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Study Antioxidant of Synthesized Nickel (II) Phthalocyanine: Characterization and Biological Activity

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Abstract

Nickel (II) phthalocyanine is a group of coordination compounds belonging to the phthalocyanines class, a macrocyclic complexes compound. It comprises a central-nickel (Ni^{2+}) ion coordinated to a large, planar ligand organization composed of four isoindole units linked by nitrogen-atom, forming a conjugated system similar to porphyrins. The complex of phthalocyanine was produced through the reaction of p - cyanobenzamide with nickel ion (Ni^{2+}) and analysis by FTIR, UV-visible and ¹HNMR spectroscopy test. The DPPH "radical-scavenging test" was using to test the antioxidant properties with varying concentrations of Nickel (II) phthalocyanine complex in methanol solution. The results confirmed the successful synthesis of high-quality "Nickel phthalocyanine complex" and confirmed by spectroscopic examinations. The complex demonstrated significant "antioxidant activity" achieving an 85% scavenging effect on the (DPPH radical) at a concentration of (25 μ g). The conclusion of this study appeal that synthesized Nickel (II) phthalocyanine shows promising antioxidant properties in optimum concentration (25 μ g).

Keywords: DPPH; Nickel II; Nickel (II) phthalocyanine; p-cyanobenzamide

Introduction

Phthalocyanine complex is a large, aromatic, macrocyclic, organic and is of theoretical or specialized interest in chemical dyes and photoelectricity. "Nickel Phthalocyanine" is considered a group of coordination complex compound belonging to the group of phthalocyanines that are macrocyclic-complexes compound. It comprises of a central-nickel II ion coordinated to a large and planar ligand-structure composed of (four-isoindoles-units) connected by nitrogen-atom forming conjugated system similar to porphyrins (Sorokin, 2019). The complex of "Nickel (II) phthalocyanine" has a planar aromatic-macrocyclic organization involving four isoindole-subunits linked by nitrogen atoms and this arrangement forms an extended conjugated (π -system) making it extremely electron-rich. The nickel ion takes the center of the "phthalocyanine ring" coordinated by the four-nitrogen-molecules in square-planar geometry. The strong coordination gives the molecule unique electronic properties and stability (Chen et al., 2007). The complex is extensively used in paints ink and plastic due to its vibrant color and stability (C. Zhang et al., 2021). The complex compound of "Nickel (II) phthalocyanine" exhibits catalytic-action in reactions such as "oxygen reduction" and "hydrogen evolution" (Bottari et al., 2010). More this complex is utilized in chemical and biological sensors to detect biomolecules or gases (Furini et al., 2020). Many new "phthalocyanine-derivative compounds" function as active material in "organic semiconductors photovoltaic cells" and gas-sensors (Kalyanasundaram et al., 1998). Its photochemical-properties make it a candidate for certain medical applications (Urbani et al., 2019). This study aims to synthesize high quality "Nickel (II) phthalocyanine" and examine its properties using (UV-visible), FTIR and ¹HNMR spectroscopy analysis as well as evaluating its "DPPH radical-scavenging activity".

Materials and Methods:

Experimental:

All chemical solvents in this experiment are distilled and dried before using and all chemicals were used for the synthetic complex compound supplied from "Aldrich Company" and "BDH Chemical Co".

Chemical synthesis

The synthesis of the last compound involving two-step process. In the first-step, **p-cyanobenzamide** was prepared by gradually adding 0.08 mL of **p-cyano benzoyl chloride** to 40mL of an amine-water solution at 60°C in a 100 mL flask (Enokida et al., 1991). The reaction mixture of compound was vigorously stirring for one hour, then allowed to cool for another hour. After cooling, the chemical-mixture was filtered by using a Büchner-funnel, and the resulting solid was thoroughly washed with ice-cold water until the pH of the washing water reached 7 (pH 7), as indicated by pH test paper. The crude-product of chemical mixture was then refluxed for 40 minutes and subsequently purified through recrystallization from hot-water (Gök et al., 2007).

