



SOLID STATE ELECTRICAL CONDUCTIVITY AND PHOTO GALVANIC STUDIES OF [Ni₂(Et₂dtc)₂Fe(CrO₄)₂(H₂O)₂]

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ABSTRACT

[Ni₂(Et₂dtc)₂Fe(CrO₄)₂(H₂O)₂] was synthesized and the structure was elucidated by elemental analyses, FT-IR, UV-Visible, FABMS and EPR techniques. The thermal behavior of the compound will be discussed. The compound exhibited both photochromism and photogalvanic behavior in chloroform solution. On exposure to sunlight and incandescent light, the complex showed photochromic changes from yellow to yellowish green to green in chloroform solution. Reversibility was established in the presence of air and in dark after three days. A similar study was conducted using a Honda cell wherein one half-cell was irradiated and the other kept in the dark for photogalvanic generation. It was noted that a maximum of 100 mV was obtained with incandescent light and the voltage generation was not linear but showed maxima and minima as a function of time. The maxima and the minima in the time – voltage curve corresponded to those obtained from photochromic curve. Thus it was established that the energy absorption led to valence changes in the trimetallic compound leading to both photochromic and photogalvanic behavior. The compound may have a potential for use in the solar energy conversion. The solid-state electrical conductivity studies indicated the ohmic nature of the compound. The dark and the photoconductivity studies along with the temperature variation conductivity studies will also be discussed.

Key words: Ni-Fe-Cr compound, solid-state electrical conductivity, photo-galvanic Studies, field dependent conductivity, photo-electrochemical studies

1. INTRODUCTION

The current search for additional energy sources has drawn renewed attention to the utilization of solar energy (Hagfeldt and Gratzel, 1995; Tan et al., 1994). Among the various schemes for its exploitation, direct conversion into electricity has obvious advantages (Clark and Eckert, 1975; Gomer, 1975). Photogalvanic cells are one such type in which certain species dissolved in a suitable solvent are the light absorbing ones (Wrington, 1983). Various Photogalvanic cells are reported in the literature (Rabinowitch, 1940; Ameta et al, 1985; Ameta et al, 1991; Dube, 1993; Eisenberg and Silverman, 1961; Gangotri et al, 1996) and cells using inorganic compounds/complexes are very rare. Nagaraja and coworkers (Raj et al, 1986; Venkatraman et al., 1992; Vasanthi et al., 1993; Edwin et al, 1999; Edwin et al, 2000) had reported heterobinuclear complexes of molybdenum, manganese and tungsten with diethyldithiocarbamates and 8-quinolinol, which were found to be highly photoactive. To calculate the activation energy of the compounds dc resistance and temperature dependence conductance measurements were carried out using a two-probe method as reported by Suman and Nagaraja, 2003. In the present study, the construction of a photogalvanic cell and thereby extension to solar cell using heterotrinuclear nickel-iron-chromium-diethyldithiocarbamate in chloroform medium is reported. The activation energy of the compound is calculated by the

solid-state field dependent and room temperature electrical conductivity studies. The conductivity in dark and sunlight will also be discussed.

2. EXPERIMENTAL

[Ni₂(Et₂dtc)₂Fe(CrO₄)₂(H₂O)₂] compound was synthesized and characterized by elemental analyses, FT- IR, UV-Visible, FABMS and EPR techniques. The thermal behavior of the compound will be discussed by TG-DTA analysis and vapor transport studies under vacuum conditions. The UV-Visible spectrum was recorded by the Lambda 25 UV-Visible spectrophotometer. The photochromic behavior of the compound was studied in chloroform at a concentration of 1x10⁻³M and the change in absorbance values were recorded by the Lambda 25 UV-Visible spectrophotometer. The photogalvanic studies (Figure 1) were carried out in a Honda cell with 'U' shaped glass compartments of 200cm³ capacity with the columns separated by a frit of 2.5cm diameter. The entire cell was surrounded by a glass jacket to circulate water and thereby to maintain the system at constant temperature. Platinum electrode of 1.0cm diameter was used in both the compartments, which were impregnated with mercury, and electrically connected to a digital multimeter in series. The distance between the electrodes was 20cm. During the investigation one limb was kept in dark and the other was irradiated with 250W tungsten lamp.

DC resistance measurements on the sample were carried out using a two-probe method (Figure 2) in which the sample was mounted on a glass slide and two thin copper wires (1.4mm diameter) were fixed by using silver paint (GE Thomson). The electrode distance was kept around 1-2mm and was measured accurately using a traveling microscope. The sample was electrically connected to a DC power supply and picoammeter Keithley 485 in series. The dark and photocurrent studies were carried out by exposing the above set up in dark and in sunlight.

The temperature dependence of conductance measurements (Figure 3) was carried out by keeping the sample inside a pyrex cylinder of 5cm diameter and 75cm length with kanthal A1 wire uniformly wound around it. The ends of the kanthal wire were connected to a variac for heating. A k-type thermocouple whose hot junction located in the close proximity of the specimen was used to monitor its temperature accurately. The electrodes of the samples were connected to the DC power supply and the picoammeter in series and the activation energy of the compound was calculated from the plot of lnI vs. 1000/T using the relation

$$I = I_0 e^{-E_a/kT}$$

Where k is Boltzmann constant and T is the temperature in Kelvin.

