

## **Nickel and copper complexes of tetrapyrazinoporphyrazine and some of their spectroscopic and electrical properties**

\*Nazar A. Hussein, Dawood S. Abid and Asawir Salim T. Al Salami

Chemistry department, College of Education, University of Basrah, Bassrah, Iraq.

\*Corresponding author: E.mail address: [naz\\_hus184@yahoo.com](mailto:naz_hus184@yahoo.com) (N. A. Hussein )

### ملخص البحث:

لقد حضرت وشخصت بعض معقدات النيكل والنحاس الثنائي لثمانى فنيلى رباعى الباييرازين البورفيرازينييه ودرست خواصها الطيفيه والكهربائيه. لقد بينت الدراسه بعض خواص هذه المعقدات الكهربائيه المميزه مقارنة لمركبات الفثالوسيانين المشابه لها. كما بينت الدراسه خاصيه التجمع في هذه المعقدات في بعض المذيبات من خلال خواصها الطيفيه.

### **Abstract:**

Some of the Nickel and copper complexes of tetrapyrazinoporphyrazine where prepared and their spectroscopic(CHN, Uv-vissible and H-NMR) and dc electrical properties were studied.

The study shows the effect of the solvent on the aggregation properties in such kind of complexes and it shows some interesting electrical properties in compared to their analogous phthalocyanicne compounds.

### **Introduction**

Tetrapyrazinoporphyrazines(AzaPc) are often termed tetrapyrazinoporphyrazine in the litratures are analogues to phthalocyanines(Pc). Due to the large planar  $\pi$ - conjugated system, they tend to form aggregates which results in poor solubility and difficulties with purification and characterization<sup>(1)</sup>. The Aggregation results in broadening along with a pathochromic shift of the well known in macrocyclic molecules Q-band<sup>(2)</sup>absorption in the visible region of the spectra<sup>(2)</sup>. An additional consequence of self-association is the quenching of the photochemically excited AzaPc, Thus reducing both fluorescence and single oxygen generation which is considered as it is primary role in photodynamic therapy(PDT)<sup>(4)</sup>. Moreover, such behavior reduces the life time of the excited state and hence may lead to negative non-linear optical responses<sup>(5)</sup>. There for, ordering these macrocycles in the condensed state is crucial to incorporate the Pc analogues into devices. In order to exploit the properties arising from both extended conjugated systems and the presence of the eight nitrogen atoms in AzaPc, many studies were carried out which results in significant modulation of their physical properties (such as colour, aggregation and optical absorption) and electronic properties<sup>(1,4,6)</sup>.

In this work a complexes of octaphenyltetrapyrazinoporphyrazine with Ni and Cu as central metal atoms were prepared and characterized by CHN, IR, U.V-Visible. The dc electrical properties and the effect of different solvents on the electronic spectra for the compounds were studied

## Experimental Section :

### Materials

The purchased chemicals were used as received. Ethanol, acetone and chloroform were purchased from GCC. Nickel acetate and HCl were purchased from BDH. HAc, DMF and Copper sulfate were purchased from RDH. Quinoline, pyridine, diaminomalonitril(DAMN), urea and iron sulfate were purchased from Fluka and hexanol was purchased from Merck.

### Instrumentation:

The elemental analysis were recorded on Euro Vector EA3000A Italy. The IR spectra were recorded on FT- IR – 8400S. The UV-Visible spectra were recorded on T80-UV/Vis spectrometer.

The H NMR(500MHz) spectra were recorded on Bruker. The dc electrical conductivity measurements were performed using an electrical circle containing power supply(Leybold Heraeus) and heating plate(TJLASSO) and avometer (DT890). The cells were prepared by casting a concentrated solution of any of the compounds in DMF on and smooth and well cleaned aluminum surfaces ( as electrode(s)).

### Preparation of Compounds :

1) preparation of 2,3-dicyano 5,6-diphenyl pyrazine (PN)<sup>(7)</sup> :

A mixture of (1g ,  $4.7 \times 10^{-3}$  mole) of benzil, 25 ml of ethanol and 25 drops of acetic acid was put in a round bottomed flask filled with condenser containing (0.5 g ,  $4.6 \times 10^{-3}$  mol) of DAMN soluble in 25ml ethanol. The total mixture were then refluxed for 4 hours. The reaction mixture then left for two days to complete the precipitation. The solid product then filtered and recrystallized from a mixture of hexanol and acetone (1:1). The product was a pale yellowish crystalline powder, (m.p = 253-255 °C) ( yield, 0.7g, 52%).

IR (KBr): ( 3055w, 1600s, 1520vs, 1070m, 700vs, 1375vs and 2235m) $\text{cm}^{-1}$ . H NMR( $\delta$  H, ppm): (7.38, 7.46, 7.54).