In the next second step, Nickel (II) phthalocyanine (Ni-Pc) was produced by reacting 5 g of the compound prepared in the first step with 1.2 g of nickel-powdered and 3 g of naphthalene(used as a diluent). The mixture was disturbed and heated in (230°C) for 1 hr (Furuyama et al., 2014). Afterward, 200 mL of acetone was boiling for 7 minutes, and the resulting powder-product was treated with a 1 M sodium-hydroxide solution(NaOH) diluted in hot-water to remove excess naphthalene (ARSLAN, 2016). The solid residue was then purified by recrystallization from benzene, yielding Ni-Pc

with a 50% recovery rate. The synthesized product was characterized using UV-Visible spectroscopy, FTIR, and ¹HNMR spectroscopy with Bruker instruments.

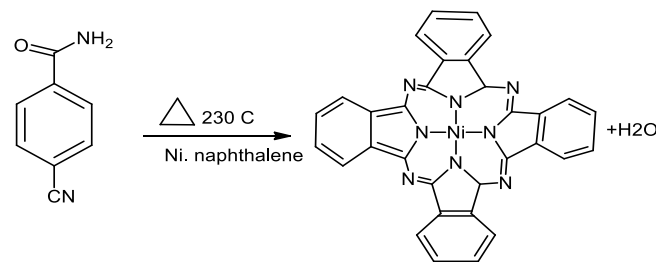


Figure (1) the synthesized of Nickel (II) phthalocyanine

DPPH Radical Scavenging Activity

Solutions of methanol containing the Nickel (II) phthalocyanine compound were prepared at a conce. of 1000ppm. Dissimilar volumes were organized at (25, 20, 15, 10, 5 μ l) of each solution of methanol, a solution of (Ni-Pc) compound in the separate tubez containing five ml of (0.004)% MeOH solution of DPPH (Marinova et al., 2011). All of tests prepared, the samples was prepared in the triplicate. The combinations were forcefully disturbed and sited in the dim condition for two hours up to constant-values were gotten. The value of absorption for the samples test was measured at wave length 517 nm and recorded (Moreira et al., 2008). DPPH root scan activity for each sample and benchmark were measured by using the chemical equation below:

$$\text{Percentage of DPPH radical-scavenging-activity} = (1 - (A_t / A_o))100$$

Where A_t represents the absorbance of the samples, while A_o denotes the absorbance of the controls. The average-values were determined from three standard samples for each compound, using "ascorbic acid" as the standard reference.

Result and discussion:

Compounds obtained from Aldrich and BDH Chemical Co. were used without additional purification. Infrared-spectra(IR) were recorded as KBr disks using a Bruker Tensor M27 spectrometer. The IR spectrum of Nickel (II) phthalocyanine (Ni-Pc) is presented in Figure 2. The compound had a melting point of 355°C and a yield of 75%. Elemental analysis yielded the following results: C: 66.17%, H: 19.88%, and the calculated values were C: 67.28%, H: 2.94%, N: 20.01%.

Key FTIR (KBr pellet) spectral data (cm^{-1}) include:

- 3000.99–3207.66 (strong, O–H stretching),
- 980.77–1200.99 (medium, CH_2 bending),
- 1607.09–1609.45 (medium, C=C stretching),
- 1700.03–1768.89 (C=N stretching),
- 1333.78–1345.50 (strong, C–N stretching),
- 540.77 (weak, Ni–N stretching).

The prominent peak at 1608 cm^{-1} corresponds to the stretching-vibration of the benzene ring within the pyrrole unit. Figure 3 illustrates the UV-Visible spectrum of Ni-Pc, confirming its structural characteristics (Abed et al., 2019; Aktaş et al., 2013; Lai et al., 2018) as appear in Figure (3) which indicated to UV-Visible spectrum of Nickel (II) phthalocyanine.

