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AC ELECTRICAL CONDUCTIVITY OF OCTAPHENY TETRAPYRAZINOPORPHRAZINE NIKEL (II)

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ABSTRACT

The ac conductivity of Octaphenytetrapyrazinoporphrazine Nikel (II) (OpTpPzNI (II),) was measured in the frequency range of 5×10^3 to 5×10^3 Hz, and temperature range 303 to 393 K. The dc conductivity was measured in the same temperature range. The measured ac conductivity, consists of frequency independent part (dc conductivity) and frequency dependent part (pure ac conductivity). The ac conductivity results from hopping of charge carriers, between localized sites around Fermi levels. The hopping site is the indication of the degree of imperfection, in the crystal. The number of the hopping sites was calculated, using Webb and William equation, which is estimated to be 7.6×10^{18} eV-1cm^3.

KEYWORDS: Octaphenyl Tetrapyrazinoporphrazine Nikel(II), Frequency Independent Conductivity(Dc Conductivity) & Frequency Dependent Conductivity (Ac Conductivity)

INTRODUCTION

Many models of ac conduction mechanisms were proposed with the semiconducting properties. Among them, the model of which the electrical transport is due to the hopping motion of small polarons, which was considered the most possible one (1), according to which most of the conductivity is a consequence of the trapping of the hole and its polarization, which was effected by the frequency of the field and affected the temperature (2). The electrical conductivity of some compounds show an agreement with Arrhenius behavior, which may be explained as the result of the presence of states in the band gap (around Femi level) (3, 4).

Ac conductivity measurements assume the existence of localized sites, between which electrons may hope in response to the alternating field. The hoping conduction is frequency dependent. The sample which show significant crystal imperfections or disorder (trapped holes), shows a significant frequency dependent conductivity, in addition to the frequency independent, that makes an assumption of both hole and electron motilities, and their temperature dependence.

Such behavior has been found in many compounds, including phthalocyanines and polymers (5-7).

Studies of frequency dependence electrical conductivity of some compounds, show an agreement with Arrhenius behavior, which may be explained as the result of the presence of states, in the band gap (around Femi level) (1, 2)

In this work, Tetrapyrazinoporphrazine cupper (II) (OpTpPzCu), was prepared and its dc and ac electrical conductivity were studied.

Preparation of the Compounds

Preparation of (2, 3-Dicyano-5, 6-Diphenyl Pyrazine) (8), DcP:

1 gm (4.7×10^{-5}mole) of Benzil was dissolved in 25 ml of ethanol and 25drop of concentrated acetic acid, and added to a round bottomed flask containing 0.5 gm ($4.6t\times10^{-3}$mole) of DAMN, dissolved in 25 ml of ethanol. The mixture then refluxed for 4 hours and the reaction mixture, was left for 2 days to be precipitated. The solid product then filtered and the product was pale brown solid, which is then re crystallized from 1:1 mixture of hexanol / acetone. The yield was 73%, mp (249-250 C). The reaction equation is shown in figure 1.

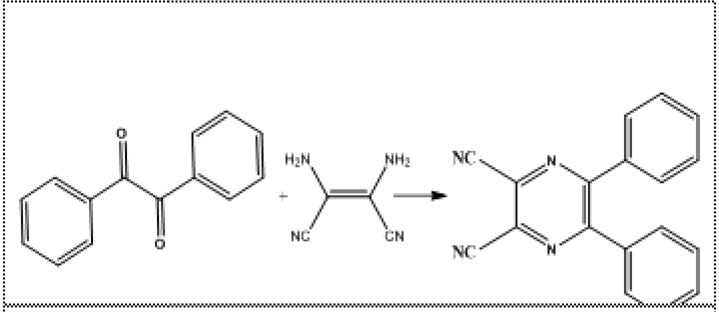

Figure 1: Preparation of DCP

Preparation of Octapheny Tetrapyrazino Porphrazine (OpPzCu(II)):

