Single pot Synthesis, Characterization of Nickel Schiff base Metal Complex by in-Situ Method

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ABSTRACT: The insitu synthesis of Schiff base metal complex using p-toluedine (p-tolu), p-anisaldehyde (p-anisal) as starting materials with Nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) used as a precursor for metal in equimolar ratio (1:1:1 M) at room temperature. The prepared metal complex is washed with several times with ethanol and boiled water for the complete removal of un-reacted species. To confirm the prepared material by the following characterization like UV-visible, Fourier Transforms Infrared spectroscopy, X-ray diffraction pattern and Cyclic Voltammetry.

Keywords: Schiff base, Metal complexes, Insitu method, cyclic voltammetry

I. INTRODUCTION

The most of the schiff base and its metal complexes are synthesized using condensation reaction, which are having the C=N functional group in it and which are synthesized usually by the reaction of amine and aldehyde [1,2]. For the past few decades, these kind of metal complexes play a vital role in various fields such as pharmacy companies, life sciences, chemical science especially inorganic and analytical field and also medical industries and it has display a broad range of utilization in various fields like antitumor, antibacterial and antifungal activity[3-8]. The presence of bulkier group in its structure having the steric hindrance and its stabilization of complexes by its metal oxidation state and it has very good solubility for the further spectral analysis to confirm the formation of metal complex [9-15]. In this present investigation, aniline based amines were used for the formation of ligand with easily reacted aldehyde and it's for metal complexes, the corresponding metal precursor is used with amine and aldehyde and especially the insitu approaches followed for the synthesis of metal complexes [16,17]. This approach has various benefits especially friendly approach to our environmental, cost effect with atom economy, less hazardous nature. Generally, the formation of schiff base ligand by the reaction of aromatic amine with carbonyl compound (aldehyde) via hemiaminal followed by the imines formation through nucleophilic addition reaction [18-27].

II. EXPERIMENTAL METHOD AND TECHNIQUES

A. *Chemicals*

The analar grade reagents only uses as received in this work for the synthesis. The high purity salts of p-toluedine, p-Anisaldehyde, Methanol, Ethanol, Zinc nitrate, Copper nitrate, Nickel nitrate were purchased from Fluka, Lancaster Chemical company.

B. *Instrumentation*

The information of the stability and structures of the materials can be discovering by UV-vis. spectrophotometer. The spectra was recorded with C-driven model UV-1800 (Shimadzu), Japan spectrophotometer (resolution 0.1 nm). FT-IR is one of the very important tool to find what are the functional groups are present in the molecules and modification on the metal surfaces (coating),which is used to prevent the growth of the nanoparticles by aggregation as well as the surface phenomenon of the inorganic metal nanoparticles. The FT-IR spectrophotometer for the analysis of the samples in Perkin-Elmer, USA Y-40 model within the range of 400–4000 cm−1. All spectra were correct with reference background spectrum of KBr. XRD pattern taken with a Philips instrument (JSO Debye Flex 2002 Seifert) at a 10°/min scanning speed from 10° to 80°. And its electrochemical measurements are carrying out using a CHI-660A (CHI Instruments Co. USA) electrochemical workstation. All the solutions were prepared for the electrochemical investigation used to purged the N_2 gas for 10 minutes before the stating the analysis

III. EXPERIMENTAL PROCEDURE

A. *Synthesis of ligand:*

About 1.07g of p-toluidine and 1.20 ml of p-anisaldehyde in methanol was allowed to stirred 5 h in inert atmosphere. A white precipitate obtained after 15 minutes, it confirms the formation of ligand successively in this methods and collected the white precipitate and washed with methanol using copious amount until the complete removal of un-reacted monomers and dried in vacuum.

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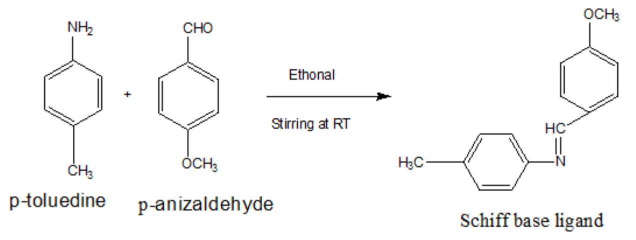

Fig 1: In-situ synthesis of Schiff base [Anil-Tolu] ligand.

B. *Synthesis of Nickel complex:*

About 1.07g of *p*-toluedine and 1.20 ml of *p*-anisaldehyde were dissolved in ethanol separately. The *p*-anisaldehyde added drop by drop wise in the stirred solution of *p*-toluedine and permissible the reaction till 10 minutes and then the methanolic solution of 1.45 g of nickel nitrate was added slowly till 10 minutes and then the reaction was allowed 5 hr. A light green coloured precipitate was formed which is confirms the formation of metal complexes and collected the pale green precipitate and washed with methanol using copious amount till the complete removal of un-reacted monomers, metal precursor and dried in vacuum.