2) preparation of 2,3,9,10,16,17,23,24-octaphenyl

1,4,8,11,15,18,22,25 – octaphenyltetrapyrazinoporphyrazine Nickel (II) TpPzNi:

Nickel (II) actate (0.24 g ,  $1 \times 10^{-3}$  mole) was added to a solution of PN(1.12g,  $4 \times 10^{-3}$  mole) in 3 ml of quinoline followed by the addition (1.5 gm ,  $2.5 \times 10^{-2}$  mole) urea, The mixture then heated at 140°C for 15 minutes with magnetic stirring. The reaction mixture then cooled, and dissolved in a least amount of chloroform and reprecipitated by adding it portion wise with stirring to 250 ml beaker containing ethanol. The precipitation process was repeated for five times, and then dried at 120 °C ,The product is a greenish powder (yield,0.17g, 15%).

CHN, calcd (C<sub>72</sub>H<sub>40</sub>N<sub>16</sub>Ni) C: 72.81, H: 3.37 , N: 18.87; found C:71.04, H: 3.12, N: 18.21; IR(KBr): (3060w, 1631s, 1558, 1155m, 767, 1346s and 1247s)  $\text{cm}^{-1}$ . UV-Vis( $\lambda_{\text{max}}$ , CHCl<sub>3</sub>): (310,642,686 nm).

3) preparation of 2,3,9,10,16,17,23,24 - octa phenyl 1,4,8,11,15,18,22,25 – octaazaphthlocyani- natocopper (II) TpPzCu :

Copper(II)sulfate(0.18 g,  $1 \times 10^{-3}$  mole) was added to a solution of (1.12g,  $4 \times 10^{-3}$  mole) of PN dissolved in 3 ml of quinoline, followed by the addition of (1.5 g,  $2.5 \times 10^{-2}$  mole) of urea. The mixture then heated at 140°C for 10 minutes with magnetic stirring. The reaction mixture then cooled, and dissolved in a least amount of chloroform and then re-precipitated by adding it portion wise with stirring to a 250 ml beaker containing ethanol. This proceed was repeated for five times,

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and then dried at 80 °C . The product is a deep brown powder, ( yield, 0.2g, 17%).

CHN, calcd (C<sub>72</sub>H<sub>40</sub>N<sub>16</sub>Cu) C: 72.51, H: 3.35, N: 18.79. found C: 72.01, H: 3.11, N: 18.23. IR (KBr): (3056w, 1612s, 1564, 1164s, 773, 1352vs, 1245s) cm<sup>-1</sup>. UV-Vis (λ<sub>max</sub>, CHCl<sub>3</sub>): (300,654 nm).

### Result and Discussion:

The little differences of the practical with the calculated elemental percentage in the CHN analysis might be due to the difficulties of purification of such compounds.

The figures (1-3) show the IR spectra of PN and its complexes with Ni and Cu respectively. It shows the aromatic C-H stretching at 3055cm<sup>-1</sup>, 3060cm<sup>-1</sup> and 3056 cm<sup>-1</sup> for PN, Ni and Cu complexes respectively and the aromatic C-H bending at 1070 cm<sup>-1</sup>, 1155 cm<sup>-1</sup> and 1164 cm<sup>-1</sup> in plane for PN ,Ni and Cu complexes respectively, and 700 cm<sup>-1</sup>,767 cm<sup>-1</sup> and773 cm<sup>-1</sup> out of plane for PN, Ni and Cu complexes respectively.

The bands 1375cm<sup>-11</sup>, 1600cm<sup>-1</sup> and 2235cm<sup>-1</sup> are attributed to the stretchy vibration for C-N,C=N and C≡N stretchy vibration respectively<sup>(9-11)</sup>. The bands at 1631cm<sup>-1</sup> and 1612cm<sup>-1</sup> for the Ni and Cu complexes which are attributed to the C=N stretching. The metal ligand band could be around the region 549 cm<sup>-1(12)</sup>.