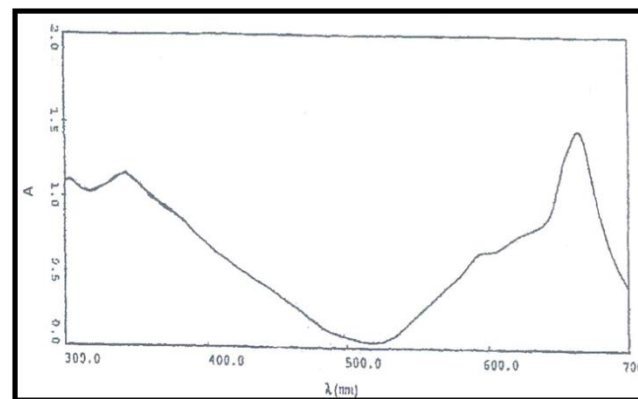
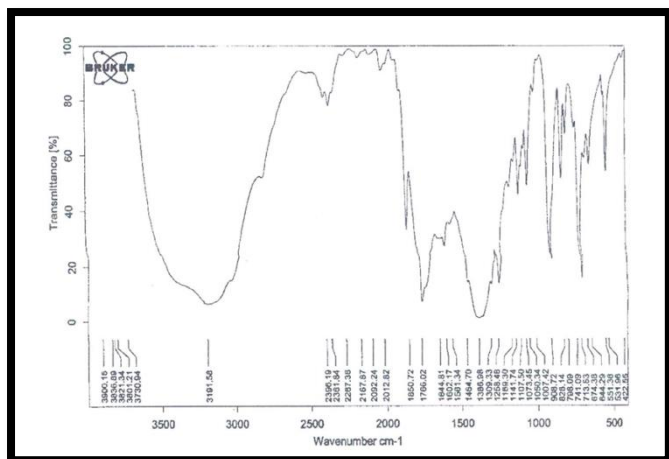


Figure (3): UV/Vis spectrum of Nickel (II) phthalocyanine

Figure (2): FTIR spectroscopy of synthesis Nickel (II) phthalocyanine compound

The ^1H NMR spectrum of the aim compound, Nickel (II) phthalocyanine (Ni-Pc), documented in DMSO, is shown in Figure 4. The spectrum exhibits a singlet in the range of 7.5–8.04 ppm, corresponding to 12 protons of the phthalocyanine aromatic CH groups (pc-CH). Additionally, a peak at 5.39 ppm is observed, which is recognized to the protons of the C=C bonds within the chemical compound. In addition, these signals confirm the successful synthesis and structural integrity of the Ni-Pc complex (Abed, 2015; Ağırtaş, 2008; Taher et al., 2024).

