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Study of optical and electrical properties of $[Co(NH_3)_3(C_{12}H_8N_2)Cl]Cl_2$ prepared by a photochemical route

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ABSTRACT

Synthesis of photoadduct ($[Co(NH_3)_3(C_{12}H_8N_2)Cl]\ Cl_2$) based on $[Co(NH_3)_5Cl]Cl_2$ and 1,10-phenenthroline ($C_{12}H_8N_2$) has been successfully achieved by a photochemical route. The as prepared photoadduct has been subjected to different spectroscopic characterizations. The empirical formula mentioned for the photoadduct has been confirmed by CHN analysis. This was also supported by FTIR spectra. UV-Visible spectroscopy reflects the material to exhibit non-linear optical (NLO) properties as the material was found to exhibit wide transparency in most part of visible region, which is an essential condition for NLO behavior. This has been confirmed by the second harmonic generation (SHG) test, which clearly revealed a greenish emission of wavelength 532 nm from an incident laser radiation of wavelength 1064 nm. The SHG efficiency for the photoadduct was found to be 0.46 times to that of standard KDP. Also, I-V characteristics shows the material to fallow ohmic behavior with a resistance of 1.2 MΩ. This has been attributed to the large band gap as obtained from UV-Visible spectra.

1.Introduction

The photosubstitution reactions in transition metal complexes provide a better and easy route for the synthesis of many metal complexes. The kinetics and mechanistic studies of these photo substituted reactions has been discussed extensively in literature [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, imidizole has been reported [3-4]. In such reactions, the prepared metal complexes (also called photoadducts) are isolated from solutions either by evaporation technique or by the use of complexing agents. The importance of making such systems lies in introducing the ligands of choice. For instance, it has been observed that the photoadducts of sodium nitroprusside with ligands like 2,2' bipyridyl, hexamine, EDTA helps to exhibit enhanced catalytic activities, EMI shielding and sensor applications, respectively, in polymer matrices [5-7]. Also, the photoadducts of $[Co(NH_3)_5Cl]Cl_2$ with ligand such as hexamine and EDTA shows essence in improving electronic properties [8-9].

Keeping this into consideration, the present work is based on the synthesis of $[Co(NH_3)_5Cl]Cl_2$/1,10-phenenthroline based photoadduct for optical and electrical properties. The method of synthesis adopted is as per the literature i.e., via a photochemical route. The material has been found to show non-linear optical (NLO) properties, hence is used in the generation of second and third harmonics. Moreover, it has been found to obey ohms law and the current carried by it lies in microamperes.

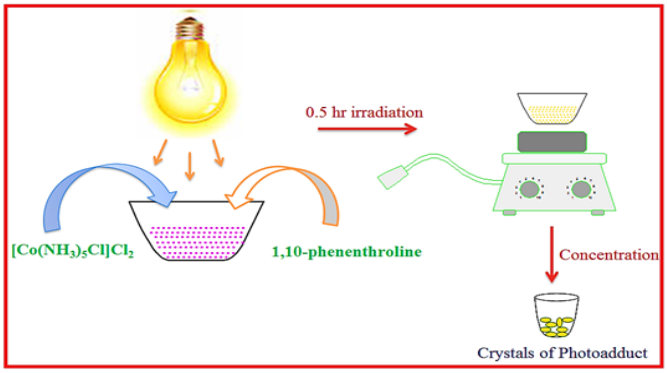
1. Experimental

2.1. Materials and Physical Measurements

Pentaamminechlorocobalt (III) Chloride (Sigma Aldridge) and 1,10-phenenthroline (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. FTIR spectra was recorded on Perkin Elmer RX-1 FTIR spectrophotometer (USA) using KBr pellets. 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.

2.2. Synthesis of photoadduct ($[Co(NH_3)_3(C_{12}H_8N_2)Cl]\ Cl_2$)

An equimolar mixture of Pentaamminechlorocobalt(III) chloride ($[Co(NH_3)_5Cl]Cl_2$) and 1,10-phenenthroline (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 golden yellow. This marked the formation of photosubstituted product called photoadduct. The mixture was concentrated on a water bath and then cooled to room temperature. Golden yellow colored crystals separated out. This is schematically shown in scheme 1. The photoadduct formed was subjected to different spectroscopic and surface characterization techniques [5].



Scheme 1. Schematic representation showing the synthesis of photoadduct ($[Co(NH_3)_3(C_{12}H_8N_2)Cl]\ Cl_2$).

