BEST: International Journal of Management, Information Technology and Engineering (BEST: IJMITE)
ISSN(Print):2348-0513; ISSN(Online): 2454-471X;
Vol. 3, Issue 8, Aug 2015, 55-60

SYNTHESIS OF OCTA (4-ACETAMEDOPHENYL) TETRAPYRAZINO PORPHRAZINE NIKEL COMPLEX AND STUDY SOME OF IT'S SPECTROSCOPIC AND ELECTRICAL PROPERTIES

NAZAR A. HUSSEIN

Department of Chemistry, College of Education for Pure Sciences, University of Basrah, Basrah, Iraq

ABSTRACT

A coplex of Octa(4-acetamidophenyl) TetrapyrazinoPorphrazine Nikel[11] were prepared and identified. The study shows some of it's spectroscopic and electrical properties. The study shows, too, the effect of some solvents on the electronic spectra. The dc electrical conductivity measurements reflects it's semiconducting properties.

KEYWORDS: Octaacetylamidophenyl Tetrapyrazino Porphrazine Nikel, Spectroscopic and Electrical Properties

INTRODUCTION

Porphyrazins are divided into two main groups, phthalocyanines (Pc) and, which is tetrapyrazinoporphrazine(Pz) which is also called azaphthalocyanines (AzaPc) [(1)].

Due to their interesting electronical and optical properties, they have potential application as biomedical agents, chemical sensors, liquid crystals and non-linear optical materials[(2,3)].

Porphyrazins have, recently, gained increasing attention. This is due to strong correlation between the nature of the electronic and optical properties of the macro cyclic ring system and the substituents (pereferal and central metalic elements)[(2)].

The Azaphthalocyanines show good solubility in organic solvent compared to phthalocyanine complexes[(4)]. In an another hand, and due to the extended π-conjugated system in phthalocyanine and Azaphthalocyanines, they exhibit a high tendency for aggregation, which causes the decrease of solubility and difficulty of purification, characterization, broadening of Q-band and the low ability to generate the singlet oxygen which is the active agent in photodynamic therapy(PDT)[(5)]. The dc electrical studies show it's semiconducting properties.

In this work a complex of octa(4-acetamedophenyl) tetrapyrazino porphyrazine with Ni as central metal atoms were prepared and characterized by CHN, IR, UV- Visible. The dc electrical properties and the effect of solvent on the electronic spectra for the prepared compounds were studied.

PREPARETION OF THE COMPOUNDS

Preparation of 4,4'- diacetamidobenzoin (6,7)

0.248g (3.875×10-3 mol) of Potassium cyanide was dissolved in 4 ml of distilled water and added to 100 ml conical flask, fitted with condenser and containing 4g(2.46 x 10-2 mol) 4-acetamidobenzaldehyde dissolved in 8 ml of ethanol. The mixture then refluxed for 2 hours. The reaction mixture then left to be cooled, The reaction mixture then added portion wise with stirring to a 200 ml beaker containing 50 ml of distilled water. A solid was precipitated, filtered

and recrystallized from chloroform and then dried at 100 °C. The product was orange powder. The yield is (1.8g, 45%).

Preparation of 4,4'- diacetamidobenzil (DAcBz) (6,7)

A mixture of 4g (1.27 ×10-2mol) of 4,4'- diacetamidobenzoin and 14 ml of concentrated nitric acid were heating in conical flask on a steam bath for 18 min until a complete disappearance of the brown nitrogen oxide fumes. A 75 ml of water was added to the reaction mixture and cooled to room temperature and left for a few minutes to coagulate as precipitated product. The brown solid then filtered and washed with distilled water on Buchner funnel, re-crystallized from ethanol and then purified by column and dried at 100 °C. The product was brown powder. The yield is (3.2g, 58%).

Preparation of 2,3-dicyano-5,6-bis(4-acetamidophenyl)pyrazine (DAcPz) (7)

A 1g (3.1×10-3 mole) of 4,4'- diacetamidobenzil was disolved in a mixture of 25 ml of ethanol and 25 drops of acetic acid and then added to conical flask containing (0.334 g , 3.1×10-3 mol) of diaminomalonitril (DAMN) soluble in 25 ml of ethanol. The total mixture then refluxed for 4.5 hours and then left for two days to complete the precipitation. The solid product filtered and re-crystallized from a mixture of hexanol and acetone (1:1). filtered and dried. The product is brown powder. The yield is (0.88g, 72%).

