

Preparation, Infra-red and solvent effects On the Electronic absorption spectra of Magnesium Phthalocyanine

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Abstract: Magnesium Phthalocyanine (abbreviated MgPc) like other methallophthalocyanines have limited solubility in most solvents this behaviour prevented complete spectroscopic studies. In this paper MgPc was prepared and Infra-red peaks were characterized, and MgPc has been found to be soluble in several solvent (DMF, DMSO, THF, Pyridine and Chlorobenzene). The study show that the position of Q-band show very small change in non aromatic solvent DMF, DMSO and THF. The blue shift was observed in aromatic solvent (chlorobenzene, this is because of the aggregation of MgPc molecules and the aggregation increase as the concentration increase. In pyridine a red shift of Q-band was observed.

الخلاصة: فثالوسيانين المغنيسيوم (يرمز له اختصاراً MgPc) كباقي الفثالوسيانينات الفلزية غير المعوضة غير ذائبة في معظم المذيبات الشائعة في الدراسات الطيفية . في هذه الدراسة حضر MgPc وشخصت حزم طيف الاشعة تحت الحمراء . كما وجد ان MgPc يذوب في بعض المذيبات مثل (THF, DMF, DMSO, Pyridine, Chlorobenzene) . سجلت أطيف الاشعة فوق البنفسجية المرئية وبيئت الدراسة ان الاطيف متشابهو في مذيبات DMF , DMSO , THF , بينما لوحظ حدوث أزاحة زرقاء في مذيب كلوروبنزين ولوحظ حدوث ان زيادة التركيز يؤدي الى زيادة الازاحة الزرقاء لحزمة - Q في البريدين لوحظ حدوث ازاحة حمراء فسرت على اساس حدوث ارتباط بين البريدين والذرة المركزية .

Introduction: Metallophthalocyanines are planar molecules Contain four Isoindole units (a pyrrole ring conjugated with a benzene ring well known for their intense blue-green color with extinction coefficients of greater than 105 L/mol.-cm in the region 650-700nm). This intense absorption has made phthalocyanine important industrial dyes. MgPc is one of these class of compounds, it is closely related to biological molecules (Chlorophyll)(2).

Phthalocyanine molecule have two main absorption band in the visible / near-uv region of the spectrum. The higher energy band occurring at around 350 nm is generally known as the B-band. The lower energy band occurring at 650 - 700 nm is generally known as the Q-band, both B and Q-band are correlated to $\pi \rightarrow \pi^*$ transition(3). In the solid state, these bands are broadened and overlap(3).

Experimentam: IR spectrum was recorded as KBr disk on a pyc-unicam SP3-300S. UV/visible spectra were recorded by cintra-5-spectrometer using 1 cm

quartz cell. Solvents were distilled and dried before use. All other chemicals were used as received from Aldrich or BDH chemical Co.

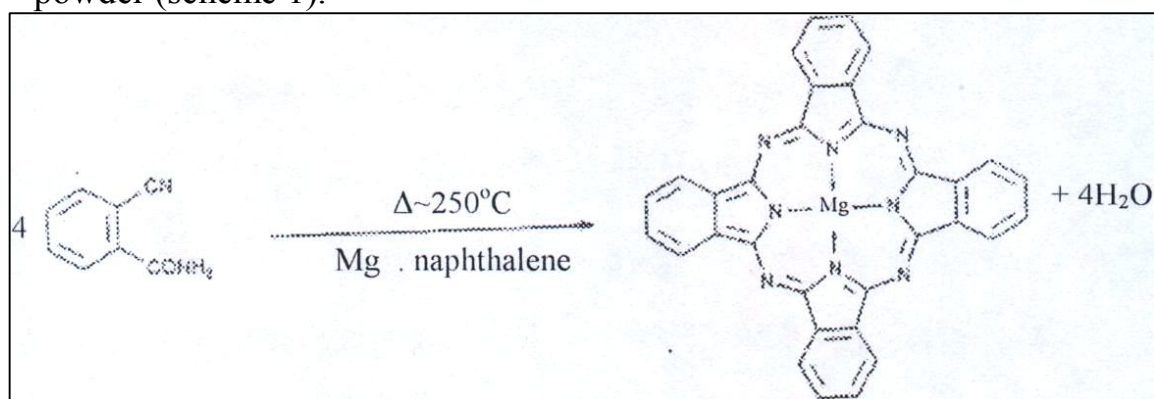
Preparation of o-Cyanobenzamide (1)