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2.Results and Discussion

3.1. Elemental analysis:

From CHN analysis, the empirical formula assigned to the synthesized photoadduct was found to be $[Co(NH_3)_3(C_{12}H_8N_2)Cl]\ Cl_2$. This is justified as the observed percentage of C, H, N i.e., 16.8, 5.14, 37.2 matched well with its calculated percentage viz 17.3, 4.8, 36.3 respectively.

3.2. FTIR Characterization:

Fourier transform infrared (FTIR) spectrum was recorded on Perkin Elmer RX-1 FTIR spectrophotometer using KBr pellets. The characteristic peaks exhibited by $[Co(NH_3)_5Cl]Cl_2$ complex are observed at 3283, 1593, 1307, 844 and 489 cm^{-1} which correspond to the NH_3 stretching vibration, degeneration deformation vibration of NH_3 ligand, symmetric deformation vibration of NH_3, rocking vibration of NH_3 and Co-NH_3 stretching vibrations respectively [8]. On the other hand, the main vibrational modes observed for 1,10-phenenthroline reflect their appearance at 2828 & 2965, 1630, 1555 cm^{-1}. These correspond to υCH, υC=C, υC=N stretching vibrations respectively.

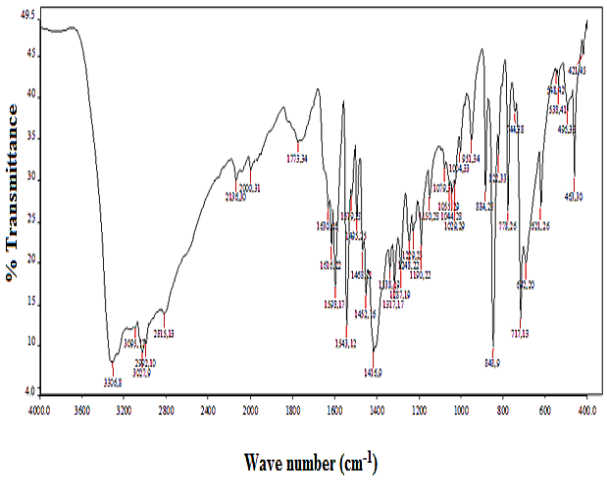
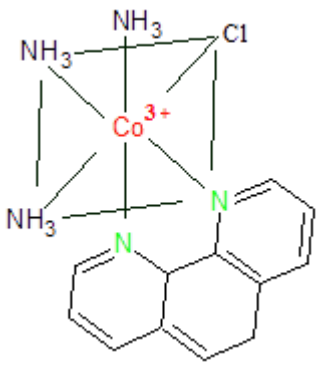


Fig 1. FTIR spectra of photoadduct.

In the FTIR spectra of photoadduct as shown in Fig. 1, all the vibrational due to Co-complex and 1,10-phenenthroline exhibit their appearance at their respective wavenumbers. However, the peaks are more or less shifted. This is owing to the introduction of 1,10-phenenthroline ligand into the coordination sphere of complex, hence confirms the formation of photoadduct. The presence of Co-Cl peak in photoadduct at 848 cm^{-1} indicated that it is the NH_3 ligand which has been replaced by 1,10-phenenthroline ligand instead of Cl. This is in accordance with the CHN results. The proposed structure for the synthesized photoadduct is shown below:



From this discussion successful synthesis of photoadduct has been proved.

3.3. UV-Visible spectroscopy and SHG study

To demonstrate the formation of photoadduct, UV-Visible spectra of the complex before and after irradiation with 1,10-phenenthroline has been carried out. Before irradiation, spectra exhibits three transition at the wavelengths of 526, 366 and 226 nm. First two transitions are attributed to the Co (d_z^2) ← π (Cl) and Co (d_z^2) ← σ (Cl) and the transition in UV-region is due to Co ← NH_3 [8]. After irradiating the mixture using osram UV-Visible photo lamp, a hypsochromic shift of the first two transitions has been observed as the peak at 526 nm has been shifted to 477 nm and the peak at 366 nm exhibits its apearance as shoulder to 227 nm peak (Fig. 2). 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 1,10-phenenthroline ligand. This indicates the formation of photoadduct. Moreover, the band gaps obtained using $E_g = hc/\lambda$ before irradiation has been found to be 2.35 (526 nm), 3.38 (366 nm) and 5.46 (227 nm) eV for the corresponding transitions as mentioned in paranthesis. However, after irradiation due to the exchange of ligands, corresponding band gaps are 3.20 (377 nm) and 5.46 (227 nm) eV.