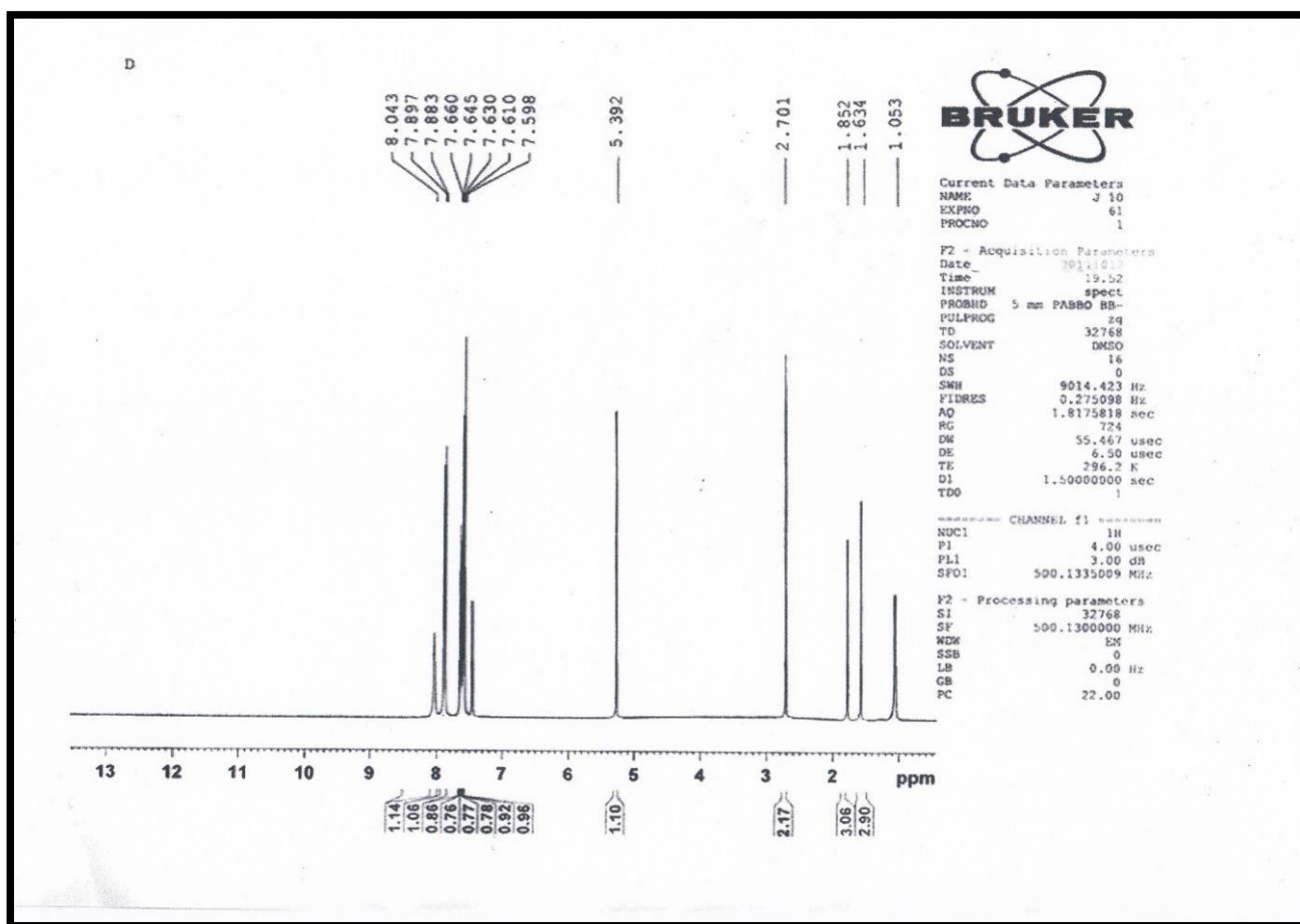


Figure (4): ^1H NMR spectrum of synthesis Nickel (II) phthalocyanine compound

Nickel (II) phthalocyanine (Ni-Pc), as shown in Figure 5, has the ability to form a variety of complexes by coordinating with different cations such as (e.g., Fe, Co, etc.) at the central metal site. This interaction includes the nitrogen atoms in the pyrrolic structure and the nickel ion, enabling the materialization of stable compounds. Many studies have demonstrated that these complexes exhibit significant industrial and biomedical applications. In industry field, the “Nickel (II) phthalocyanine” products play a key role in the increasing development of advanced materials such as “carbon nanotubes” owing to their robust metal-ligand bond. In the medical field, the “Nickel (II) phthalocyanine” compounds

have showing promising properties including “antitumor and antibacterial activities”. More addition the complex usually are instrumental in enhancing the efficacy of certain medications by increasing the degree of inhibition against specific biological-targets and contributing to their vital role in therapeutic advancements(Ali et al., 2024; Couto et al., 2020; Y. Zhang et al., 2017).

