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AC ELECTRICAL CONDUCTIVITY OF OCTAPHENYL ETRAPYRAZINOPORPHRAZINE CUPPER (II)

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ABSTRACT

Ac conductivity in the frequency range of 5×10^{3} to 5×10^{3} Hz of Octapheny tetrapyrazinoporphrazine Cupper (II) (OpTpPzCu) was measured, which consists of frequency independent (Dc conductivity) and frequency dependent part. This kind of conductivity results from hopping of charge carriers between localized sites around Fermi levels. The hopping sites is 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 1×10^{20} $eV^{-1}cm^{-3}$.

KEYWORDS: Octaphenyl Tetrapyrazino Porphrazine Cupper (II), Frequency Independent (Conductivity, Frequency Dependent Conductivity.

INTRODUCTION

Studies of temperature dependence of 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)(1,2) AC conductivity measurements assumed the existence of localized sites between which electrons may hope. In response to the alternating field. The hoping conduction is frequency dependent ($\sigma\alpha\omega^{n}$), where ω is the angular frequency. The sample which show significant crystal imperfections or disorder, show a significant frequency dependent conductivity in addition to the frequency independent. Which make an assumption of both hole and electron motilities and their temperature dependence.

Such behavior has been found in many compounds, such as, TCNQ complex salts,

Phthalocyanines and polymers (3, 4, 5).

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

PREPARATION OF THE COMPOUNDS

Synthesis of (2, 3-Dicyano-5, 6-Diphenyl Pyrazine)(6), 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 recrystallized from 1:1 mixture of hexanol / acetone. The yield was 73%, mp (249-250 C). The reaction equation is shown in figure 1.

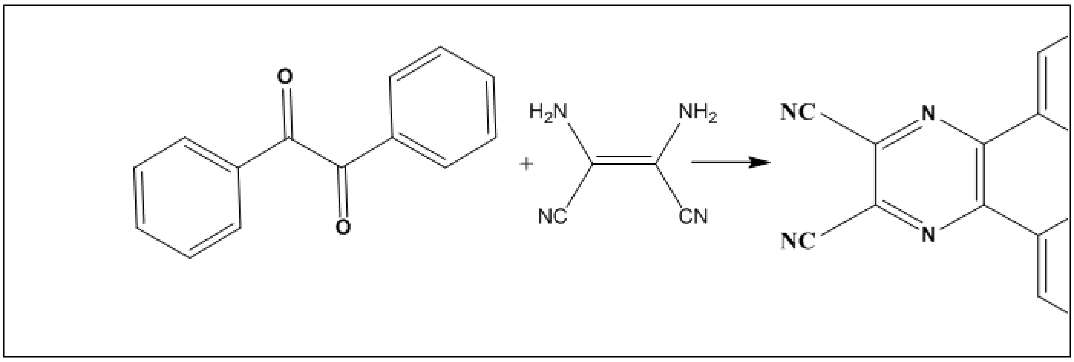

Figure 1: Preparation of Dcp

Synthesis of Octapheny Tetrapyrazino Porphrazine (OpPzCu(II))

5.92gm(0.04 mole) of DcP 1.71gm(0.01mole) of dihydrated Copper dichloride($CuCl_2$).2 H_2O, 10 gm of urea, and 0.01 gm of Ammonium Molbdate dissolved in 5 ml of quinolone. The reaction mixture then refluxed for 5 hours. The precipitate then filtered. The solid product then purified by its reflux with water, acetone, hexane and CCl_4 each time the solid product is filtered to dissolve the impurities. The solid then dried at 110 ^{0}C. The product is dark blue solid decomposes at about 290 ^{0}C. The yield is 52.13%. The preparation is shown in figure 2.