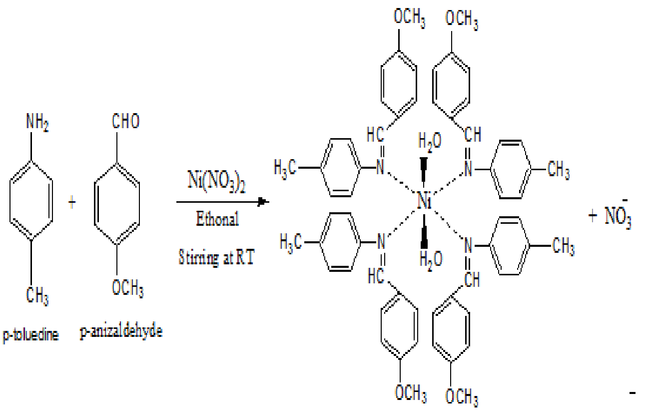

Fig 2: In-situ synthesis of Schiff base [Ni(Anil-Tolu)$_4$ (H$_2$O)$_2$] ligand

IV. RESULTS AND DISCUSSION

A. *UV-visible Spectral analysis*

Figure 1 shows the UV-visible spectrum of ligand and its corresponding metal complexes, which are (a) pure ligand, (b) Nickel, schiff bases. When UV-visible spectra were recorded in CH_3CN solvent, some of the charge transferred bands are observed. The spectrum shows three responses at 250-280 nm, 290-320 nm, and 412-455 nm. The obtaining of broad band due to the presence of the charge transfer of ligand to metal (LMCT) and the ligand to ligand charge transfer transition (p–p') response obtained at below 300 nm and it have weak d-d transition over at 400 nm and finely one shoulker peak was obtained at ~335 nm is responsible for the π-π*transition. These spectra were confirmed the formation of metal complexes successfully using in-situ preparation at room temperature.

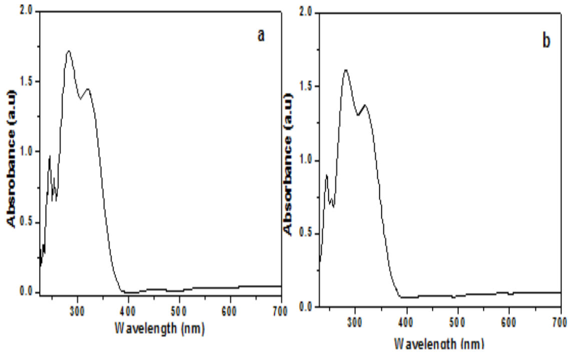

Fig.1. UV-visible spectra of Schiff base (a) and Schiff base nickel complex

B. *Fourier Transforms Infra-red Spectroscopy*

Figure 2 shows the FT-IR spectra of ligand and its corresponding metal complexes, which are (a) pure ligand, (b) Nickel, schiff bases. The ligand has average intense peaks at 1249, 1610, and 1695 cm^{-1} are for ν(C-O), ν(C=N) and ν(C=O), respectively. The response in the region of 540-590 cm^{-1} and 470-500 cm^{-1} are assigned to ν(M—N) and ν(M—O) stretching vibrations were conform the metal are strongly bound with ligand successively. The wide response between in 3149-3300 cm^{-1} observed the complex having hydrated by its broad response. The bands at 2800-3000 cm-1 due to the stretching of ν(C-H) and the band at ~1598 cm^{-1} due to the stretching vibration of ν(C=C) and the responses of aldehyde ν(C-H) obtained at 1309 cm^{-1}. Some of the bands of metal complexes are observed at slightly lower region compared with pure ligand, which confirms the metals were coordinated with Schiff base ligand.

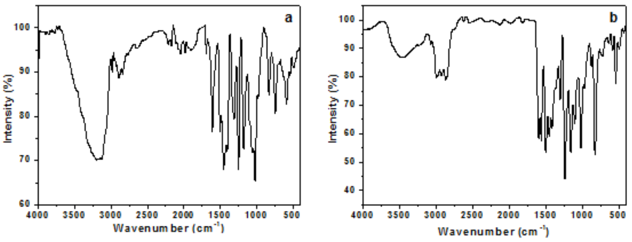

Fig.2. FT-IR spectra of Schiff base (a) and Schiff base nickel complex

C. *X-ray Diffraction studies*

Figure 3 shows the XRD spectra of ligand and its corresponding metal complexes, which are (a) pure ligand, (b) Nickel, schiff bases. The prepared metal complexes having well crystalline sharp peak in its pattern due to its well crystalline nature and also it has considerable change in its pattern [22,23]. The grain nature and its size obtained using Scherre's formula using it's the value of full width half maximum peak value. By these spectra we can easily find out the nature of crystallinity of the metal complexes by the observation of the broad bands at 2θ= 15-30.