o-Cyanobenzamide (1) was prepared according to the method of Lowery et al (4). 20 g. (0.316 mole) of Phthalimide was stirred with 100 ml of one. ammonium hydroxide (25%) for 24 hours at room temperature. The produced phthalamide was then filtered off washed with water and ethanol and dried at 100 °C (yield 20.759, 93%). A mixture of phthalamide 16 g (0.0975 mole), acetic anhydride 60 ml and 10 ml of acetic acid was refluxed for 45 min. and the resultant solution was filtered and the filtrate allowed to cool to 40 °C and then re-filtered. The solid product (o-Cyanobenzamide) was washed with acetic acid, water and re-crystallization from ethanol and dried at 110 °C for 24 hours (yield 6.5 g, 45%) m.p 170-171, lit 172.(4).

Preparation of MgPc: 4 g. of o-Cyanobenzamide, 1 g. of powdered magnesium and 2 g. of naphthalene (as diluent) were heated at ~ 240-250 °C for 1 hour.

The powdered product was treated with boiling acetone, 1 M NaOH and hot water to remove naphthalene and phthalimide. The

residue was recrystallized from quinoline (yield 35%) as blue powder (scheme 1).



(1)

(2)

Scheme (1)

Results and Discussion:

Infra-red : Fig 1 shows the Infrared spectrum of MgPc from 2000-20 cm⁻¹ range.

In the 1610-1250 cm⁻¹ range there are several peaks which are attributed to both C = C and C - N stretching vibrations from benzene and pyrrole units (2). In the 1250-1000 cm⁻¹ range the strong peaks are characterized by the C - H in-plane bending. The medium peak at 890 cm⁻¹ is attributed to Mg - N (6). The strong peaks in the range 800-730 cm⁻¹ are attributed to C-H out-of-plane bending.