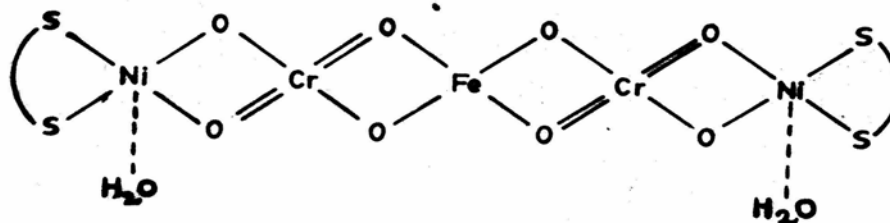
3. RESULTS AND DISCUSSION

Synthesis, Characterization and proposed structure

The compound [Ni₂(Et₂dtc)₂Fe(CrO₄)₂(H₂O)₂] was synthesized from [Ni(et₂dtc)₃][FeCl₄] and K₂CrO₄ (Judith Vijaya and Nagaraja, 2004) and characterized by FT-IR (Figure 4), UV-Visible (Figure 5), FABMS (Figure 6) and EPR techniques. The weak broadband observed around 3450cm⁻¹ is assigned to γ(OH) indicating the presence of coordinated water molecule. The band observed around 1600cm⁻¹ is attributed to δ(H₂O). The presence of coordinated water is also supported by thermogravimetric data. The band around 1250-1350 cm⁻¹ is assigned to the presence of C-N single bond. The band at 1440 cm⁻¹ is due to the presence of C=N stretching mode. The sharp band at 900cm⁻¹ shows the presence of γ(Mo=O) moiety. The absorption at 490 cm⁻¹ is assigned to the presence of γ(Ni-H₂O) and the presence of γ(Ni-O-Cr) is confirmed by the absorption bands at 850 and 570cm⁻¹. The band at 510 cm⁻¹ is due to the presence of γ(Ni-S) (Chatt et al, 1956). From the UV-Visible spectra (Figure 5) the peaks at λ 380nm (oxygen to chromium charge transfer transition), 420nm (sulfur – nickel charge transfer transition), 550nm and 560nm (four coordinated nickel center) are assigned. The base peak at

354 corresponds to $[\text{Ni}(\text{et}_2\text{dtc})_2]^+$ and the peaks at The complexes at a very low energy itself fragments and no molecular ion peak is found in the analysis. The complex $\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2$ shows the base peak at 354 (m/z value) which is due to $[\text{Ni}(\text{et}_2\text{dtc})_2]^+$ fragment. The peaks at 560, 503, 414, 307, 289, 206, 148 and 116 corresponds to $[\text{Ni}_2(\text{et}_2\text{dtc})\text{Fe}(\text{CrO}_4)_2]^+$, $[\text{Ni}(\text{et}_2\text{dtc})\text{Fe}(\text{CrO}_4)_2]^+$, $[\text{Ni}_2(\text{et}_2\text{dtc})_2]^+$, $[\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})]^+$, $[\text{Fe}(\text{CrO}_4)_2]^+$, $[\text{Ni}(\text{et}_2\text{dtc})_2]^+$, $[(\text{et}_2\text{dtc})]^+$ and $[(\text{et}_2\text{dtc})\text{-S}]^+$ respectively.

The EPR studies show no characteristic peaks except DPPH peak. Hence the complexes are found to be diamagnetic. With all the above results proposed structure of the compound is drawn.



Thermal behavior of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

Thermal behavior of the compound $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ was studied by TG-DTA analysis (Figure 7) which showed the presence of 40% residue corresponding to the formation of $\text{Ni}_2\text{Fe}(\text{CrO}_4)$. When the same study was done under vacuum using the set up as shown in Figure 8 it showed the loss of 64% and the qualitative analysis was carried out for both the residue and the vapors deposited along the sides of the flask. The residue showed the presence of nickel, iron and chromium and the vapor showed the presence of chromium.

Photochromic and photogalvanic studies

The compound $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ exhibit both photochromism and togalvanic behavior, particularly when sunlight is a source of energy. The photochromic behavior of the compound was studied by dissolving the compound in chloroform at the concentration of $1 \times 10^{-3}\text{M}$. On irradiation with sunlight / incandescent light for about 1h, the color of the compound changed from yellow to yellowish green and in about 4h, the color turned to green and the reversibility was established in the presence of air and in dark after three days. The absorption was measured in chloroform solution as a function of time on irradiation at the above four λ values. Reversibility was established in the presence of air and in dark after three days as shown by Figure 9a & 9b.

The photogalvanic studies in chloroform solution were carried out using a Honda cell (Figure 1) and the concentration of the complex was fixed as $1 \times 10^{-3}\text{M}$. Initially the solution was yellow in color, which turned to yellowish green to green on exposure to light as a function of time. The potential values at different time intervals were recorded and the maximum potential of 100mV was obtained. Later the whole set up was stored in dark and the potential was recorded for the next three days. The system became reversible on the third day and the yellow color of the solution was regained. The same experiment was repeated to establish that the reversibility is reproducible (Figure 10).