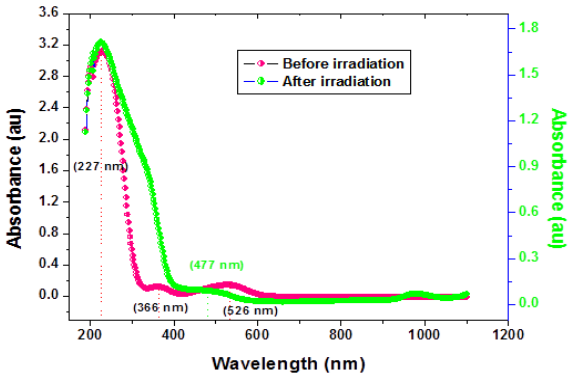


Fig 2. UV-Visible spectra of $[Co(NH_3)_5Cl]Cl_2$/ $C_{12}H_8N_2$ mixture before and after irradiation.

Moreover, there is a wide transparency in most part of visible region which is an essential condition for a material to exhibit NLO properties. This has been justified by conducting a second harmonic generation (SHG) test. Second harmonic generation (SHG) of the synthesized photoadduct was evaluated by the Kurtz and Perry powder technique. The powered photoadduct was packed in a microcapillary of uniform bore and was exposed to laser radiation. A Q-switched Nd-YAG laser beam of fundamental wavelength 1064 nm (8 ns pulsed width and 10 Hz pulse rate) was made to fall normally on the sample cell. The emitted light was focused by a lens and detected by the photomultiplier tube, a green emission of wavelength 532 nm was observed which confirmed the generation of second harmonics. During the experiment, KDP was used as reference. It is observed that the SHG efficiency of the present photoadduct sample is 0.46 times that of KDP.

3.4. Current-Voltage (I-V) Characteristics

The current-voltage characteristics for the photoadduct has been carried out by a two probe technique. The behavior observed is shown in Fig. 3, which clearly shows a gradual increase of current with the applied voltage. The mechanism of conduction in such a material can be either Richardson Schottky (RS)/Pole Frenkel (PF) or Space charge limited current (SPLC) or Ohmic conduction.

Schottky emission occurs due to thermal activation of electrons over the metal-insulator or metal-semiconductor interface barrier because of lowering of barrier height due to the applied field. PF is similar to schottky except that it is applied to the thermal excitation of electrons from traps into the conduction band of insulator. In both cases, lnI vs $V^{1/2}$ characteristics is expected to be linear. For SCLC model as described by Mott Gurney law, current varies with the square of voltage i.e. I α V^2.

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 0.98 (~ 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 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 1.2 MΩ. 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.

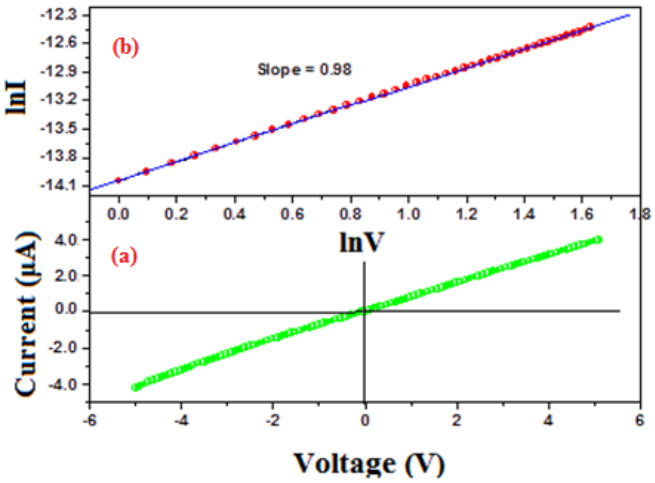


Fig 3. I-V characteristics (a) and its logarithmic plot (b) for synthesized photoadduct.

Conclusion

A photoadduct based on $[Co(NH_3)_5Cl]Cl_2/C_{12}H_8N_2$ has been successfully prepared by photochemical route. This is justified by CHN analysis, UV-Visible and FTIR spectroscopy. Moreover, wide transparency in the entire visible region indicates the material to exhibit NLO properties which has been justified by second harmonic generation (SHG) test. The SHG efficiency of the sample was found to be 0.46 times the standard KDP. Also from I-V study, the material obeys ohms law in the given voltage range with a resistance of the order of 1.2 MΩ.

Note

The authors declare no competing financial interest.

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Conflict of Interest Statement:

There is no conflict of interest between authors and the organizations in which the present work has been carried out.

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