Synthesis, Characterization and I-V characteristics in $[Co(NH_3)4(C_3H_4N_2)Cl]Cl_2$ prepared by a photochemical route

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Abstract: Synthesis of photo substituted product ($[Co(NH_3)_4(C_3H_4N_2)Cl]\ Cl_2$) based on $[Co(NH_3)_5Cl]Cl_2$ and imidazole ($C_3H_4N_2$) has been successfully achieved by a photochemical route. The as prepared photoproduct has been subjected to different spectroscopic characterizations. The empirical formula observed for the material has been confirmed by CHN analysis. Photo substitution of ligands has been envisioned by UV-Visible spectroscopy, which clearly showed the perturbation of energy levels as hypsochromic shift occurs during irradiation. This leads to the change of color to yellowish orange from red. The material was found to consist of two band gaps corresponding to 3.75eV and 4.56eV.XRD showed sharp intense peaks, reflecting the crystalline nature of material. These peaks have been indexed by powder-X software and it crystalizes into an orthorhombic structure with a space group of pnnm. Lattice parameters and unit cell volume has been obtained after refinement. Debye Scherrer formula has been used to determine the crystallite size which was found to 25.3 nm. Also, I-V characteristics shows the material to fallow ohmicbehavior with a resistance of 20kΩ. This has been attributed to the large band gap as obtained from UV-Visible spectra.

Key words: Pentaamminechlorocobalt(III) Chloride, imidazole, UV-Visible, XRD and I-V characteristics.

Introduction

Since transition metal complexes are known to exhibit many special properties ranging from catalysis to chromism, water softening to some material applications etc., therefore they have been the focus of interest across the globe. Moreover hybrid complexes wherein organic substances are used as ligands have been explored. Among many synthetic routes, photochemical route has been the better and an easy route for their synthesis along with the kinetic and mechanistic studies [1-2]. Photo reactivity of octacyanometallates of Mo (IV), W (IV), and Fe (III) with many ligands like 2,2' bipyridyl, ethylenediamine, 8-hydroxyquionoline, pyrazine, ethanolamine, imidazole has been reported [3-4].The importance of making hybrid complexes allows it to tune the properties of complexes as the ligands of choice can be inserted into thecoordination sphere of parent complex. They have also be used as dopants in many polymer matrices for specific applications viz the helps to exhibit enhanced catalytic activities, EMI shielding and sensor applications, respectively, in polymer matrices [5-7]. Also, the photo substituted product of $[Co(NH_3)_5Cl]Cl_2$ with ligands such as hexamine and EDTA shows essence in improving electronic properties [8-9].

In view of above, the present paper involves the synthesis of a photo substituted product called photoproduct of pentaamminechlorocobalt(III) chloride ($[Co(NH_3)_5Cl]Cl_2$) with imidazole ligand via a photochemical route. The material has been found to exhibit ohmicbehavior as revealed by I-V characteristics.

Materials and Methods

Pentaamminechlorocobalt (III) Chloride (Sigma Aldridge) and imidazole (Loba chemicals) were used of analytical reagent grade. All solutions were prepared in triply distilled water. Irradiation was done with Osram UV-Visible photo lamp. UV-Visible spectroscopy has been carried out using T80 double beam spectrophotometer. Crystalline

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structure and lattice parameters of the sample has been observed by Rigaku X-ray Diffractometer. Current-voltage (I-V) characteristics has been done by a two probe technique. For mechanistic studies of charge transport, Richardson Schottky/Pole Frenkel, SCLC and ohmic conduction has been envisioned.

Synthesis of [Co(NH_3)$_4$($C_3H_4N_2$)Cl] Cl_2

Photo substituted product has been prepared as per the procedure mentioned in literature [5]. The procedure adopted is: An equimolar mixture of Pentaamminechlorocobalt(III) chloride ([Co(NH_3)$_5$Cl]Cl_2) and imidazole (0.5M) in 1:1 ratio was irradiated for half an hour using Osram UV-Visible photo lamp. During irradiation for half an hour, color of the mixture was found to change from pink to yellowish orange. This marked the formation of photosubstituted product called photoadduct. The mixture was concentrated on a water bath and then cooled to room temperature. Yellowish orange colored crystals of the photoproduct separated out. The photoproduct formed was subjected to different spectroscopic and surface characterization techniques.