Mechanism of the photogalvanic behavior

Studies were done using nickel-diethyldithiocarbamate $[\text{Ni}(\text{et}_2\text{dtc})_2]$, nickel-iron-diethyldithiocarbamate $[\text{Ni}(\text{Et}_2\text{dtc})_3][\text{FeCl}_4]$ and chromium-diethyldithiocarbamate $[\text{Cr}(\text{et}_2\text{dtc})_3]$ complexes in a Honda cell under identical conditions, to understand the role played by the individual metal centers in the heterotrinnuclear complex. $[\text{Ni}(\text{et}_2\text{dtc})_2]$ in chloroform was green in color which changes to dark green in the presence of light with the maximum potential of 45mV and $[\text{Ni}(\text{Et}_2\text{dtc})_3][\text{FeCl}_4]$ complex in chloroform with reddish brown color changed to dark red on irradiation showed the maximum potential of 47mV and both the systems were not reversible. Neither voltage generation nor color change was observed for $[\text{Cr}(\text{et}_2\text{dtc})_3]$ or K_2CrO_4 . But $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ in chloroform was yellow in color which changed to green on irradiation with light. Thus the irradiation of $[\text{Ni}(\text{et}_2\text{dtc})_2]$ and $[\text{Ni}(\text{Et}_2\text{dtc})_3][\text{FeCl}_4]$ resulted in photochromism with potential generation whereas chromium center was found to be photochemically inactive. Hence it can be concluded that in the complex $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ the photochromism and potential generation could be attributed to the nickel center and the reversibility to the chromium center and iron was not involved in this process since the potential values of $[\text{Ni}(\text{et}_2\text{dtc})_2]$ and $[\text{Ni}(\text{Et}_2\text{dtc})_3][\text{FeCl}_4]$ were approximately the same. An interelectronic transfer mechanism is proposed for the redox behavior of the complex in chloroform. Ni(II) undergoes photo oxidation to Ni(III) and Cr(VI) reduces to Cr(V) in the presence of light and Cr(V) and Ni(III) reverts back to Cr(VI) and Ni(II) in dark which is confirmed by the fact that the solution is initially yellow in color which could be due to the presence of Cr(VI) and changes to green in the presence of light that could be due to the presence of Cr(V). On dark storage it attains the original yellow color and shows the formation of Cr(VI). Thus in the photogalvanic behavior the redox reaction is responsible for the potential generation.

Electrical conductance studies

Field dependent conductivity

At room temperature the current values as a function of field were recorded and a plot of field vs current was obtained which was found to be linear (Figure 11). The linear plots indicated the Ohmic contact over the range of applied field.

Photo and dark current studies

The same set up for electrical conductivity studies was kept in sunlight and in dark and the corresponding increase in the current values at different potential intervals were recorded. In the presence of light there is an increase in the current values as shown in Figure 12.

Temperature variation conductivity studies

When the temperature of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ was increased up to 200K with the constant applied field of 100V/cm the current increased exponentially and the plot of $\ln I$ vs $1000/T$ was drawn which gave a straight line with a negative slope as shown in Figure 13. From the slope the energy of activation (E_a) was calculated and it was found to be 0.14eV.

4. CONCLUSIONS

It is concluded that the compound $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ is reversibly photosensitive with redox action. Thus it is a promising candidate for photogalvanic and photoelectrochemical cells which can be extended to solar energy conversion.

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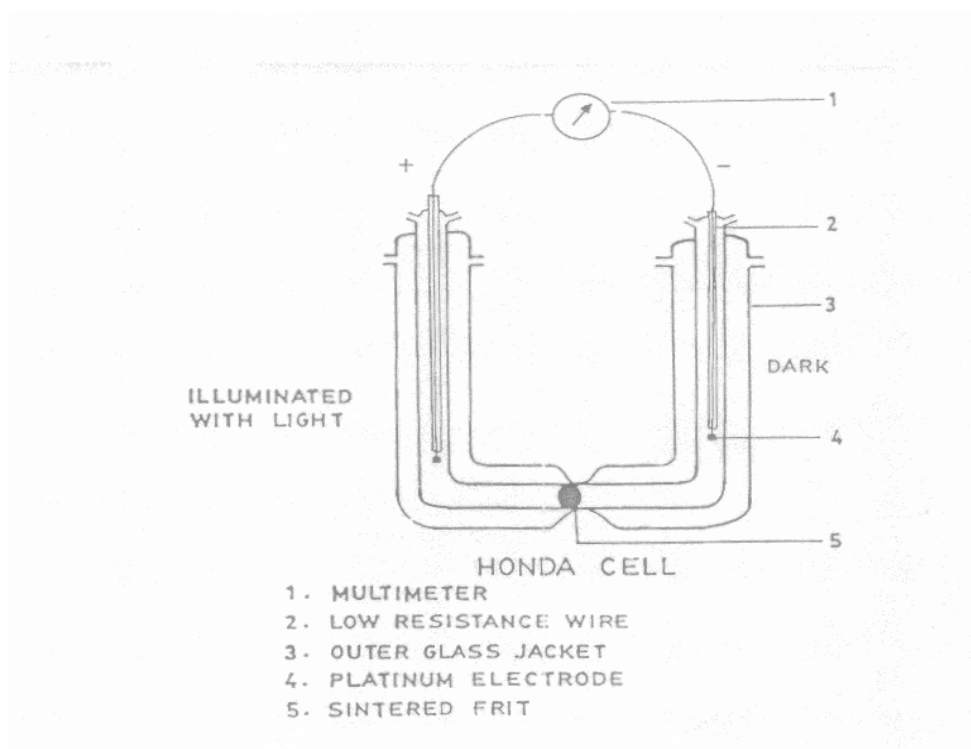