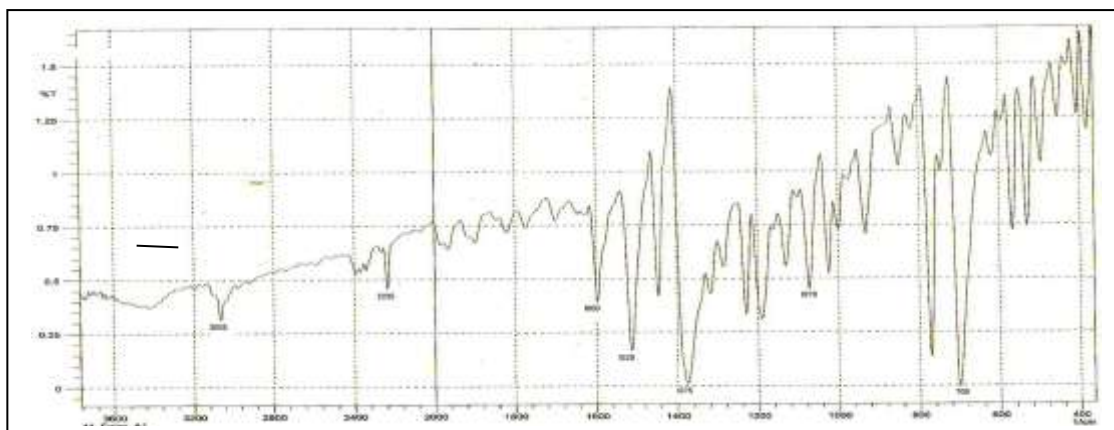
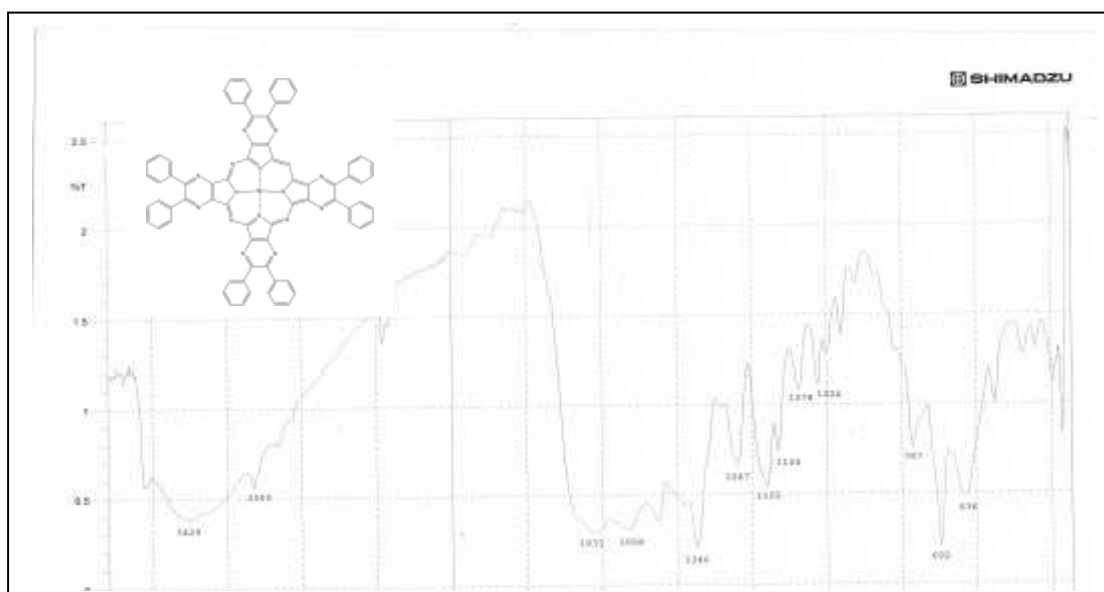
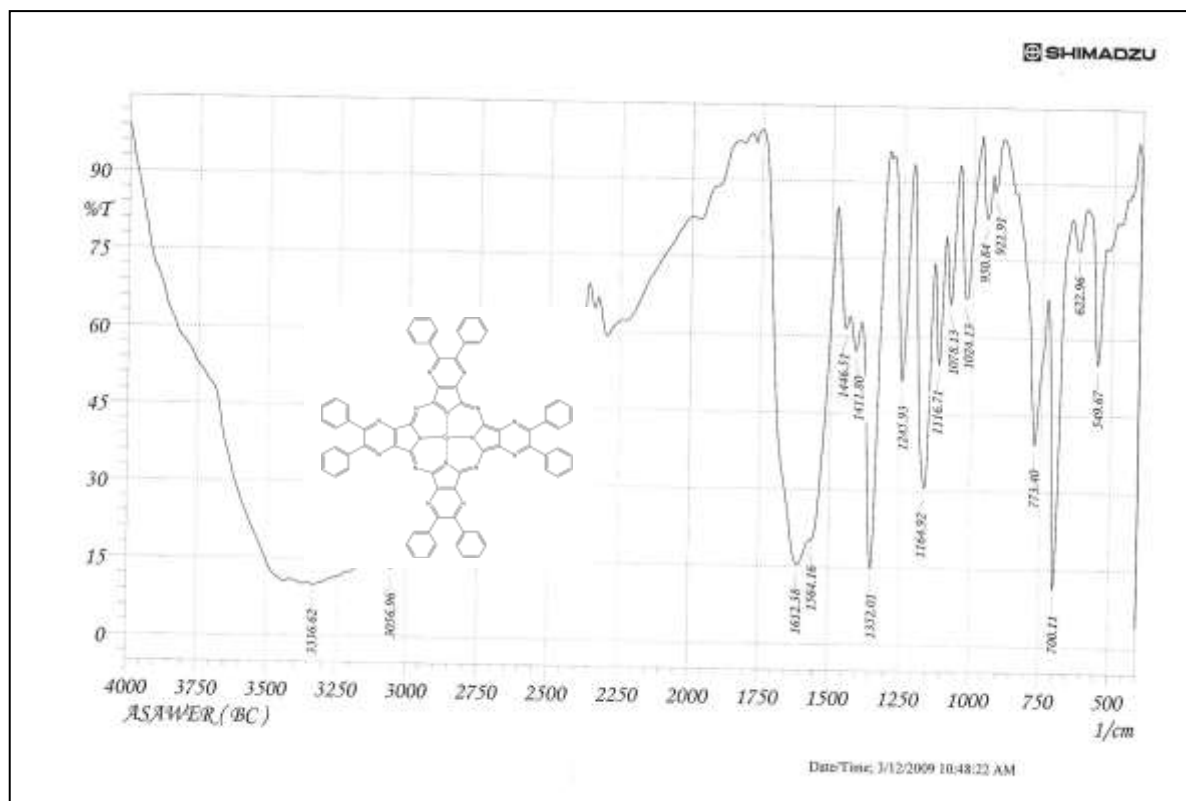