0.5 (0.0018 mole) of DcP, 0.107gm (0.00045mole) of 6 hydrated Nickel (dichlorided) NiCl2. 6 H2O, 0.67 gm of urea, and 0.01 gm of ammonium molb date, were dissolved in 5 ml of quinolone. The reaction mixture then refluxed for two hours. The deep green precipitate, then filtered. The solid product was purified by its reflux with water, acetone, hexane and CCl4, respectively, to dissolve the impurities. Each time the solid precipitate filtered and dried at 110 0C. The product is dark green solid, decomposes at about 250 0C. The yield is 20.16%. The preparation is, shown in figure 2. CHN (C72H40N16Ni): Calculated; C: 72.78%, H: 3.36%, N: 18.87%; Found; C: 72.60, H: 3.20, N: 17.99

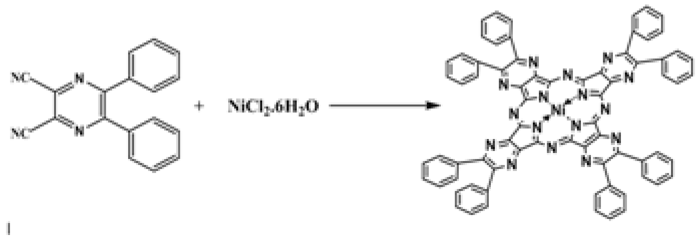

Figure 2: Preparation of OpTpPzNi (II)

RESULTS AND DISCUSSIONS

IR: The disappearance of the nitrile peak, at 2240 cm-1 and the carbonyl group at 1700 cm-1, and the band around 3100 is due to C-H aromatic stretching are the characteristic IR spectrum, of Octapheny Tertrapyrazinoporphrazine. The width of the band around 3400, might be due to moisture. The peak at 1640 cm-1 is due to the C=N stretching (9) Figure 3.

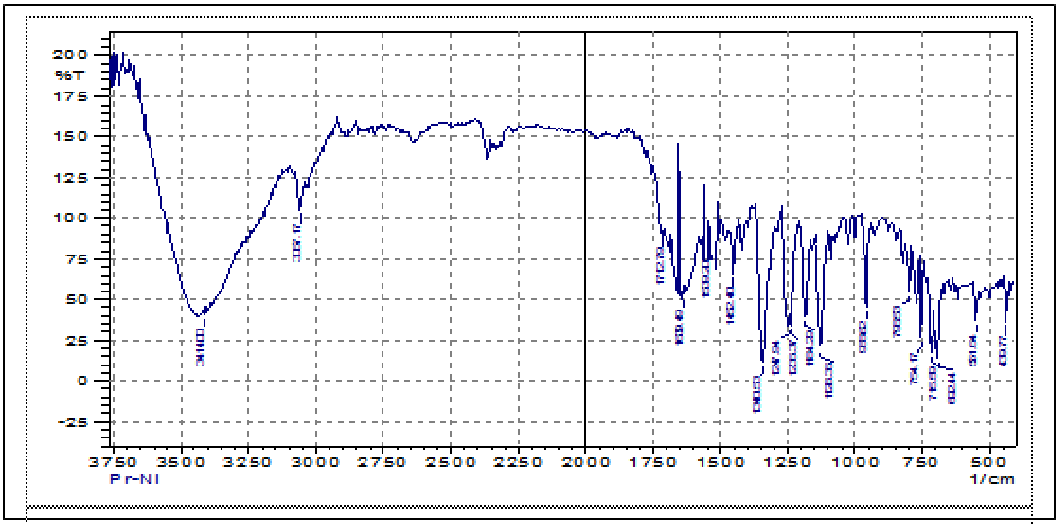

Figure 3: IR Spectrum of TpPzNi(II) (KBr Disc

The electronic spectra of the complexes, Octaphenyl Tetrapyrazino Porphrazine shows the characteristic (Soret band) at 353 nm and, due to, π-π* and n-π* transitions, and Q band at 680.5 nm, which is due to, π-π* and weak d-d transition of the central metal atom hidden inside the Q-band (3, 9, 10), with an extinction coefficient (ε) $1.2x10^4$ L.mol-1.cm-1. The solvent DMF was used to prevent or reduce aggregation of the complex molecules.

