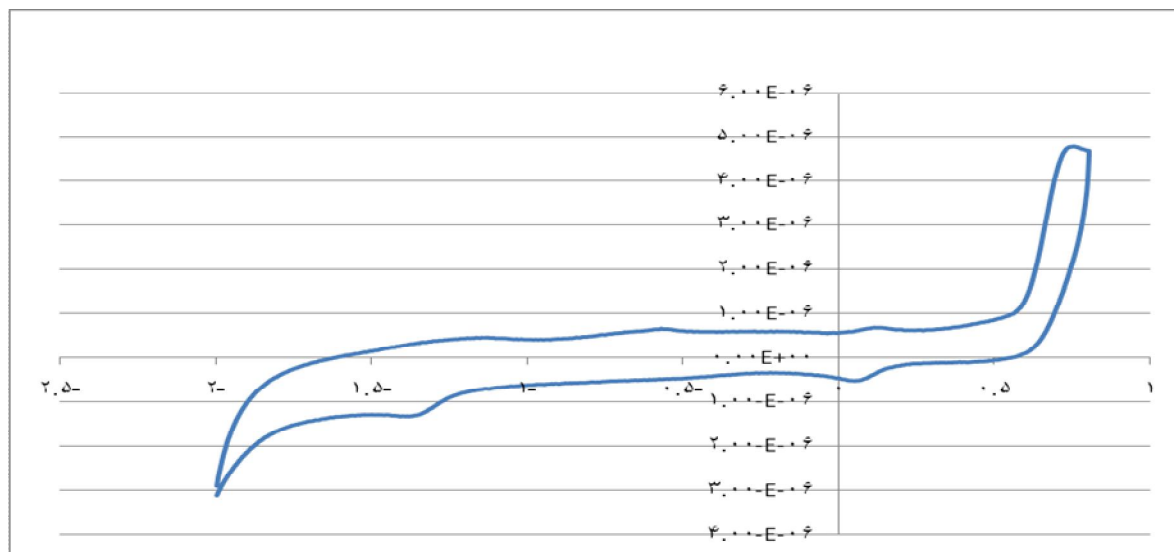


Figure 4. Spectrum CV / Vis combination of cobalt (II) plus ligand along with thiocyanate

Spectrum CV/ Vis combination of nickel (II) plus ligand along with thiocyanate:

Cyclic voltamogram of complex synthesized with speed of 0.1vs^{-1} and in the range of 0.8 to -2 V were investigated in DMSO solution. In comparing of ligand chart with complex obtained in the upper range of the chart, namely in the oxidation part, a long peak was observed in the range of 0.58 to 0.8 V and also two peaks were seen in the range of -0.1 to 0.25v and -0.4 to -0.91 that was shifted relative to the ligand peak. At the bottom of the chart, namely in reduction part, three peaks were respectively seen in areas of -0.13 to 0.22 v and -0.68 to -0.91v and -1.12 to -1.6 which was displaced than the ligand peak.

After comparison of oxidation and reduction peaks obtained in this chart, we concluded that every three peaks appeared in the oxidation region were observed in the reduction region. Therefore, its electrochemical behavior indicated the state of being reversible of complex and broad oxidation peak was due to the ligand and metal, which appeared in close location. Displacements which had taken place in both oxidation and reduction region, were confirmed the formation of the desired compound and prepared complex with electroactive thiocyanate.

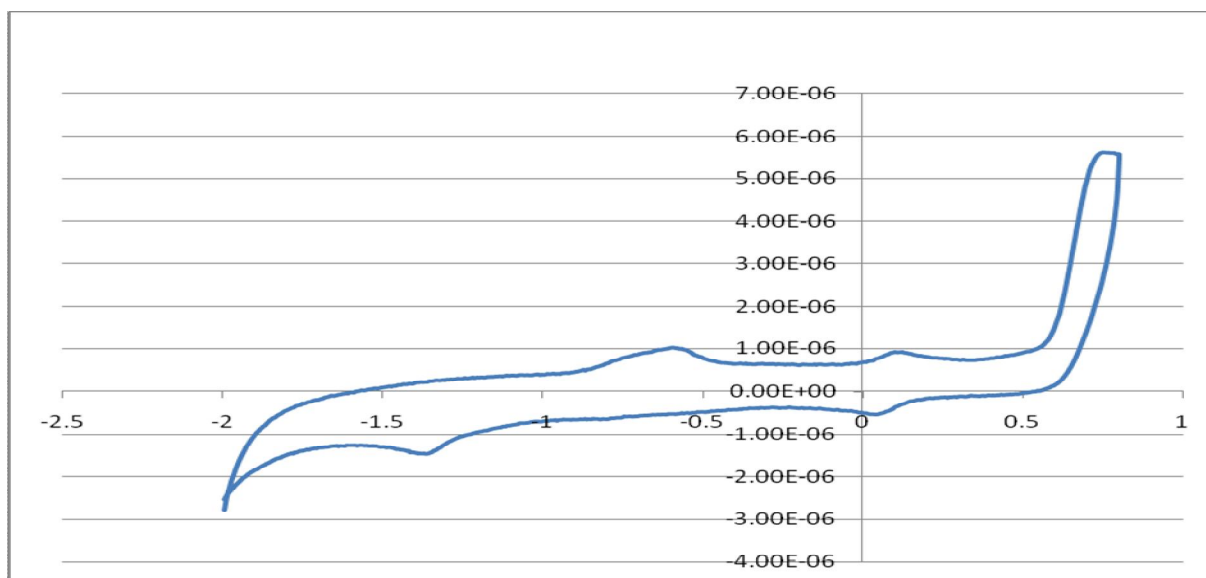


Figure 5. Spectrum CV/ Vis combination of nickel (II) plus ligand along with thiocyanate

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