Figure (1): The IR spectrum for PN

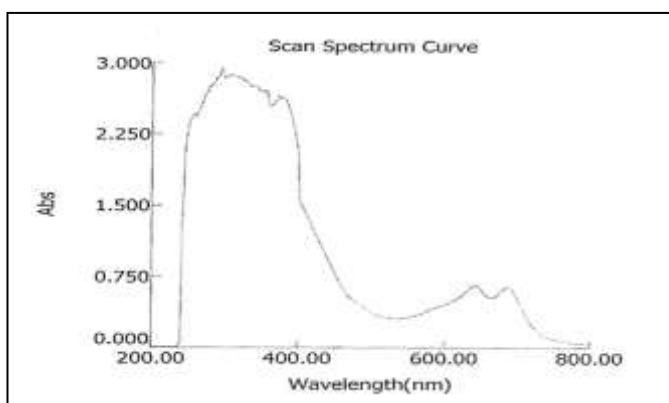


Figure(2): The IR spectrum of TpPzNi

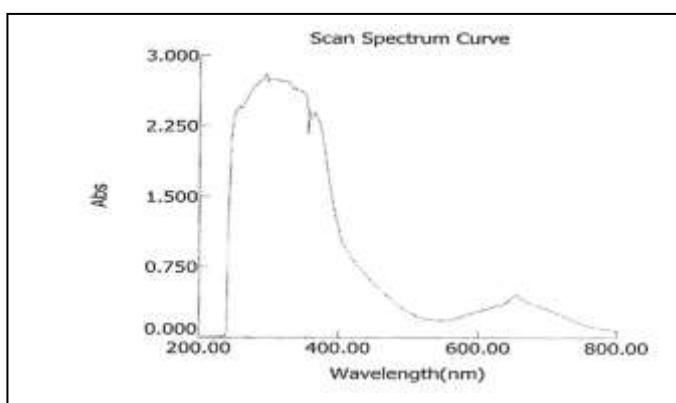


Figure(3): The IR spectrum of TpPzCu

The U.V-Visible spectra figures (4) and (5), show the main two band types, at( 642 and 686) nm and 654 nm (Q band) and 310 nm and 300 nm (soret band) for Ni and Cu complexes respectively, Which could be attributed to the ( $\pi-\pi^*$ ) transitions. The soret bands is also attributed to the coupling of electrons of the nitrogen atoms to the  $\pi$ -system. The d-d transitions, due to the metals appears as small peaks in the same positions of Q and soret bands<sup>(13)</sup>.



Figure(4) : The U.V-Visible for TpPzNi



Figure(5) : The U.V-Visible for TpPzCu

The H NMR spectra for PN, figure (6), shows a mixed band at 7.5 ppm which is related to the benzene protons. It appears by higher resolution as two triplets at 7.38 ppm and 7.46 ppm and doublet at 7.54 ppm which is attributed to the meta, para and ortho protons, respectively (figure (7)).