Results and Discussion

Elemental Analysis

The empirical formula assigned to the synthesized photo substituted product, from CHN analysis, is [Co(NH_3)$_4$($C_3H_4N_2$)Cl] Cl_2. This is based on the observed percentage of C (11.5%), N (27.6%) and H (5%) against the calculated percentage of C (11.8%), N (27.8%) and H (5.3%) respectively. This clearly shows the replacement of one NH_3 ligand by an imidazole ligand. Since imidazole being a neutral ligand, no change in the oxidation state of metal is observed.

UV-Visible spectroscopy

In order to demonstrate the formation of photo substituted product, UV-Visible spectra of the complex before and after irradiation with imidazole ligand has been carried out. Before irradiation, spectra exhibits two transition at the wavelengths of 338 and 270 nm corresponding to Co (d_z^2) ← σ (Cl) and Co ← NH_3respectively [8]. After irradiating the mixture using osram UV-Visible photo lamp, a hypsochromic shift of the peaks has been observed to 330 nm and 267 nm as shown in Fig. 1. This shifting of peaks is due to the perturbation of energy levels which can occur via the exchange of ligands. Hypsochromic shift can be attributed to the replacement of weaker field ligand NH_3 by a comparatively stronger imidazole ligand. This indicates the formation of photoproduct. Moreover, the band gaps obtained using $E_g = hc/\lambda$ before irradiation has been found to be 3.6eV (338 nm) and 4.6eV (270 nm) eV for the corresponding transitions as mentioned in paranthesis. However, after irradiation due to the exchange of ligands, corresponding band gaps are 3.75eV (330 nm) and 4.56eV (267 nm) eV.

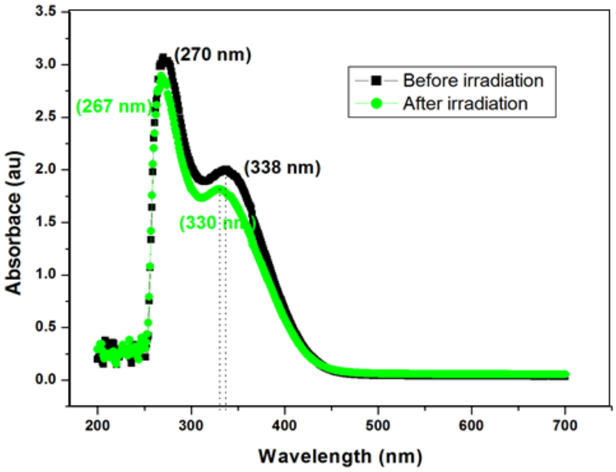

Figure 1: UV-Visible spectra of[Co(NH_3)$_5$Cl]Cl_2 with imidazole ligand before and after irradiation.

X-ray Diffraction (XRD)

X-ray Diffraction of the synthesized photo substituted product is shown in Fig. 2. Photoproduct clearly reflects sharp peaks thereby illustrating the material to be crystalline in nature. These peaks have been indexed using Powder-X software. This has been crystallized into an orthorhombic structure with a space group of *pnnm*. which matches well with the JCPDS-International Centre for diffraction data, file no. 73-1449.

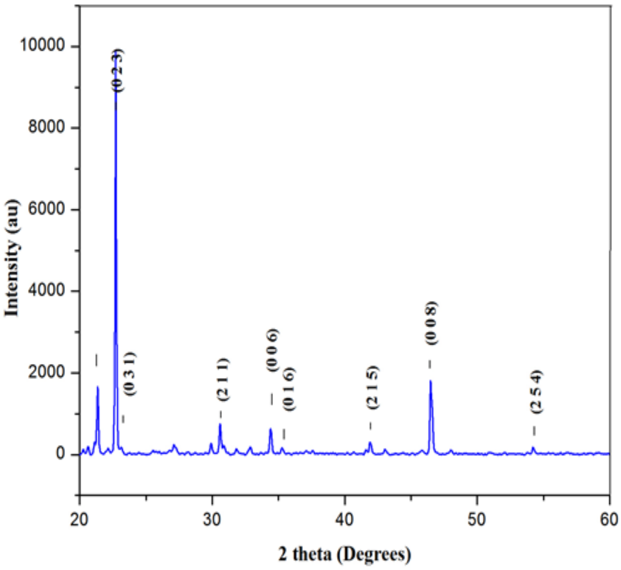

Figure 2:XRD pattern of photo substituted product (photoproduct).