Figure 1. Schematic diagram of Honda cell for the photogalvanic studies

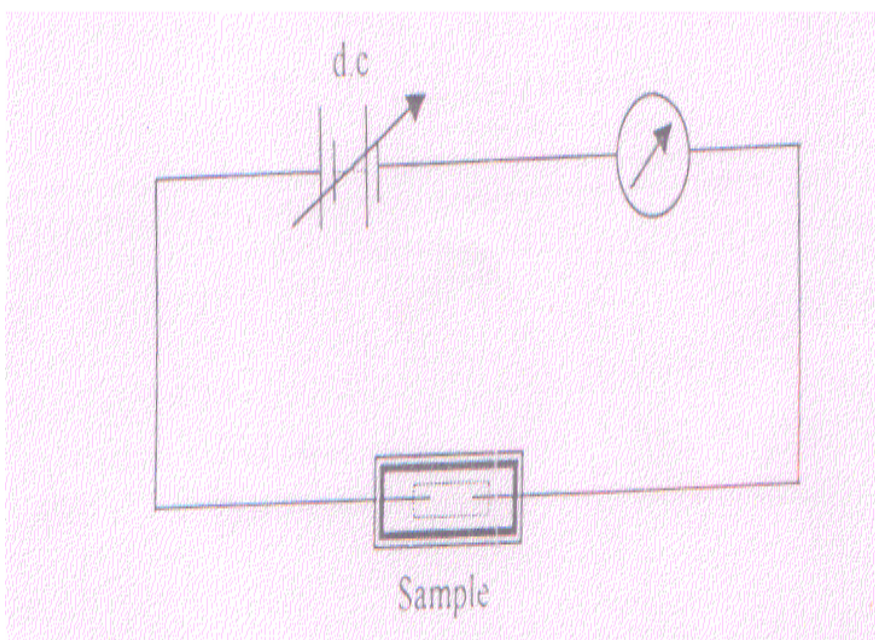


Figure 2. Two-probe set up for electrical conductivity studies

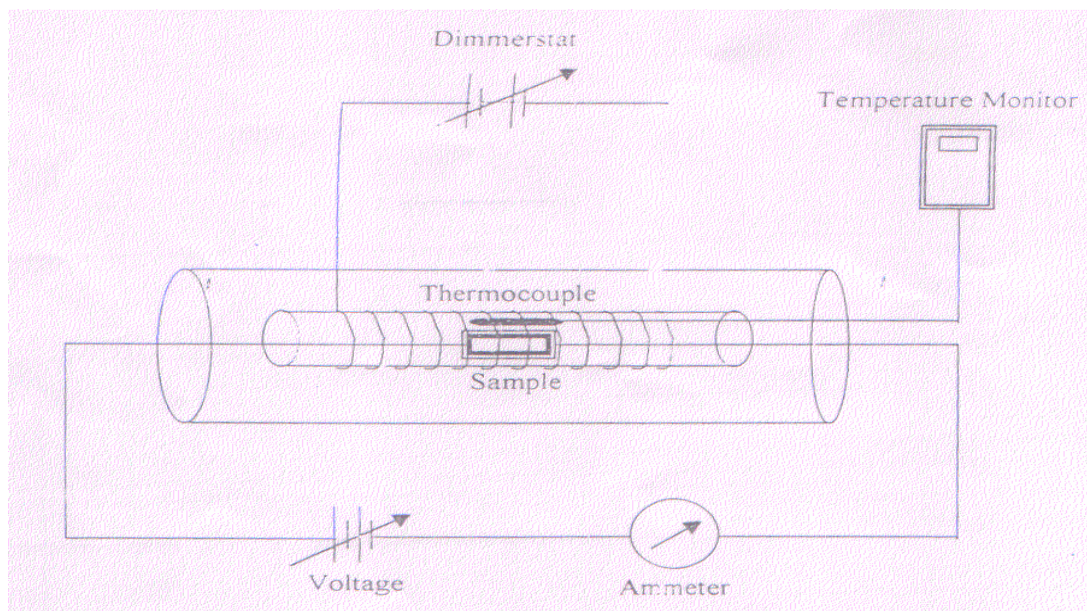


Figure 3. Set up for Temperature Variation conductivity studies