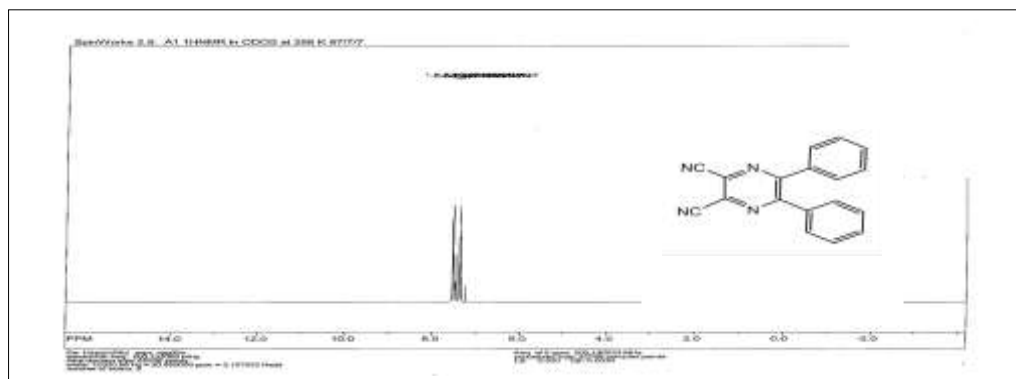


Figure (6): The H NMR spectrum for PN

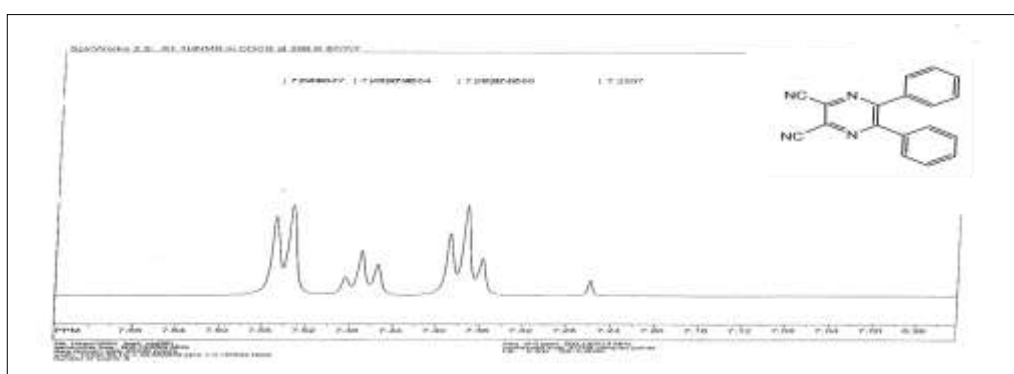


Figure (7): The H NMR spectrum for PN higher resolution.

**Effect of Solvents:**

Figures (8,9 ) show the UV-Visible spectra for the Cu and Ni complex, in chloroform, chloroform with acid (HCl) (0.6M), and in pyridine.

The figure (8) shows a single and wide peak at 654 nm for the Cu and complex. The width of the peak refers to the aggregation of the molecules<sup>(14)</sup>.

These peak become increasing in width at 658 nm with the use of acidic chloroform, figure(9), which relates to the aggregation. In pyridine the peaks become higher and extra thinner which is due to the higher polarity of pyridine which could make extra coordination with the central metal atoms that reduce the aggregation<sup>(15,16)</sup>.

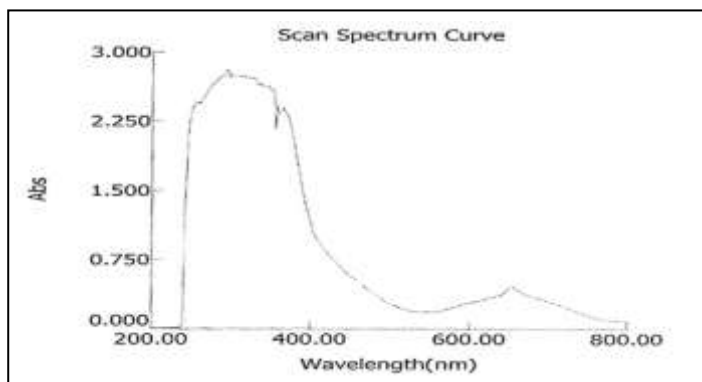


Figure (8): The U.V-Visible spectra for Cu complex in chloroform

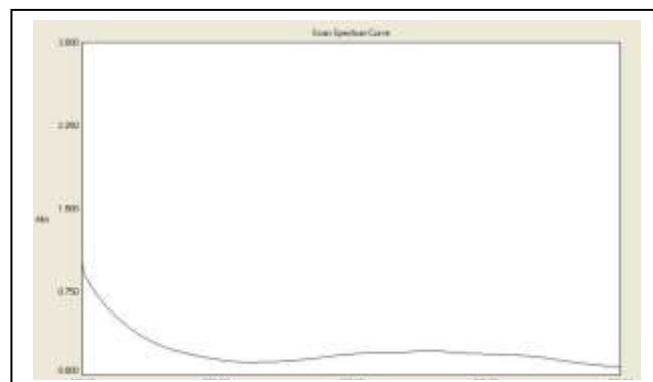


Figure (9): The U.V-Visible spectra for Cu complex in chloroform with acid (HCl) (0.6M)

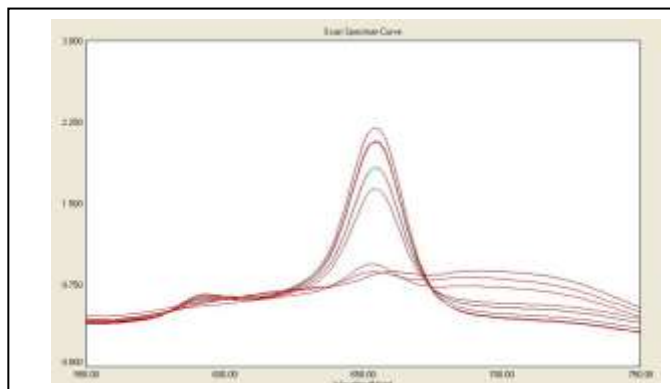


Figure (10): The U.V-Visible spectra for Cu complex in pyridine

Figure (10) shows the Q-band of the complex with time. The height of the peak decreases with time which might be related to increased aggregation.

Figure (11) shows a double and wide peaks at 686 nm and 642 nm for Ni complex which due to the  $\pi$ -  $\pi$  coupling<sup>(17)</sup>.