The lattice parameters obtained after refinement and volume of unit cell are shown in Table 1. Particle size (D) of photoadduct has been obtained using Scherrer formula:

$$D = 0.89\lambda/\beta Cos\theta$$

whereλ is the wavelength used (Cu K_α = 1.54Å), β is the FWHM and θ is the Bragg angle.

I-V Charactristics

The current-voltage characteristics for the photoproduct has been carried out by a two probe technique. As is evident from Fig. 3a, an increase in current takes place with the increase in applied voltage. Different mechanisms have been given for the conduction of such materials. The Richardson Schottky (RS) or Pole Frenkel (PF) mechanism occurs due to thermal activation of electrons over the metal-insulator/metal-semiconductor interface or from traps into the conduction band of insulator respectively. In both cases, lnI vs $V^{1/2}$ characteristics is expected to be linear. Spacecharge limited current (SPLC) on the other hand is described by Mott Gurney law where incurrent varies with the square of voltage i.e. I α V^2 [8].

Since the I-V plot appears to be linear, it is expected to have ohmic behavior. To account for the actual conduction mechanism in the present material, I-V plot has been drawn on logarithmic scale to fit the power law

$$I = KV^m$$

where$K$ is a constant and the value of the exponent m helps us to identify the conduction mechanism. Fig. 3b shows I-V plot on logarithmic scale, which revealed the value of exponent (m) to be 0.81 (approaching 1) throughout the applied voltage range. This clearly shows an ohmic conduction mechanism to be operative in the present material and is in accordance with ohms law. This means that the

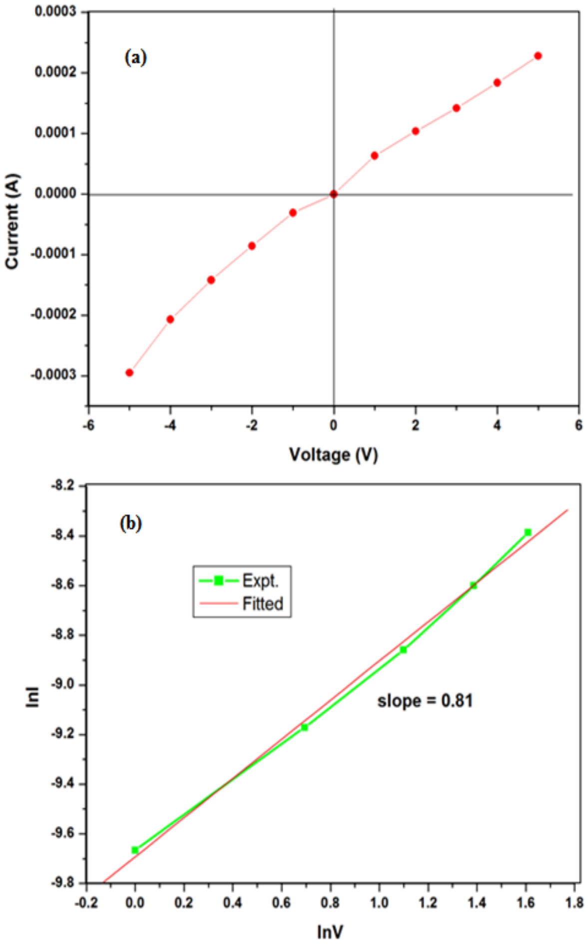

Figure 3: I-V characteristics (a) and its logarithmic plot (b) for synthesized photoproduct.

Table 1 Geometrical parameters and crystallite size in the synthesized photoproduct.

Sample (D)	Lattice Parameters (Å)	Structure	Volume (Å3)	Crystal Size
Photoproduct	a= 6.153, b= 11.895, c= 15.732 & α=β=γ=90°	Orthorhombic	1151.4	25.3 nm

thermally generated free charge carriers in the nanocomposite material are predominant over injected charge carriers owing to contacts. The resistance of the synthesized photoadduct has been found to be 20 kΩ. This high value of resistance can be attributed to the large band gap as shown by UV-Visible spectra, due to which there are less number of charge carriers available in the conduction band.

Conclusion

A photoproduct based on $[Co(NH_3)_5Cl]Cl_2/C_3H_4N_2$has been successfully prepared by photochemical route. This is justified by CHN analysis, UV-Visible. Moreover, XRD showed its crystalline nature with an orthorhombic crystal structure. Lattice parameters, unit cell volume and crystallite size have been obtained. Also from I-V study, the material obeys ohms law in the given voltage range with a resistance of the order of 20kΩ.

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