# Synthesis, Characterization and Molar

# conductivity study of some

# phthalocyanine Palladium(II)

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#### Abstract:

The study includes the preparation of Phthalocyanine compounds with general formula PePd and  $(NO_2)$ 4PcPd where NO are a peripheral substituted in position 3- and 4-on the benzene rings. All compounds were characterized by UV-Visible and IR spectroscopy. Molar conductivity was studied in N, N-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) indicated that all these solutes behave as weak electrolytes.

## Introduction:

The earlier interst in metal phthalocyanines was mainly because of their importance as dyes and pigments. In the last twenty years phthalocyanine chemistry was undergoing a renaissance because phthalocyanine and many of its derivatives exhibit singular and conventional physical properties interesting for applications in materials science. Recently expanding a many either into applied field such as photovoltaies, optical data, liquid crystals, chemical sensors, electrical conductivity and thermally stability The present work described the synthesis, characterization and molar conductivity of new complex of phthalocyanine palladium and new complexes derivative.

# **Experimental:**

The prepared compounds were prepared using synthetic route as shown in scheme 1.



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## Scheme 1.

Preparation of nitro phthalic acid:

3- And 4- nitrophthalic acid were prepared by nitration of phthalaic anhydride. 50 gm Phthalic anhydride was dissolved in 50 ml of sulphuric acid at 75 °C. Then 21 ml fumming nitric acid was added with vigorous stirring at 90 °C. 15 ml of sulfuric acid was added dropwise for I hr. then 90 ml of nitric acid was added and heated at 90 °C with continuous vigorous stirring for 3 hrs. After cooling filtration under vacuum remove the excess of nitric acid and sulphuric acid. The curde product washed several times with cold distilled water. The 3- nitro Phthalie acid was obtained by recrystallization of the product from distilled water (three times) (yield 35%), Pall yellow crystals were obtained m.p 220 °C (lit. 220 °C). The washing distilled water was collected and concentrated. 4- Nitro phthalic acid was extracted from washing water by diethyl ether several times, collected and evaporated to form yellow crystalline product (yield 43%), with m.p 165 (lit. 165 °C).

Fumming nitric acid was prepared by distillation of a mixture of equal volume of conc. HNO, and conc. H-SO, and first third of the volume of HNO, was taken.

Preparation of Phthalocyanine Palladium [I](PcPd) (9);

(0.016 mole) K2PdCl4, (0.062 mole) phthalic anhydride, (0.2g) ammonium molbdate tetrahydrate, 0.5g ammonium chloride and excess urea (0.5 mole) were finally grounded and placed in 250 ml round bottom flask containing 50 ml of nitrobenzene. The temperature of the stirred reaction mixture was slowly increase to 185 °C and maintained at 185 °C for 4 hrs.

The hot mixture was filtered and solid product washed with ethanol many times until free completely from nitrobenzene solvent. The product was then dried and added to 200ml of IN HCI and then refluxed for two hours, cooled to room temperature and filtered. The residue was added to 200ml IN NaOH and refluxed for two hours then filtered and washing with distilled water until the washing water was neutral, dried at 100 °C for Shrs.And solid powder was collected then kept in a desicator.

Preparation of 4,4,4,4-(NO<sub>2</sub>)PePd [III] and 3,3,3,3-(NO2)4 PcPd [II];

(0.016 mole) K<sub>2</sub>PdCl2, (0.062 mole) 4-nitroPhthalic acid (or 3-nitroPhthalic acid), (0.2g) ammonium molbdate tetrahydrate, 0.5g ammonium chloride and excess urea (0.5 mole) were finally grounded and placed in 250 ml round bottom flask containing 50 ml of nitrobenzene. The temperature of the stirred reaction. mixture was slowly to 185 °C and maintained at 185 °C for 4 hrs.

The remaining steps as same as prepared of compound PePd to collected the products  $4,4,4,4-(NO_2)4PcPd$  and 3,3,3,3-(NO2)4 PcPd and stored at desicator.

## **Appartus:**

Melting points were measured on Gallen Kamp melting point apparatus. Infrared spectra were recorded on a Pye unicam model SP3-300 spectrophotometer. UV-Visible spectra were measured by thermospectronic Helios a V4.60 using DMSO as solvent in concentration 10 M. Conductivity measurements were measured using Konduktoskop model 365B conductivity meter using standard conductivity cell constant equal to 0.785 cm.