Preparation of Octa(4- acetamidophenyl)- Tetrapyrazino porphrazine Nickel (II) (OAcPzNi)

0.1115 g (6.3 × 10-4mole) of nickel actate was added to a solution of 1g (2.52 × 10-3 mole) of DAcPz in 3 ml of distilled quinolone. 1.2 gm (2×10-2 mole) of urea were added to the mixture and the reaction mixture refluxed with magnetic stirring for 15 minutes and then cooled and filtered. The solid product dissolved in a least amount of chloroform and re-precipitated by adding it portion wise with stirring to a beaker containing 200 ml ethanol. The precipitation process was repeated for three times, and then dried at 120 ºC. The product is a brown powder. The yield is(0.6 g, 57.8 %). CHN($C_{88}H_{64}N_{24}O_8Ni$): calcd; C:66.88 ,H:4.50 ,N:21.28; Found; C:65.02 ,H:4.22 , N:20.01 .

RESULTS AND DISCUSSIONS

The little differences between the practical CHN values with the calculated percentages might be due to the difficulties of purification of such compounds.

Figures (1) and (2) shows the IR spectra of DAcPz and its complex (OAcPzNi) respectively. They show, respectively, the aromatic

C-H stretching at 3190 cm -1 and 3091 cm-1, the aromatic C-H in plane, at 839 cm-1 and 923 cm-1 and 669 cm-1 and 773 cm-1 out of plane.

The bands, 1384 cm-1 and 1344 cm-1, for the respective compounds are attributed to the stretching vibration for C-N, and the bands 1683 cm-1 and 1670 cm-1 are attributed to the C=N stretching vibration for both compounds respectively, and C≡N stretchy vibration for PAcPN is at 2214 cm-1(8,9), which is disappeared in the complex.

The bands 3348 cm^{-1} and 3304 cm^{-1} are attributed to the stretching vibration for

N-H respectively.

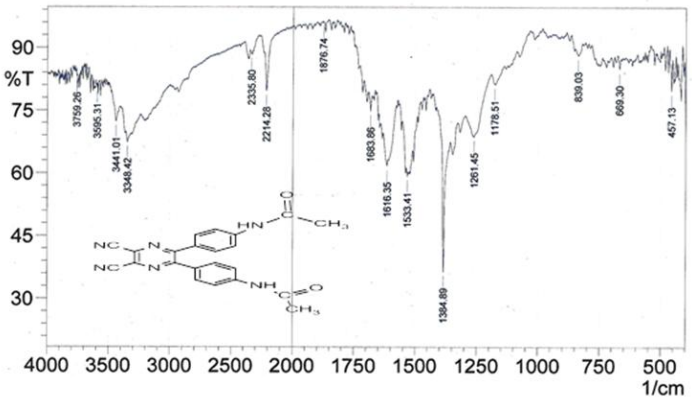


Figure 1: The IR Spectrum of DAcPz

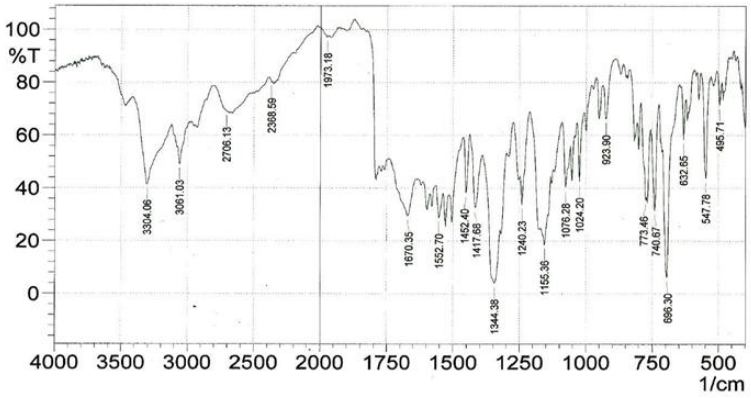


Figure 2: The IR Spectrum of OAcPzNi (11)

The U.V-Visible spectrum, figure(3), shows the two main bands, at 675 nm (Qband) and 395 nm (Soret band) for OAcPzNi complex, Which could be attributed to the π-π^* transitions in addition to the n-π^* coupling of electrons of the nitrogen atoms to the π-system[(1-10)].