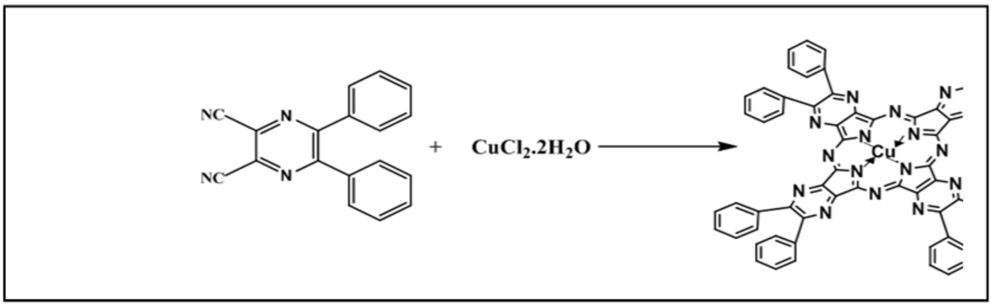

Figure 2: Preparation of OpTpPzCu

RESULTS AND DISCUSSIONS

IR: The disappearance of the nitrile peak at 2240 cm^{-1} and the carbonyl group at 1700 cm^{-}1 and the presence of the C-H aromatic at 3151 and C=N at cm^{-1}are the most characteristic I Rspectrum[(7)] of OctaphenyTetrapyrazinoporphrazine, Figure 1

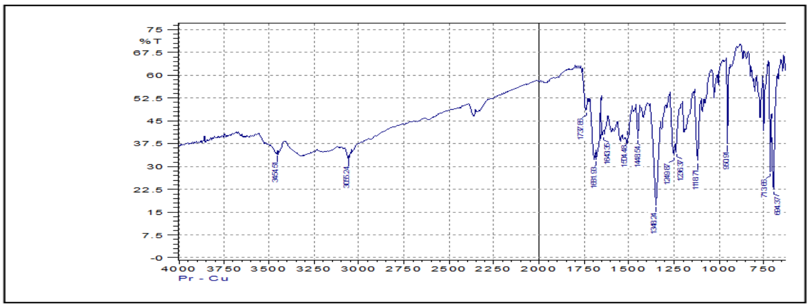

Figure 3: The IR spectrum of OpTpPzCu(KBr disc)

The electronic spectra of the complexes, Octaphenyl Tetrapyrazino Porphrazine, shows the characteristic (Soret band) at 300 nm and, due to, π-π* and n-π* transitions, and Q band at 703 nm, which is due to, π-π* and weak d-d transition of the central metal atom hidden inside the Q-band [1, 7, 8], with an extinction coefficient (**ε**) 1.2x104 $L.mol^{-1} cm^{-1}$. The solvent DMF was used to prevent or reduce aggregation of the complex molecules.

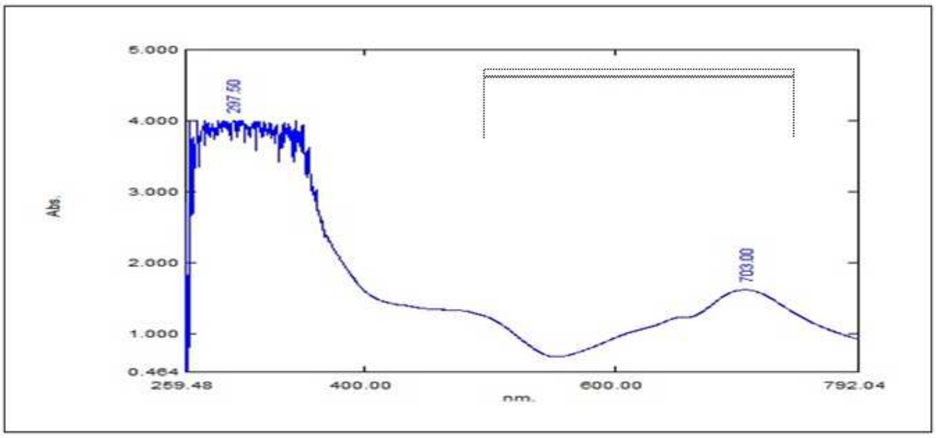

Figure 4: The Electronic Spectrum of OpTpPzCu

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.