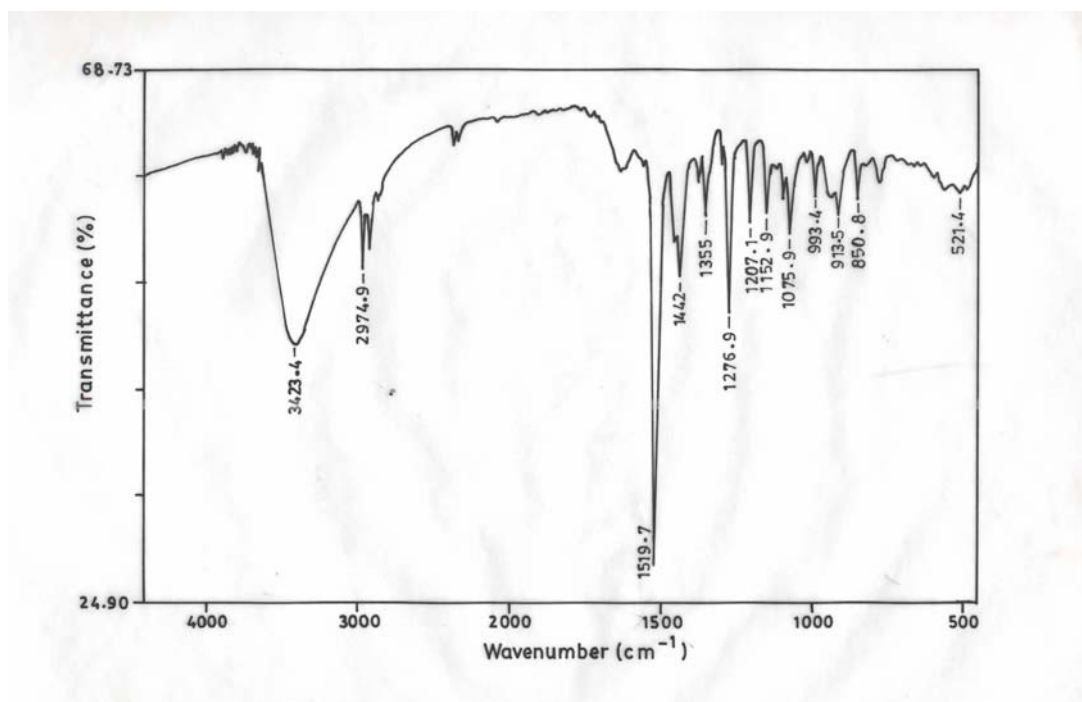


Figure 4 FT-IR spectrum of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

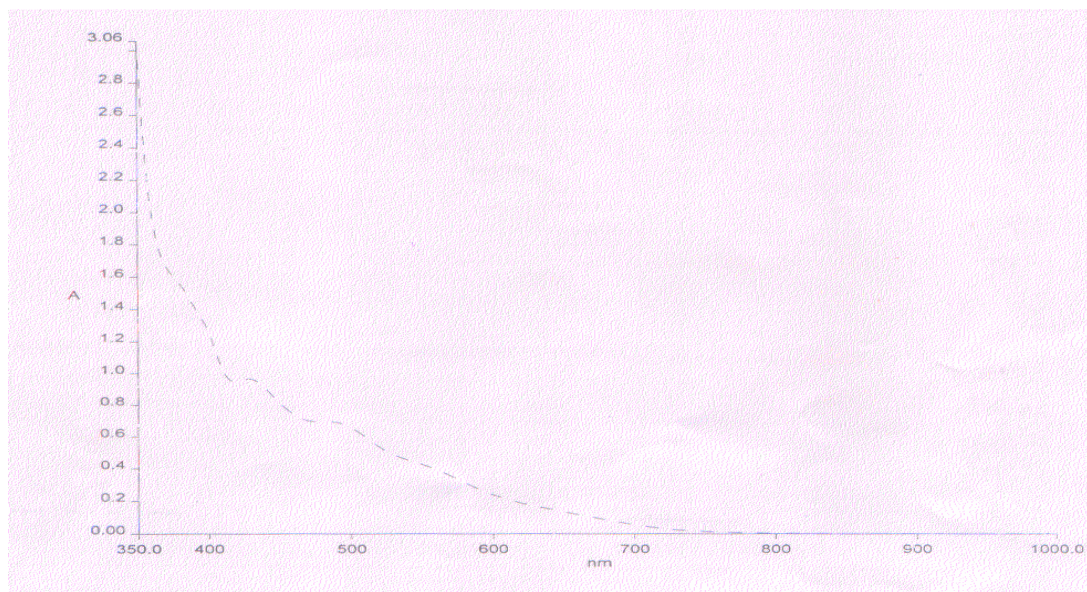


Figure 5 UV-Visible spectrum of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