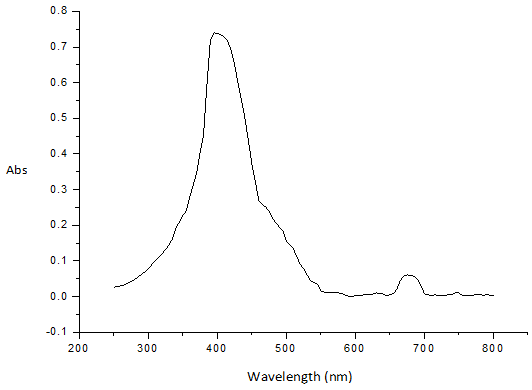


Figure 4: The U.V-Visible of OAcPzNi in Chloroform

The visible spectrum, figure(4), shows the variation of Q band of the complex, at 675 nm with time. It shows that the absorption intensity increases with time which could be attributed to the separation of the aggregated species in the presence of the pyridine molecules whicht makes the peaks higher and sharper[(11.12)].

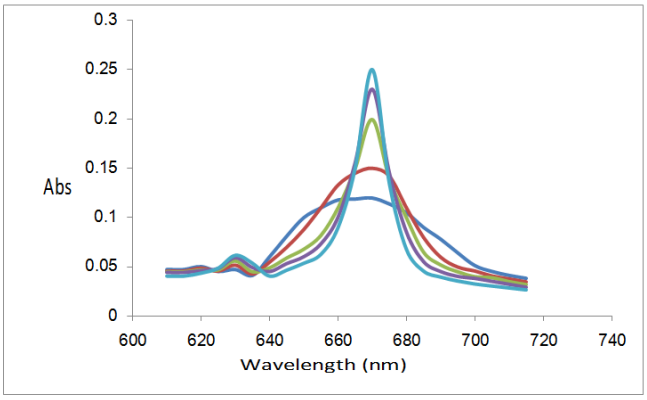


Figure 5: The Visible Spectra for OAcPzNi Complex in the Presence of Pyridine with Time at 675 Nm from Lower to Higher

1) 5 min 2) 15 min 3) 30 min 4) 60 min 5) 90 min .

Figure (6), shows the relation between ln $\frac{D-D0}{D\infty-D}$ and ln [py] and according to the relations(13,14):

OAcPzNi + 2Py ↔ OAcPzNi(Py)2-1

$$ln\frac{D-D0}{D\infty-D} = lnK + \text{n ln}[Py]\text{-2}$$

Where Py is the pyridine molecules . D, D0 and D∞ are the optical density for the complex with our pyridine, with pyridine and at equilibrium respectively. K and n are the equilibrium constant and the number of pyridine molecules attached to the complex molecule.

The calculated lnK from the intercept in figure (6) is 0. 75.

From the slope of figure(6)), n is equal to 1.62, and from figure(7), n is calculated to be 2 which refers to the attachment of 2 pyridine molecules to the central atom. From the formula: ΔG = -RT lnK, (T=295, R=8.314 J.mol-1) the change in free energy, ΔG, is calculated(– 2.45 kJ/mol-1) at 22 0C. The negative is related to the spontaneity.

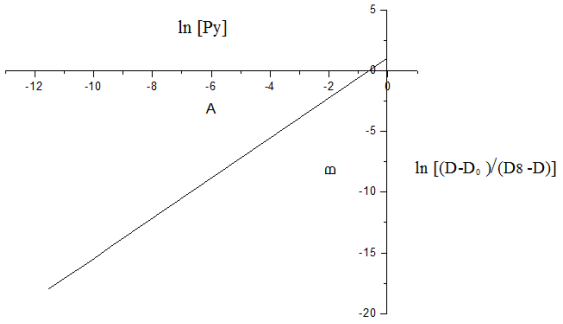
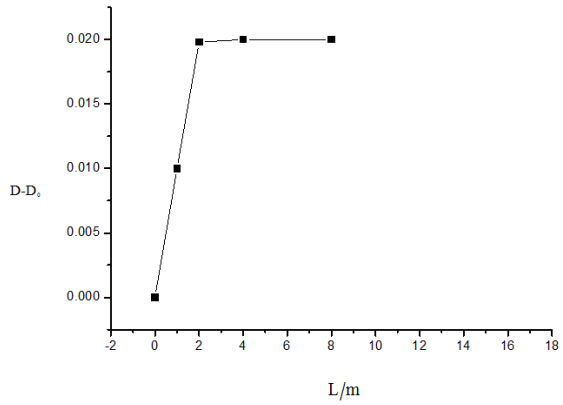


Figure 6: Variation of the [(D-D0)/(D∞-D)] with Ln [Py] for the Opacpni Complex



Figures 7: The Relation of D-D0 with L /M for the OAcPzNi Complex

L/m = number of ligands/number of molecules

Figure (8) shows the the variation of current with voltage at room temperature 220C for surface film of the complex with aluminum electrodes vaporizeon glass substrate. The figure shows an Ohmic relation in the voltage range 0-10 volts.