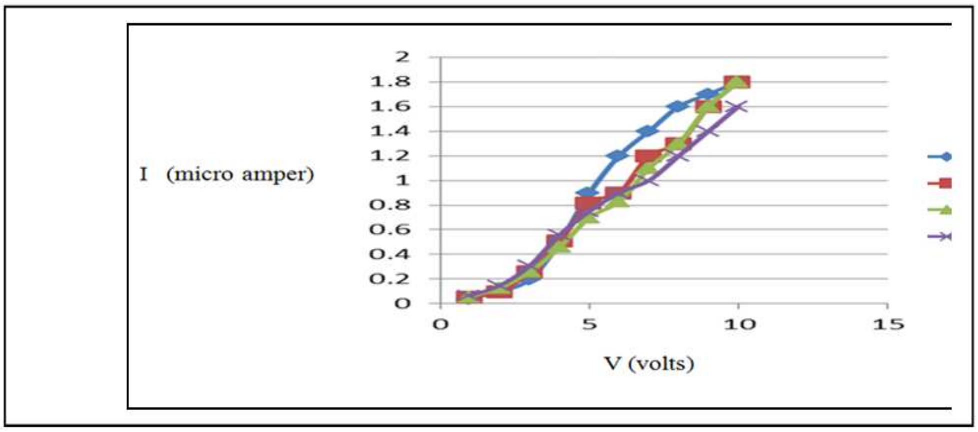

Figure 5: I/V Curve at Different Temperatures for OpTpPzCu

Figure 5 shows the I/V curve for the complex (OpTpPzCu(II)) at 30 ^{0}C, voltage range is 0-10 volts. It shows an ohmic relation especially at lower voltages where there is no space charge limited current.

Figure 6, shows the relation between log conductivity (log σ) and log angular frequency (log ω) 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 7 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 (σ_T) contains ac and dc conductivities [3, 9].

$$\sigma_T = \sigma_{dc} + \sigma_\omega$$

Where $\sigma_\omega = \omega^n$ (varies with frequency, n is constant), and σ_{dc} follows Arrhenius equation, $\sigma_{dc} = \sigma_0 e^{-\frac{\Delta E}{kT}}$

Figure 8, 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, 10]. $C = C_\infty + A\,\omega^{n-1}$

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 10^5 Hz. A and n are constants.

Using Mott and Davis equation [11, 12].

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

N (E_F), the number of energy states around Fermi level, is estimated to be 9.6×10^{19} 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 interplanner spacing which is calculated from X-ray diffraction(Figure 10, 2Θ=25^0). ϑ_{ph} is the phonon frequency taken as 10^{12} Hz [3, 5] and ω is taken as 5 kHz.

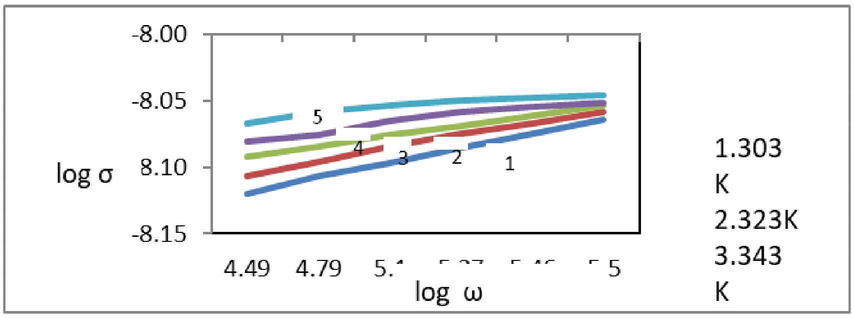

Figure 6: Relation between log σ and log ω at different Temperatures, for OpTpPzCu.

Figure 7: 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.