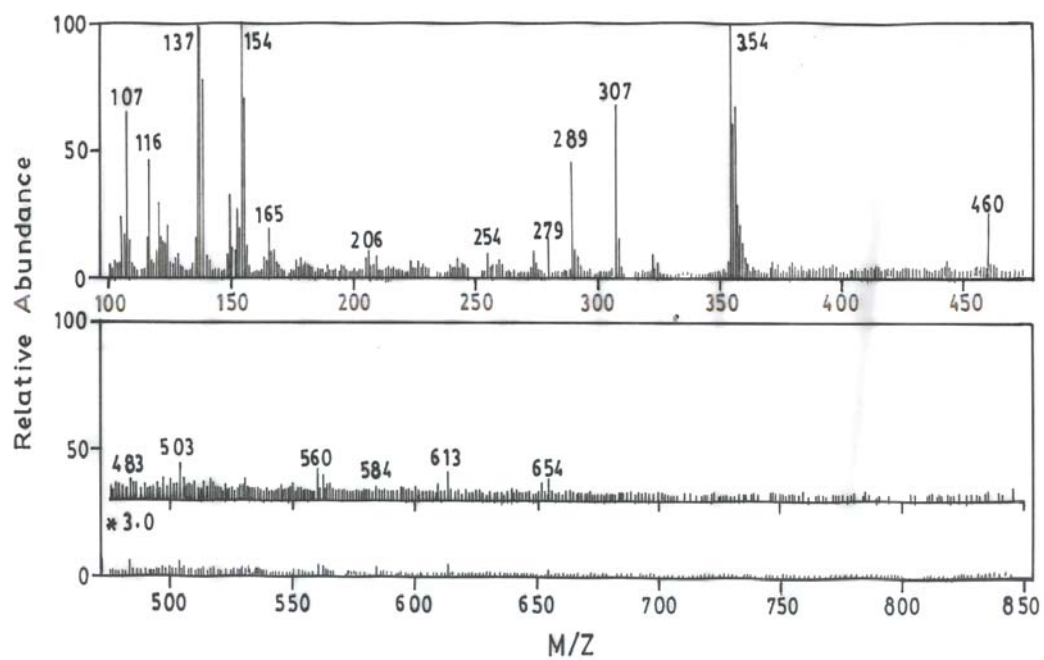


Figure 6 FABMS of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

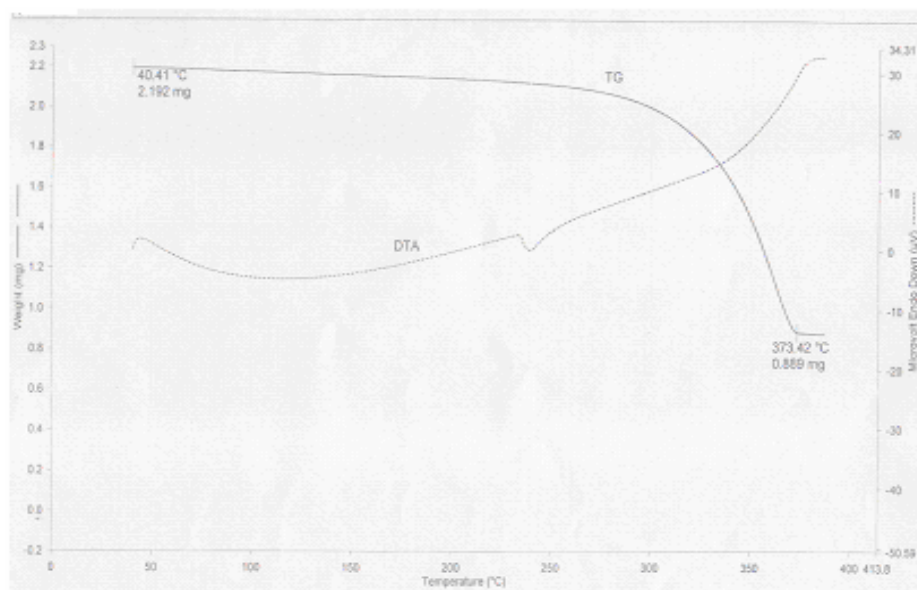


Figure 7 TG-DTA analysis of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

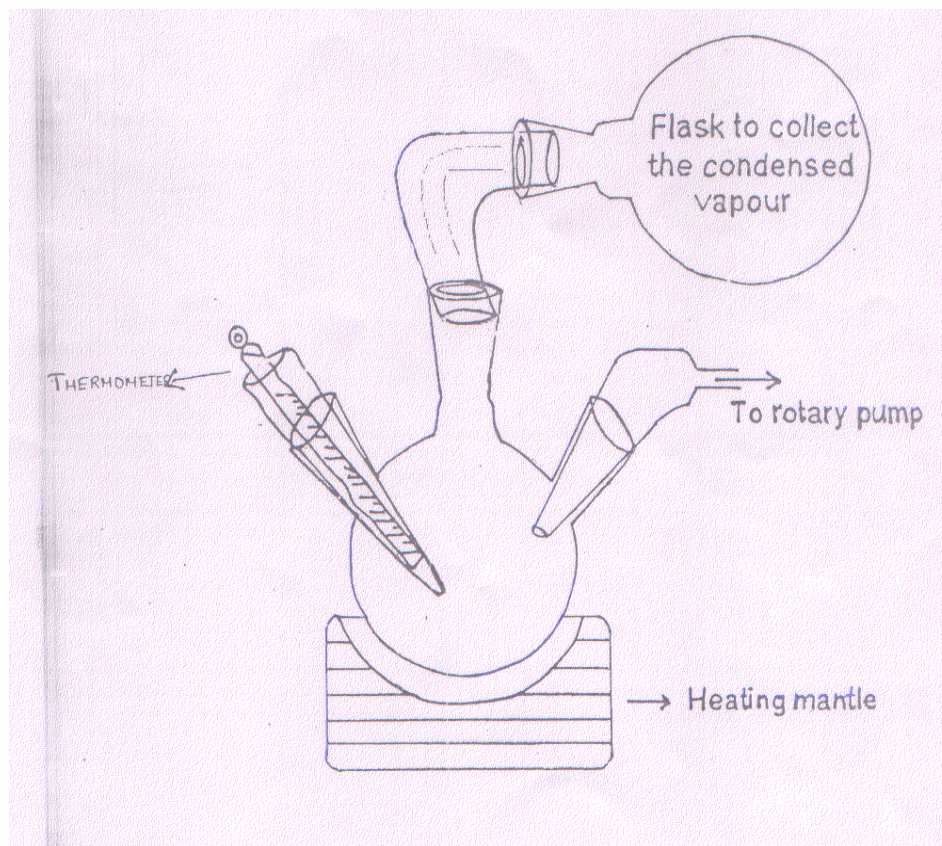


Figure 8 Schematic diagram for the vapor transport studies under vacuum