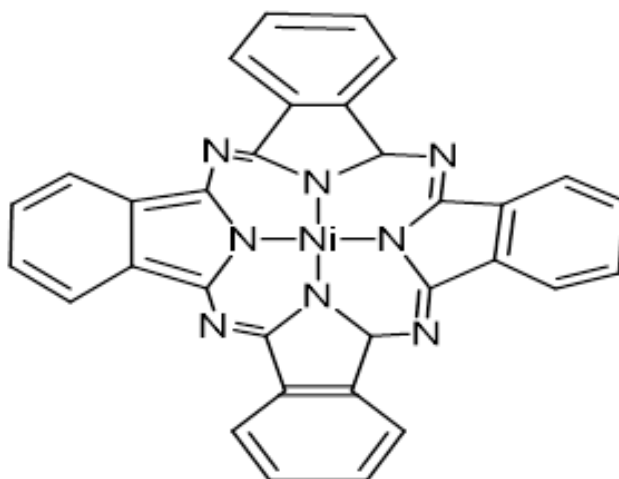


Figure (5): Structure of Nickel Phthalocyanine complex

Antioxidant characterizations of “Nickel (II) phthalocyanine” are recognized for their ability to suppress the formation of “reactive oxygen species” (ROS) through the chelation of trace elements. The DPPH test is usually used to assess the “free radical scavenging activity” of antioxidant of natural compounds (Nimse et al., 2015). DPPH test stable-free-radical generate a purple-colored solution in meOH and exhibits strong absorption at wavelength of 517nm(Xu et al., 2007). This test depending on measure the ability of antioxidants to scavenge “DPPH-radicals” with antioxidants-reducing these radicals by donating electrons which results in the loss of (purple color) of the solution Results showed in Table 1 and Figure 6 appeal to the significant “scavenging activity” of phthalocyanine complex against “DPPH radical” comparing favorably with Vitamin C “ascorbic acid”. At a concentration of (25 µg) the complex of phthalocyanine exhibited 85% scavenging effect on the “DPPH radicals” highlighting its potential as an effective antioxidant.

Table (1): The DPPH-free radical scavenging activity of Nickel Phthalocyanine complex on in-vitro assay

Comp	Conc. 1000 ppm														
	5 µL			10 µL			15 µL			20 µL			25 µL		
	A _a	A _o	(I%)	A _a	A _o	(I%)	A _a	A _o	(I%)	A _a	A _o	(I%)	A _a	A _o	(I%)
Ni.Pc	0.306	0.655	53	0.252	0.655	62	0.191	0.655	71	0.144	0.655	78	0.101	0.655	85
Vit. C	0.245	0.655	63	0.19	0.655	71	0.121	0.655	82	0.085	0.655	87	0.044	0.655	93

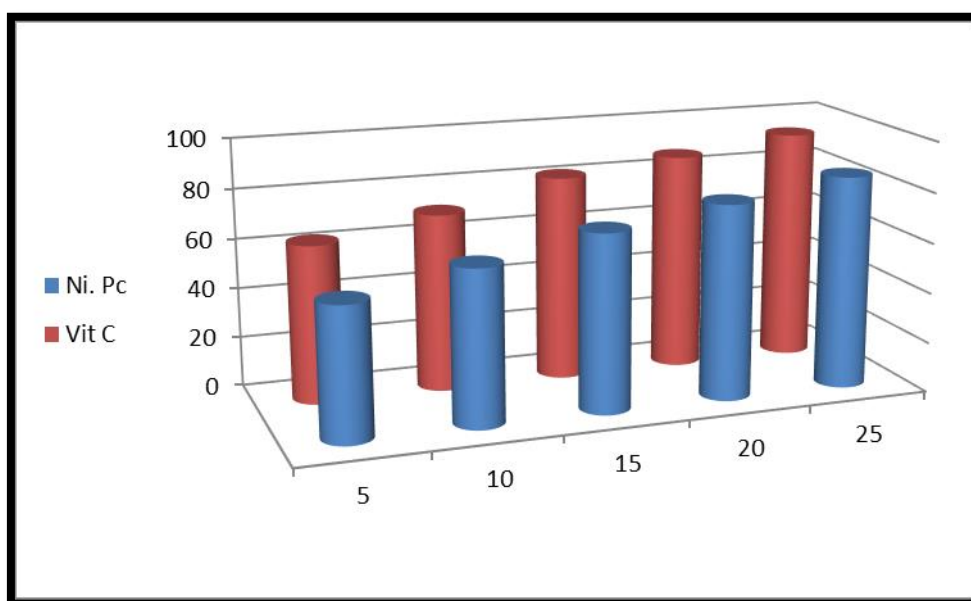


Figure (6): DPPH-free radical scavenging action of Nickel (II) phthalocyanine compound on in-vitro assay

Conclusion:

Study conclude the role of synthesis Nickel (II) phthalocyanine as anti-oxidant using free radical scavenging effect of Ni-Pc on DPPH and its role as strong.

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