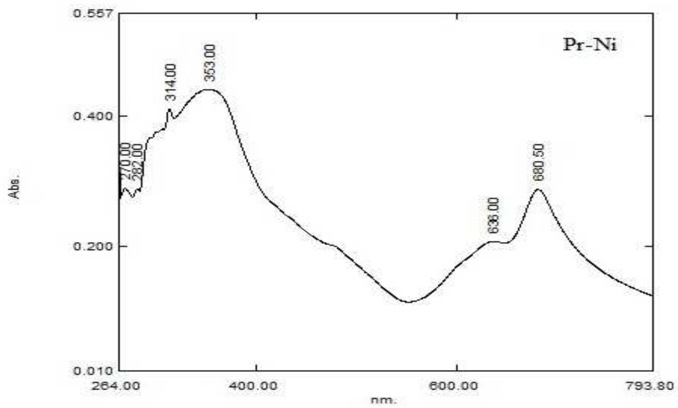

Figure 4: The Electronic Spectrum of TpPzNi (II)

Electrical Properties

Preparation of the samples: The samples were casted, as sandwich cells on fluorine doped tin oxide (FTO) glass substrate, which is conducting from one side with 1 cm^2, surface area. The thickness of the casted film is 0.5 mm and then the cell constant is 10^{-2} cm-1. The sample cell is put in cryostat, which is supplied with variable heating element and cell electrode holder and voltage supply. The cryostat is connected to voltmeter and ammeter (8), to measure the voltage and the current. The temperature was measured using copper-constantan thermocouple placed near the sample. The dc electrical conductivity measurement were carried out in the temperature range of (303- 393) K and at 3 volts. The Ac electrical measurement, were measured in the frequency range of (5 -50) KHz and temperature range of (303 – 393) K. The ac electrical conductivity was measured, using 4800A Vector impedance

The I/V characteristic curve study for the complex (OpTpPzCu(II)), in the voltage range 0-10 volts and at 30 0C shows an ohmic relation, especially at lower voltages, where there is no space charge limited current

Figure 5, shows the relation between log conductivity (log σ) and log angular frequency (log ω), and at different temperatures for the complex, where ω is the angular frequency (2πf), and f is in hertz. The figure shows the increase of ac conductivity, with frequency and temperature.

Figure 6, shows the variation of log conductivity with inverse temperature at different frequencies, for both dc conductivities at different frequencies. It shows that, the measured ac conductivity is higher than dc conductivity, and dc conductivity is approaching the ac conductivity at lower frequency. The ac conductivity, increases with increasing temperature and frequency

The measurement shows that, the measured conductivity (σT) contains ac and dc conductivities (2, 9).

σT = σdc + σω

Where, σω = ωn (varies with frequency, n is constant), and σdc follows Arrhenius equation, σdc = $\sigma_0 e^{-\frac{\Delta E}{kT}}$

Figure 7, shows the variation of log Capacitance (log C) in pF, with log ω in Hertz. The figure shows the increase of the capacitance with temperature, and decreases with frequency, which tend to approach common value.

Figure 9, shows the variation of log (C∞ –C) with ln ω at different temperature, according to Kramer Kronig relation (3, 5).

C = C∞ + A ω n-1

Where C, is the capacitance at any frequency and C∞ the capacitance at infinity (which means at common value of capacities), which is assumed to be at 105 Hz A and n are constants.

Using Mott and Davis equation (11, 13)

$$\sigma_{\omega} = \frac{4\pi}{3}(ln2)e^2kTN(E_F)^2\alpha^{-5}[ln\frac{\vartheta_{ph}}{\omega}]^4\omega$$

N (EF), the number of energy states around Fermi level, is estimated to be 7.6×1018 eV-1 cm^{-3}, where charge of electron is 4.8×10^{-10} esu, k is 8.617×10^{-5} eV/K, T is taken as 303 K, α is the reciprocal inter-planner spacing which is calculated from X-ray diffraction, with Cu as anode and CuKα of wave length of 1.5406(Figure 10, 2ϴ=240). ϑph is the phonon frequency taken as 10^{12} Hz (5, 7) and ω is taken as 5 kHz.