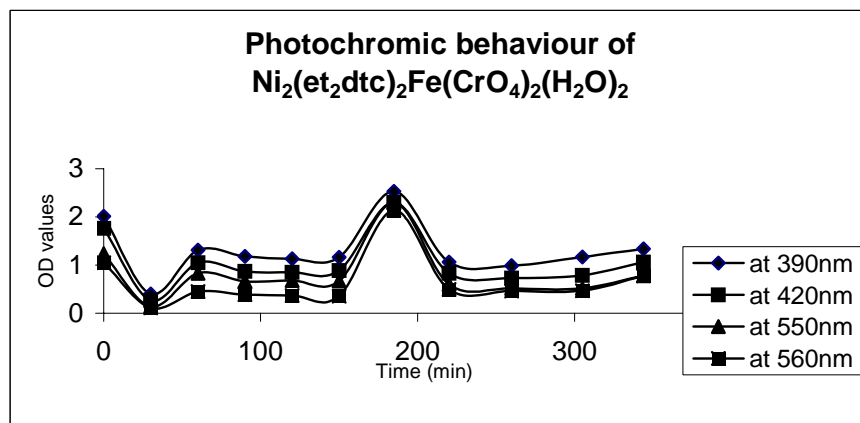


Figure 9a. Effect of sunlight on $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ with respect to time

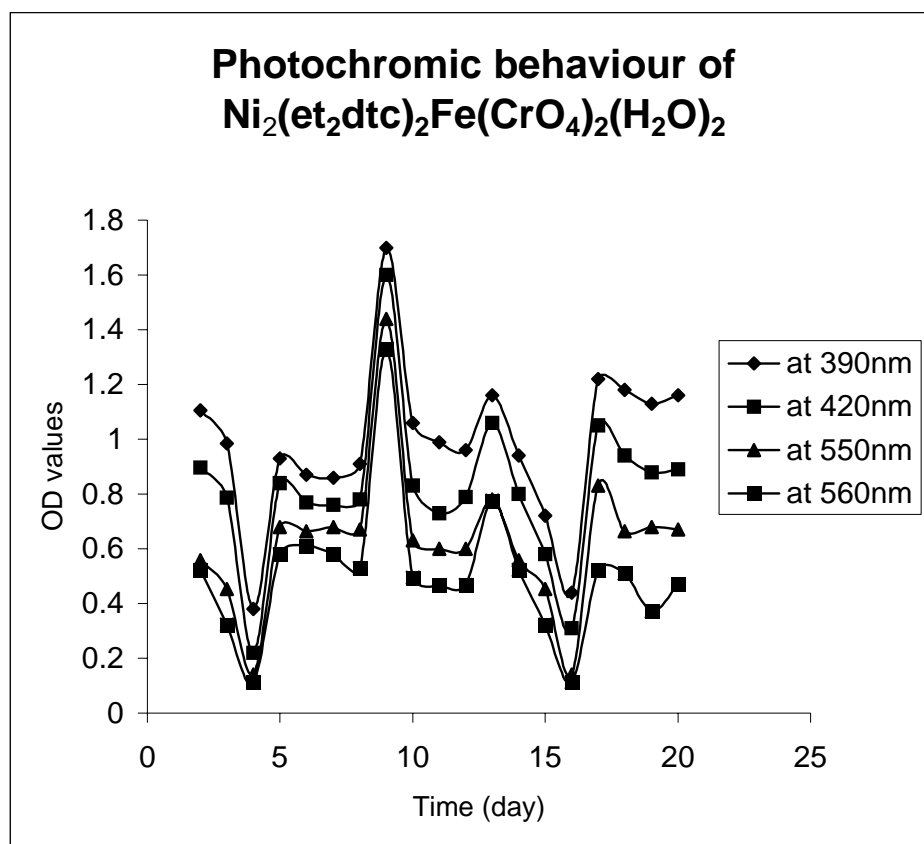


Figure 9b. Effect of sunlight on $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$ with respect to days