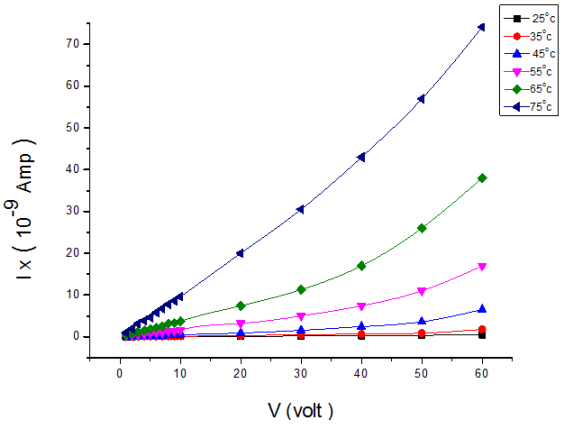
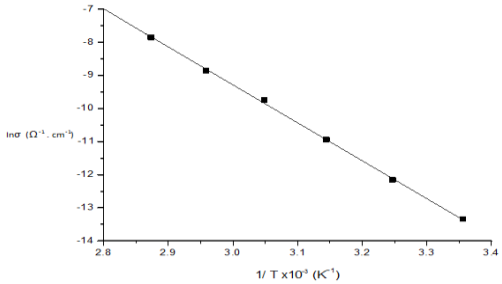


Figure 8: The Current Voltage Relation for the OAcPzNi Complex

Figure(9) shows the relation between $\ln\sigma$ and $\frac{1}{T}$ according to arrhenius relation(15),where, σ is the specific conductivity, ΔE is the activation energy,k is Boltzman

constant. The calculated activation energy and the pre-exponential factor were calculated from the graph of figure(8) and shown in table (1).



Figures 9: The Relation between Lnσ and 1/T for OAcPzNi Complex at the Teprature Range 298-.at

Table 1: The ΔE and Σo for the Complex

Compound	EΔEv	σ0Cm -1 -1 Ω
OAcPzNi		9.1 x 10-4

RFERENCES

1. J. Simon and J. J. Andr'e;*"Organic Semiconductors*" John and Willy, London (1985).
2. E. Gonca., Highly symmetrical polyfluorinated porphyrazines., "J. fluorochem"., 149.65-71 **(2013)**.
3. J. M. Fox.; T.J. Katz.; S, Van Elshocht.; T, Verbiest.; M, Kauranen.; A. Persoons.; T,; Krauss,T. Th. Chang.; and L. Brus.; J. Am. Chem. Soc. 121, 3453-3459**(1999**).
4. M. P. Donzello, C. Ercolani and P. A.Stuzhin, *"Coordination Chemistry Reviews*", 250, 1530 **(2006)**.
5. M. Kostka., P. Zimcik., M. Miletin., P. Klemera., K. Kopecky and Z. Musil., *"J. photochem. Photobiol, A-Chem"* 178, 16-25**(2006**).
6. L. F. Fieser and K L. Williamson. ; "*Organic Experiments*" D.C. Heath and Company 263 (**1974**).
7. Nazar A. Hussein and Raheem K. Zobon; International Journal of Applied and Natural Sciences 3(1), 57 (2014).
8. S. Makhsee, J. Samuel and F. Ibrahim, *Tetrahedron*, 64, 8871**(2008)**.
9. G. Socrates, "*Infraed Characteristic Group Frequecies*" John Wiley Sons, Ltd, New York, Copyright **(1980)**.
10. R. M. Silverstein and F.X-Webster, "*Spectroscopic Identification of Organic Compounds*", 6th Ed, John Wiley and Sons, Inc.,New York **(1996)**.
11. M. Kostka, P. Zimcik, M. Miletin, P. Klemera, K. Kopecky and Z. Musil; J. Photochemistry and photobiology A: Chem., 178, 16**(2006)**.
12. K. Kopecky, P. Zimcik, V. Novokova, Miletin, P. Klemera, K. Kopecky Z. Musil, J. Stribna; *Dyes and Pigments*,78, 231**(2008).**
13. O. I. Koifman, T. A. Koroleva and B. D. Berezin; *Soviet J. Coord. Chem.*, 3(12), 1420 **(1977)**.
14. S. F. Ginzburg, L.P. Brinina, G. V. Ponomarev and V. V. Khrapov; *Soviet J. Coord. Chem.*, 3(12), 1394 **(1977)**.
15. J. P. Linsky and T. R. Paul., *Inorg. Chem*., 19, 3131, **(1980)**.