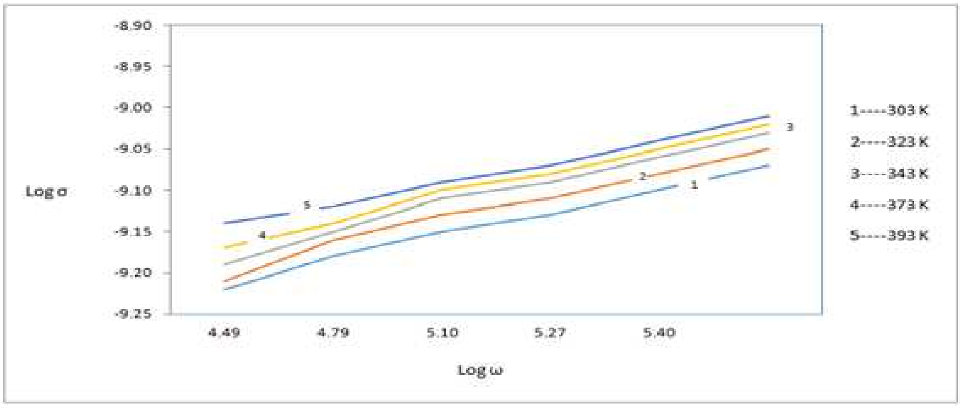

Figure 5: Relation Between log σ and log ω at Different Temperatures, for TpPzNi(11)

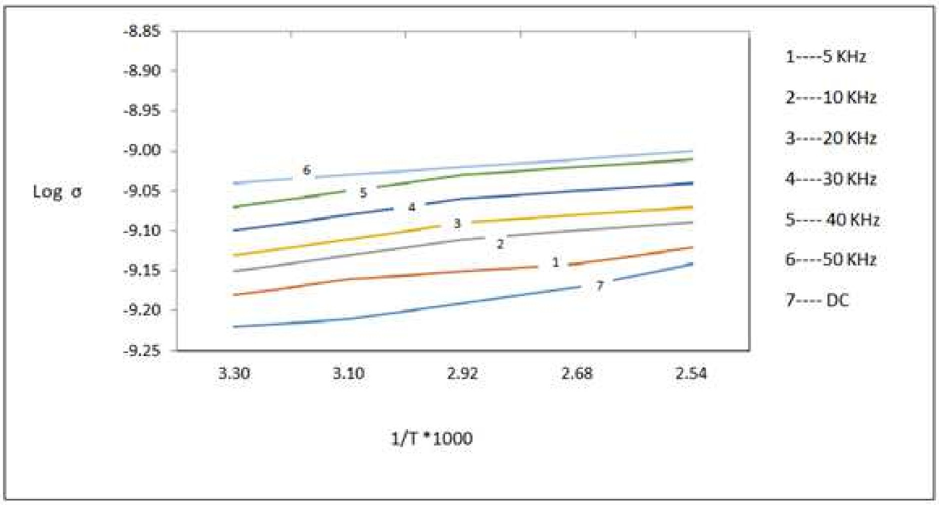

Figure 6: The Relation Between log σ and Reciprocal Temperature for the Frequency Independent Part (Dc Conductivity (1)) and for Frequency Dependent Part (Ac Conductivity at Different Frequencies (2-5, 3-10, 4-20, 5-30, 6-40, 7-50) KHz