The figure (12) shows single and wide peak for Ni complex with the use of acidic chloroform which relate to the reduce of aggregation<sup>(17)</sup>.

The figure (13) shows a double peak for Ni complex in pyridine at 686 nm and 640 nm the peaks increasing with time in pyridine, which is due to the higher polarity of pyridine which could make extra coordination with Ni complex<sup>(15,16)</sup>.

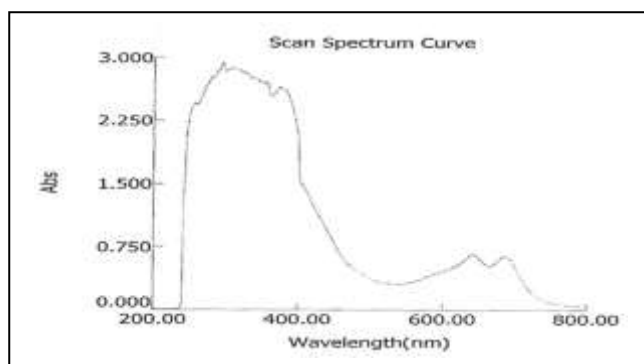


Figure (11): The U.V-Visible spectra for Ni complex in chloroform

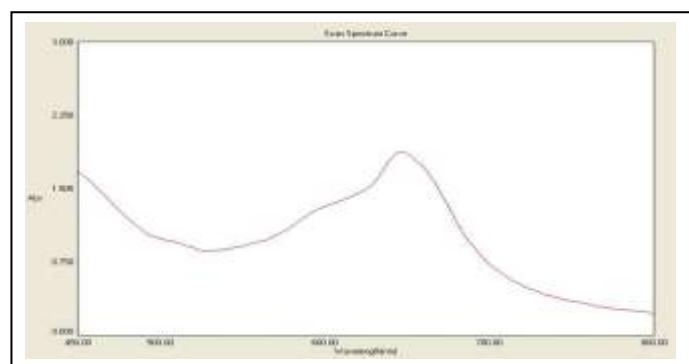


Figure (12): The Q-band spectra for Ni complex in chloroform with acid (HCl) (0.6M).

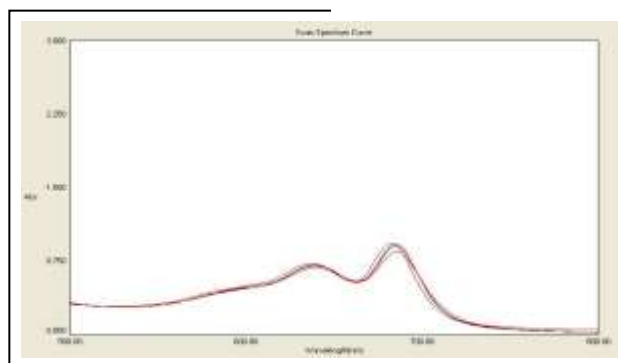


Figure (13): The U.V-Visible spectra for Ni complex in pyridine with time.

**D.C Electrical Conductivity:**

The studied electrical conductivity of the prepared compounds (Ni and Cu complexes) as thin films which their thickness between (1 $\mu$ -4 $\mu$ ) are shown in the figures (14 – 21).

Figures (14) and (15) show the relation of the flowing current with time for both complexes. During the first period the relation is exponential and the current reached to a constant value after 240 second for Cu complex and 500 second for Ni complex. The decrease in the conductivity with time might be due to the evaporation of some solvent molecules and movement of some of the complex molecules<sup>(18)</sup>.

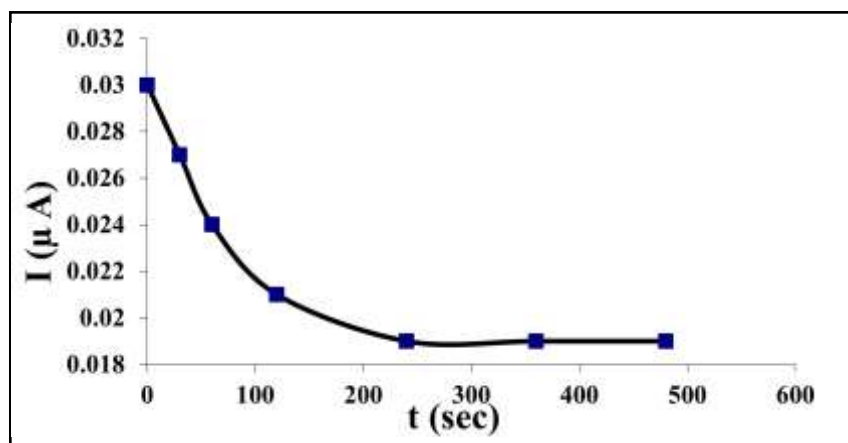


Figure (14): The relation of the current flow with time( $\mu$  amper) for TpPzCu at 9 volts.