## **Results and Discussion:**

The IR spectra of all prepared compounds showed a medium band at 1600 cm which attributed to C-N stretching vibration of pyrrole dominate, a medium band at 1590 cm which attributed to C-C stretching of aromatic groups, a strong band at 1140-1000 cm and a medium bands at 920, 810, 770, 720 and 690 cm appear in the spectra assigned to phthalocynine skeletal vibration (1-11), the IR spectrum of compound (II) showed a strong band at 1530 and 1330 cm which attributed to asymmetric and symmetric stretching vibration of NO2 groups and IR spectrum of compound (III) showed a strong band at 1530 and 1335 cm which attributed to asymmetric and symmetric stretching vibration of NO2 groups. Typical IR spectra for these compounds shown in Figs. (1 and 2).

UV-Visible spectra of the prepared compounds are summarized in the Table (1). Typical UV-Visible spectra for these compounds are shown in Figs. (3-5)



The molar conductivity have been measured for all the prepared compounds in both DMSO and DMF solvents, all these compounds are exhibited a weak electrochemical behavior as shown in figures (6-11). The molar conductivities are equal to 198, 186 and 18tohm cm<sup>2</sup> mol for compounds I, II and III respectively in DMSO solvent and are equal to 101, 145 and 140 ohm cm<sup>2</sup> mol for compounds I, II and III respectively in DMSO solvent and detectable no the properties of the solutions were allowed to age for up to a week and detectable no change in molar conductivity were observed as shown in Table (2). The non changed molar conductivity was high enough to suggest that all the complexes stable in both the solvent and do not hydrolysied.

In order to know the stability of the prepared complexes, we calculated the dissociation constant (Kd) and molar conductivity in zero concentration (A) by using Krauss equation (2),

Table(2): Molar conductivity in different times, Molar conductivity in zero concentration and Dissociation constant for prepared compounds.

Compound	5 <sub>0</sub> (0M9O)		A <sub>0</sub> (DMF)		DMSO		DMP	
	T=0	T=7daye	T=0	T=7days	As	Kd*10*	A.	Kd*10
1	198	300	101	101	83.3	2.1	40.8	23
1	186	185	145	145	87.56	(2	45,5	0.5
0	181	181	[.40	HI	76 <u>f</u>	07	42.7	45



Fig. (1): IR spectra of compounds (1)











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#### **References:**

1. C. G. Claessens, W. J. Blau, M. Cook, M. Hanack, R. J. M. Nolte, T. Torres and D. Wohrle. Monatshfets fur chemie., 132, 2(2002).

2. M. P. Somashekarappa and J. K. eshavagya, metal.org. chem., 29, 767(1999).

3. J. Sleven, T. Cardinaels, C. Gorller-Walrand and K. Binnemans, ArKivoc (2003) Internet.

4. K. Ban, K. Nishizawa, K. Ohata and H. Shirai, J. Mater. Chem., 10, 1083 (2000).

5. K. Ban, K. Nishizawa, K-Ohata A. M. Van de Craats, J. M. Warman, I. Yamamota and H. Shirai, J. Mater. Chem., 11, 321 (2001).

6. N. B. McKeown, "Phthalocynine Materials: Synthesis, Structure, Function", Cambridge University Press (Cambridge) 1998.

7. W. A. Lawrance, J. Am. Fabric. Soc., 1871 (1920).

8. The Merck index, 10th Edt., Merk and Co. Inc., New Jersey, p.943 (1983).

9. B. N. Achar, G. M. Fohlen, J. A. Parker and Keshavayya, J. Polyhydron 6, 1463 (1987).

10.C. J. Brown, J. Chem. Soc., A 2494 (1968).

11.R. M. Silverstein, G. C. Bassler and T. C. Morrill.

"Spectrometric Identification of Compounds", Wiley, New York, 1998. Organic

12.P. W. Atkins, "Physical Chemistry" Oxford University (1998).

الخلاصة:

تضمنت الدراسة تحضير بعض المركبات الفثالوسيانين ذات الصيغة العامة PePd و (NO Ped حيث NO Ped في NO Ped و NO Ped حيث NO

شخصت هذه المركبات بالاطياف الالكترونية في المنطقة فوق البنفسجية - المرئية ومطيافية الاشعة تحت الحمراء. درست التوصيلية المولارية في المذيبين ثنائي مثيل فورما مايد وثنائي مثيل سلفوكسايد حيث تسلك كل هذه المذابات كالكتروليتات ضعيفة.