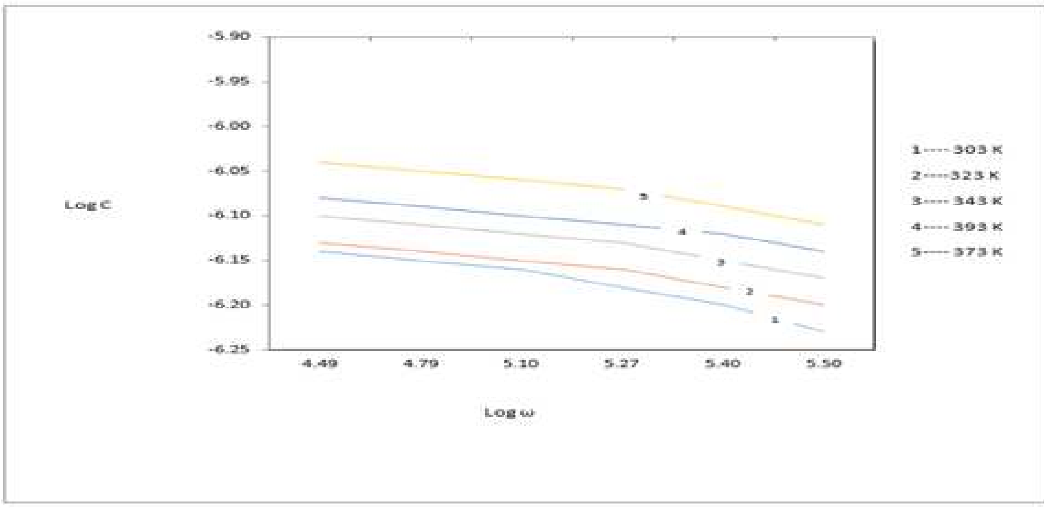

Figure 7: The Relation Between log C and log ω at Different Temperatures for (TpPzNi(II)

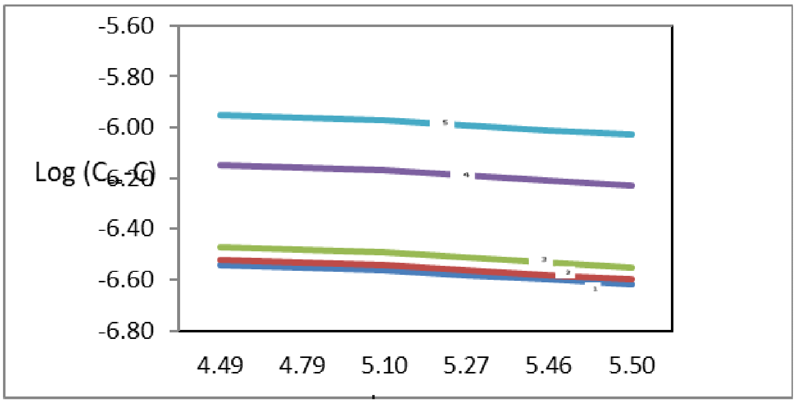

Figure 8: The Relation Between log (C00 – c) and log ω at Different Temperatures, for OpTpPzNi(II)

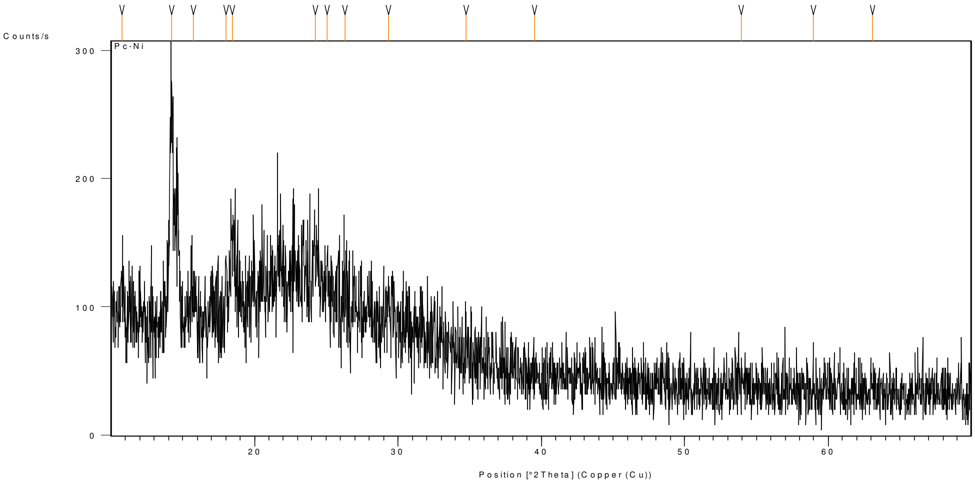

Figure 9: The x-Ray Diffraction of OpTpPzNI (II)

CONCLUSIONS

A sandwich thin film of TetrapyrazinoPorphrazine Ni (II), acts as semiconductor. Ac conductivity increases with frequency and temperature, and its Capacitance decreases with both Frequency and Temperature. The number of energy states around Fermi level, is estimated to be 7.6×10^{18} eV-1 cm^{-3}.

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