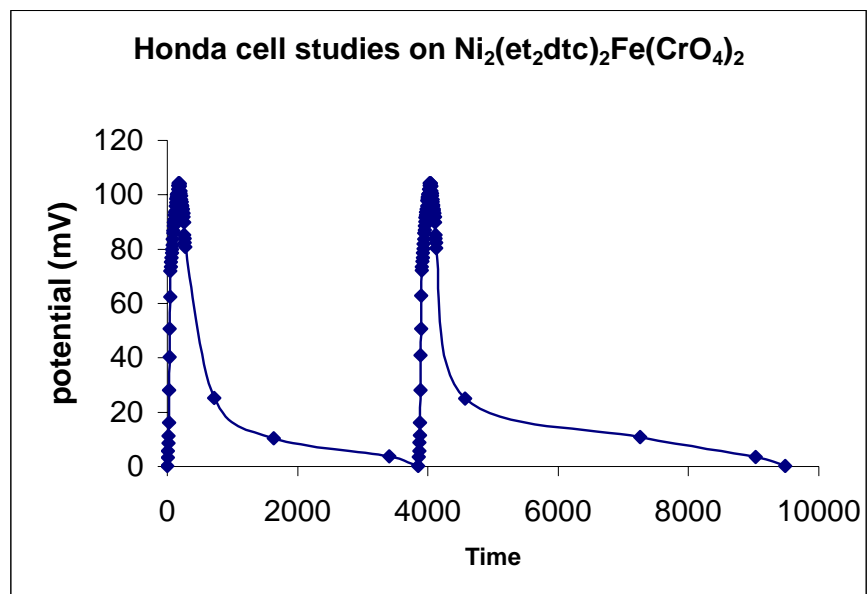


Figure 10. Photogalvanic behavior of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

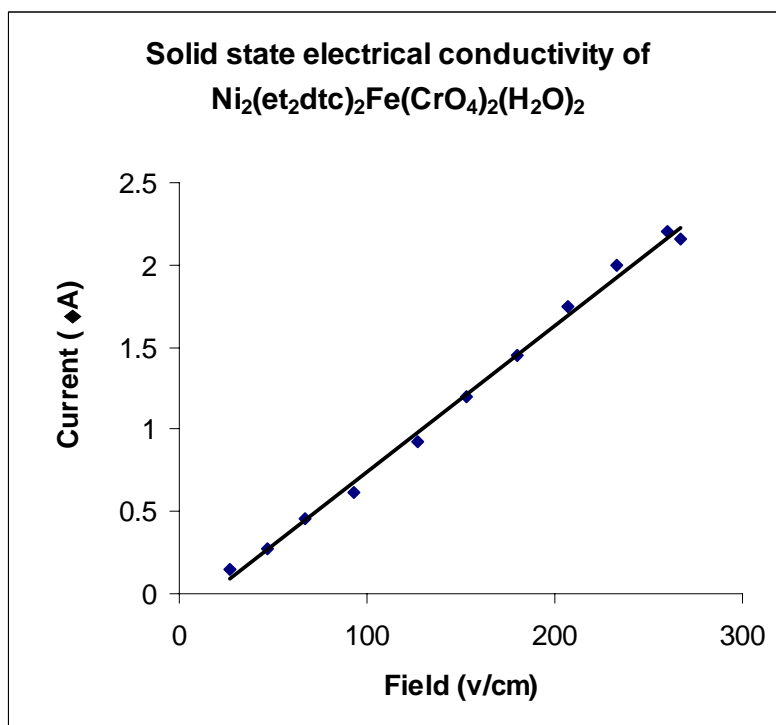


Figure 11. Field vs current plot of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

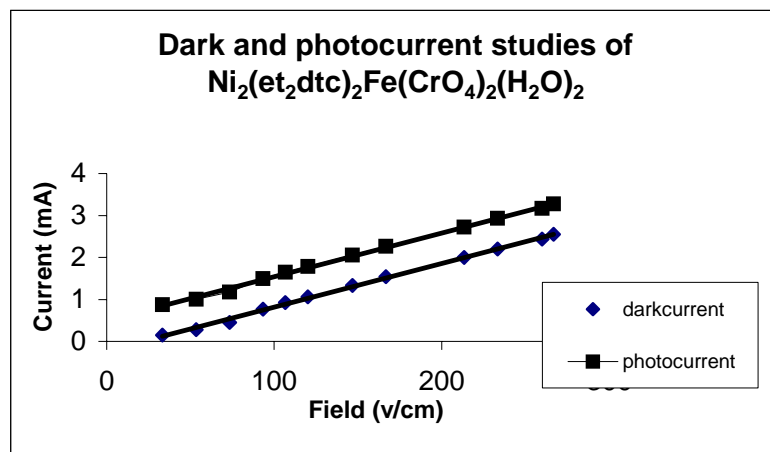


Figure 12 Photo and dark current studies of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$

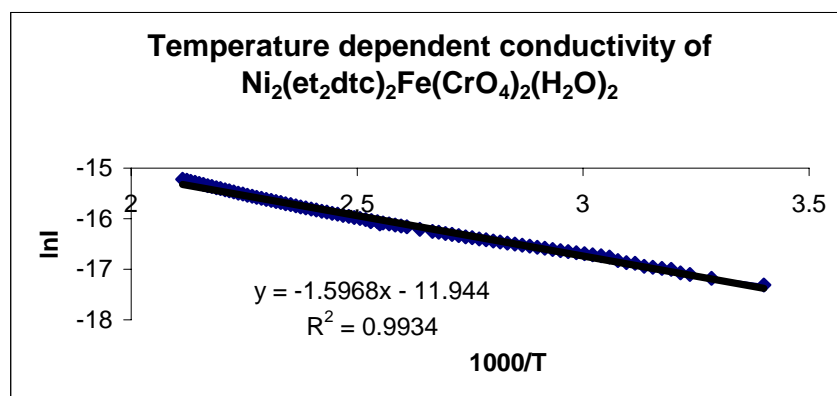


Figure 13 $\ln I$ vs $1000/T$ plot of $[\text{Ni}_2(\text{Et}_2\text{dtc})_2\text{Fe}(\text{CrO}_4)_2(\text{H}_2\text{O})_2]$