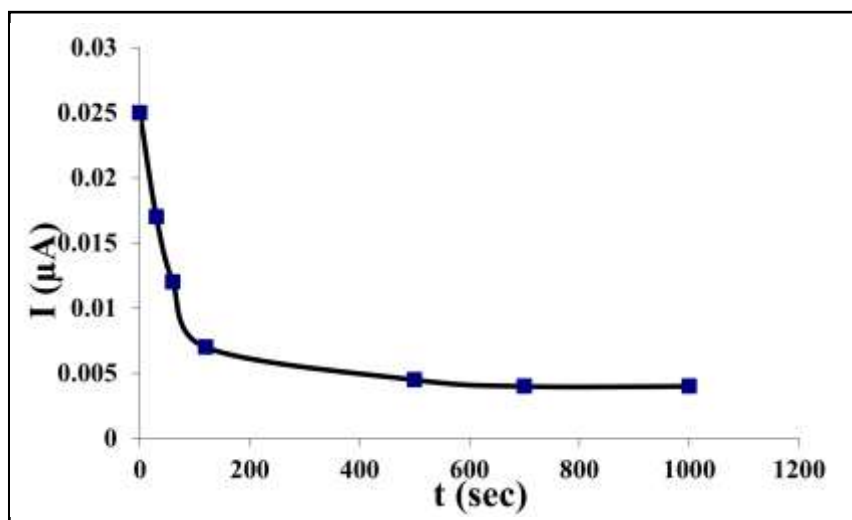


Figure (15): The relation of the current flow with time( $\mu$  amper) for TpPzNi at 9 volts.

Figures (16) and (17) show a current voltage relation, for both complexes. The figures show an ohmic relation in the range with in 10 volts.

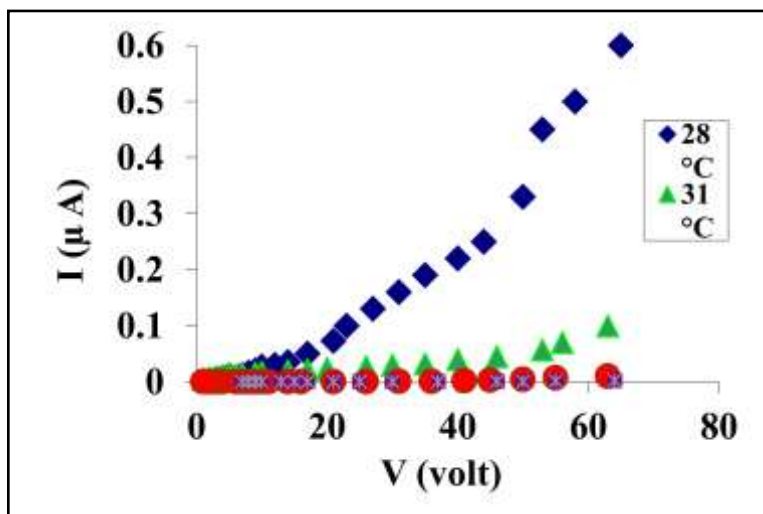


Figure (16): The current voltage relation for TpPzCu.

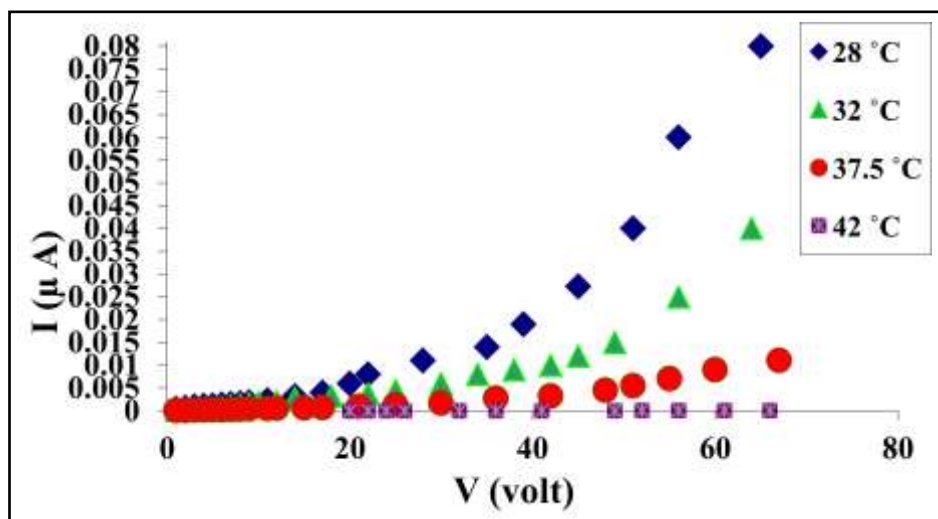


Figure (17): The current voltage relation for TpPzNi.