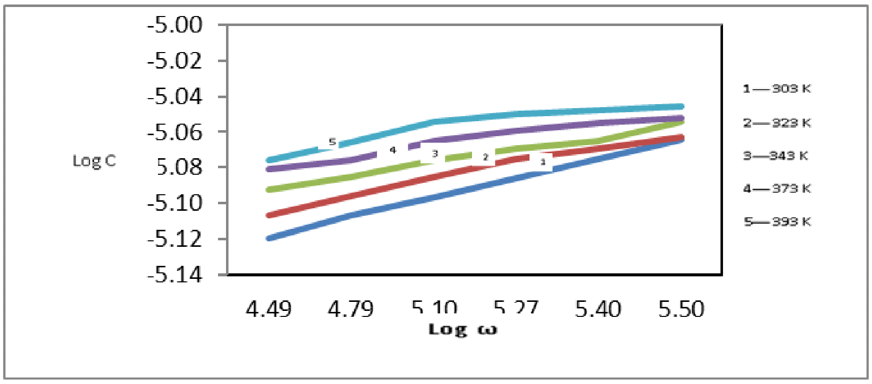

Figure 8: The Relation between log C and log ω at Different Temperatures for (OpTpPzCu).

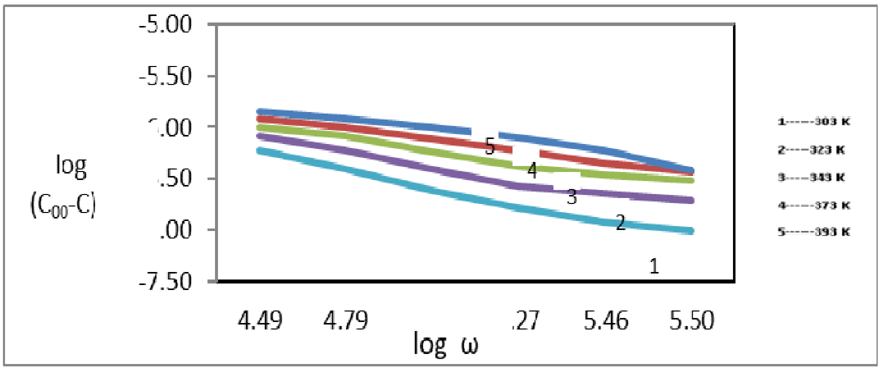

Figure 9: The Relation between log (C00 – c) and log ω at Different Temperatures, for OpTpPzCu.

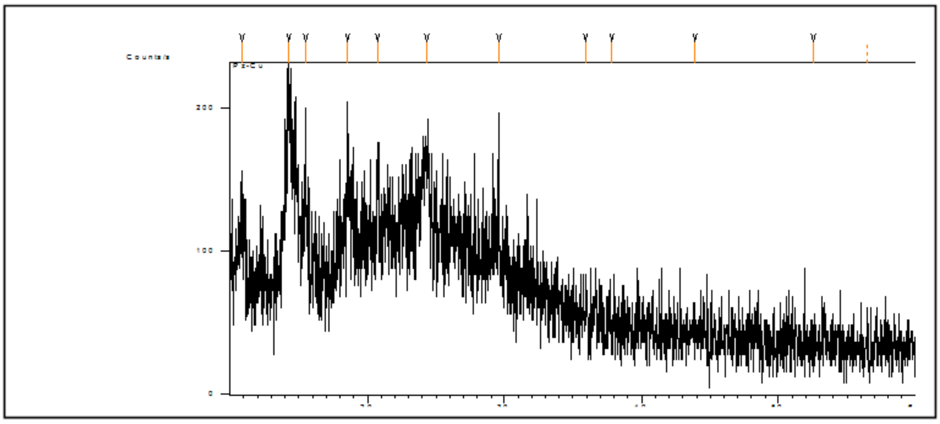

Figure 10: The X-ray Diffraction of OpTpPzCu.

CONCLUSIONS

Thin film of Octaphenyl TetrapyrazinoPorphrazine Cu (II) act 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 9.6×1019 eV-1 cm-3.

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