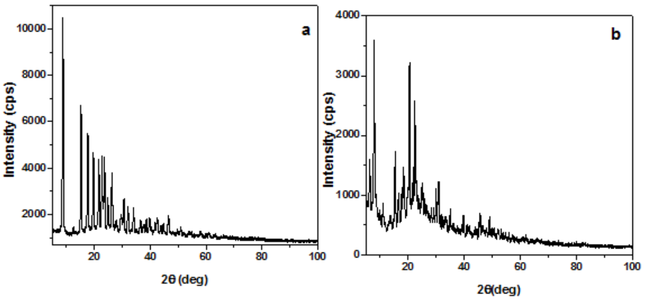

Fig.3. XRD spectra of Schiff base (a) and Schiff base nickel complex

The modified electrode was prepared after polishing with alumina powder with washing with water, sample amount near 2 mg of complex placed on micro slide and add few drop of methanol for making it wet and rub over the surface of GCE for adhering the metal complex on the GCE surface and dried well. All the solution were prepared with purity and purge with N2 air to remove the presence of oxygenated air making it fit for analysis before 10 minutes of measurements.

D. *Electrochemical responses of anizaldehyde-toluidine based Schiff base metal complexes*

Figure 4 shows the electrochemical responses of anizaldehyde-toluidine based Schiff base metal complexes which are Nickel Schiff base ligands in 0.1 M PBS (pH 6) at scan rate 50 mV. The metallic Schiff base complexes has strong peak at 0.84 V due to its irreversible anodic responses of the one-electron oxidation for the bulk species. Two coupled peaks, a reversible but smaller oxidation responses observed at (+0.45 V, +0.73 V and +0.83 V, +1.35 V), which is attributed for the transformation of the metal (M) like M(II)/M(I) and M(I)/M(0) corresponding redox couples and it confirms the electrochemical nature of the reversibility of ligand. The one broad strong irreversible peak observed for the electron transfer in the ligand to metal.

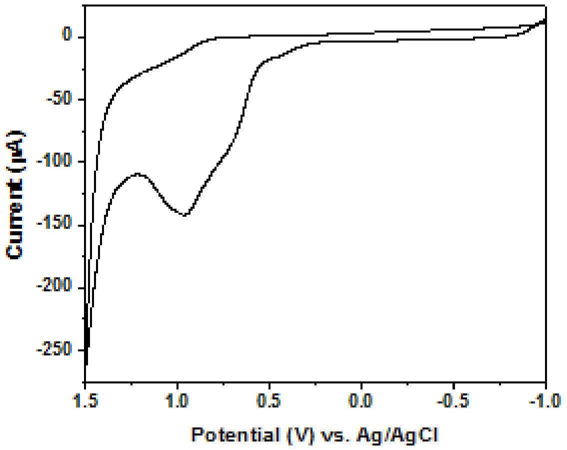

Fig.4. Cyclic voltammogram of Nickel Schiff base metal complex in 0.1 M PBS (pH 6) at scan rate 50 mV.

V. CONCLUSION

The developments of synthesizing new metal complexes have grown rapidly. The transition metal complexes have numerous applications in various fields. In this present study, we synthesized the Schiff base metal complexes using in-situ root of complex formation in room temperature. For the ligand preparation *p*-anizaldehyde and *p*-toluidine was used as monomer and nitrate salt of Ni is used as metal precursor. Three types of metal complexes are prepared in the inert atmosphere, which are Nickel Schiff base metal complex [Ni(Anil-Tolu)$_4$ (H$_2$O)$_2$]. To confirm the formation of ligand and its complexes by some spectral studies which are UV-Vis, FT-IR, XRD and CV, which are confirms the metal are present in the complex.

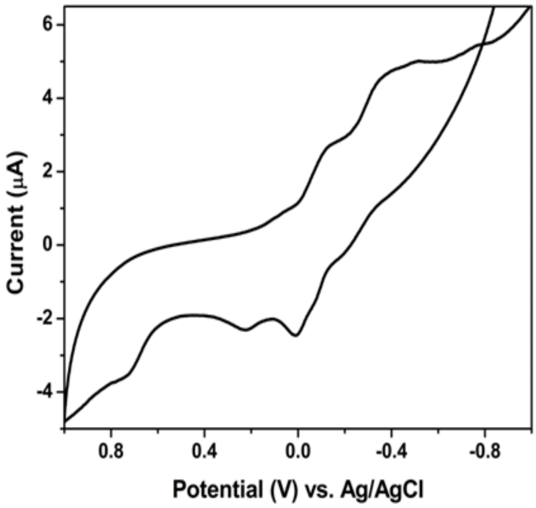

Fig.4. CV spectrum of [Sa(*p*-anisal-DA)$_4$(H$_2$O)$_2$] in 0.1 M PBS (pH 6) at scan rate 50 mV

VI. CONCLUSION

The developments of the field of synthesizing new metal complexes are grown rapidly. The Schiff base transition metal complexes have numerous applications in various fields. In this present work, we followed the in-situ root to synthesize the Schiff base Samarium complexes using in-situ root of complex formation in room temperature. For the ligand preparation p-anizaldehyde and p-toluidine was used as monomer and nitrate salt of Samarium was used as metal precursor. The ligand and its Pd complex are prepared under inert atmosphere, which are Samarium Schiff base metal complex [Sa(p-anisal-DA)4(H2O)2]. To confirm the formation of ligand and its complexes by some spectruml studies which are UV-Vis, FT-IR, XRD and CV, which are confirms the synthesis of [Sa(p-anisal-DA)4(H2O)2] were synthesized successfully by using in-situ method.

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