Figures(10-21) show the relation between the conductivity with temperature, and the natural logarithm of conductivity with the inverse temperature respectively for each complex according to the relation  $\sigma = \sigma_0 \exp(-\Delta E / kT)$ , where  $\sigma$  and  $\sigma_0$  are the conductivity and the pre-exponential conductivity respectively.  $\Delta E$  is the band gap.  $K$  and  $T$  are the Boltzmann constant and the temperature in Kelvin. The figures show that the conductivity decrease with increasing of temperature. The decrease in conductivity might be due to a decrease in the crystal structure order which means increases the crystal disorder. The disorder was found by other works<sup>(19)</sup>.



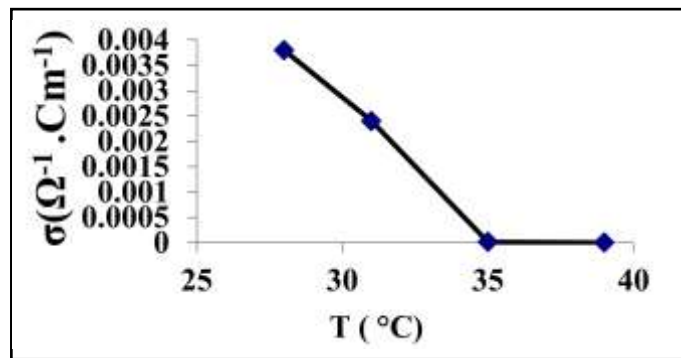


Figure (18): The relation between the conductivity and temperature for TpPzCu

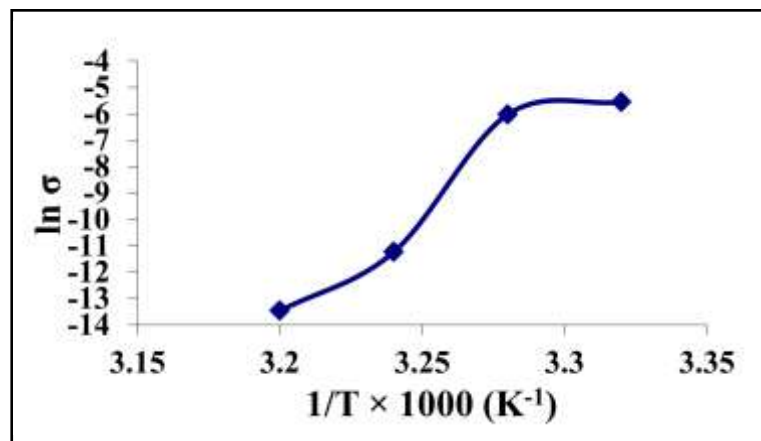


Figure (19): The relation between the pre-exponential conductivity and reverse temperature for TpPzCu

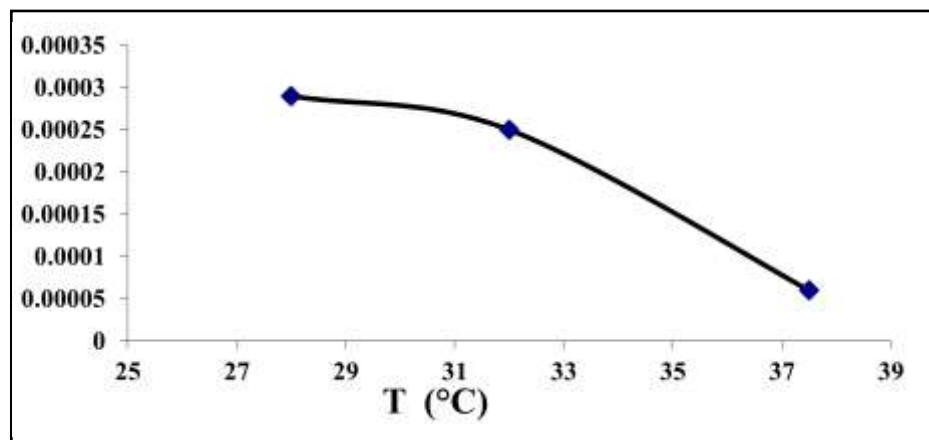


Figure (20): The relation between the conductivity and temperature for TpPzNi

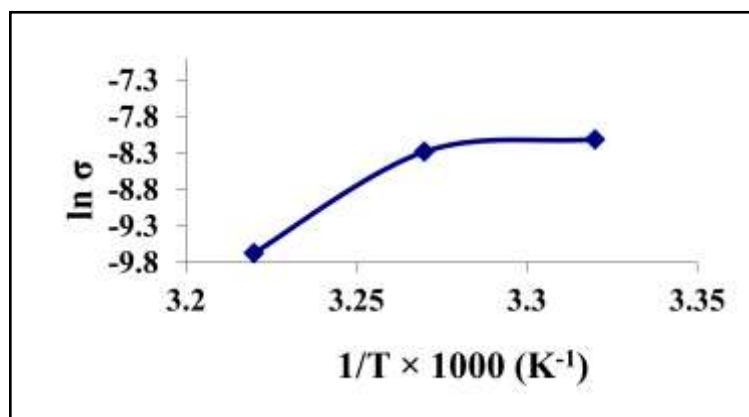


Figure (21): The relation between the ln conductivity with temperature for TpPzNi

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