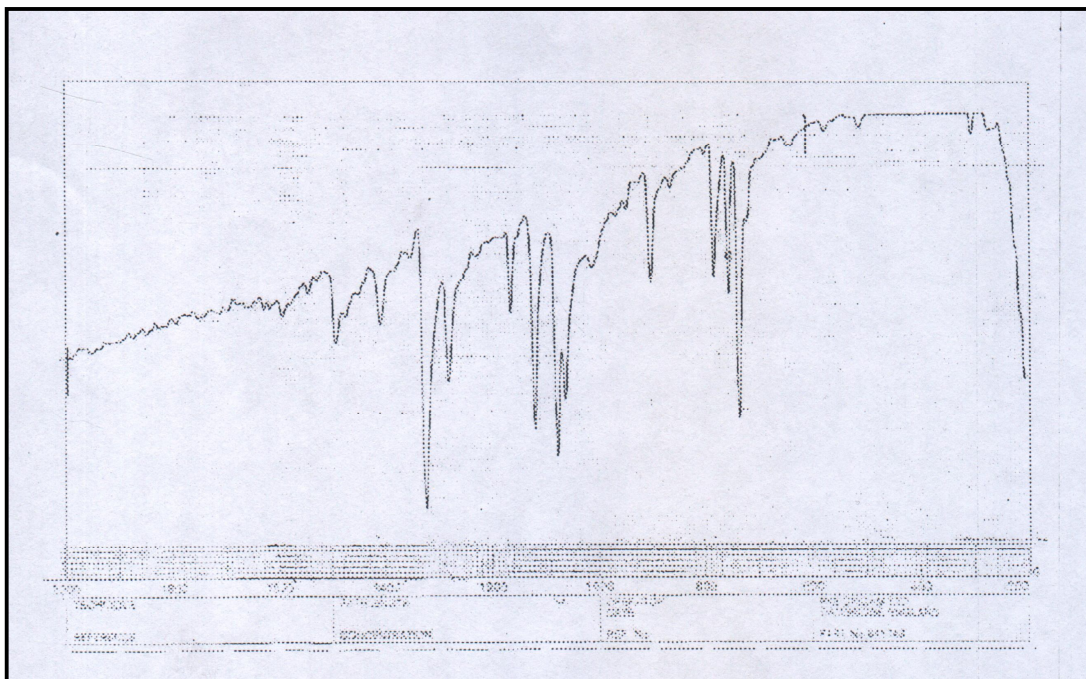


Fig. 1:1. R. Spectrum of MgPc as KBr disc

UV - Visible: UV -Vis spectra of MgPc in different solvents are illustrated in Figs 2-3. The wavelength of maximum absorbance (λ_{\max} nm) molar extinction coefficient ($\log \epsilon$) values are summarized in Table 1.

In THF, DMSO and DMF the electronic spectra of MgPc are similar and show the characteristic Q-band absorption centered around 670 nm and B-band around 344-348, both bands are attributed to π - π^* transitions(2).

Table (I): Electronic spectra data of MgPc in different solvents.

Solvent	Q - band λ_{\max} nm ($\log \epsilon$)	Other band	B - band
THF	670 (4.98)	607 (3.8)	344 (4.05)
DMSO	672 (5.07)	608 (3.77)	348 (4.08)
DMF	671 (5.02)	. 610 (3.66)	345(4.16)
Pyridine	678 (4.97)	650 (4.4), 610 (4.51)	348 (4.7)

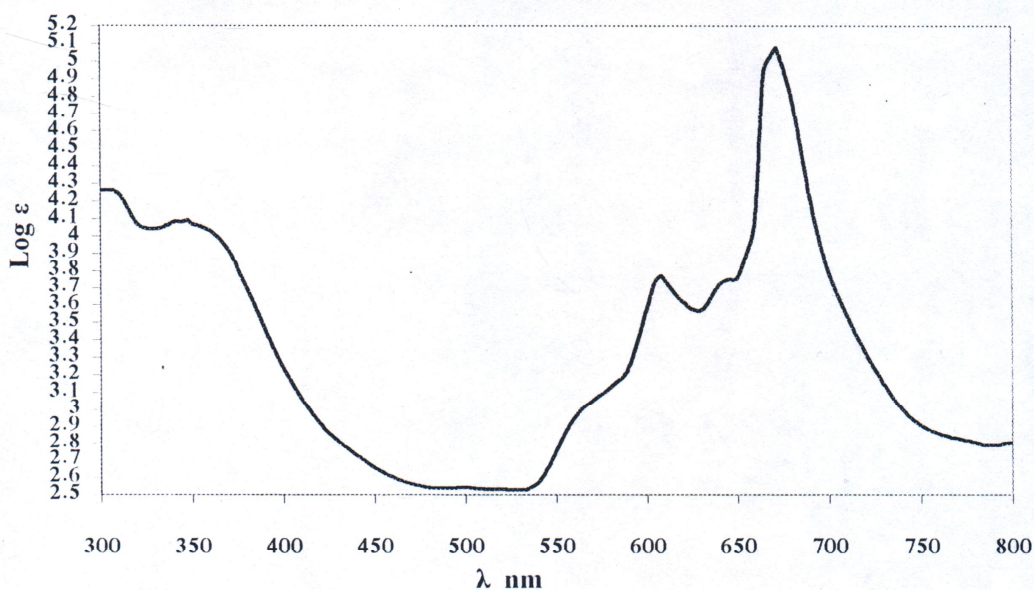


Fig 2: Electronic absorption spectrum of MgPc in DMSO

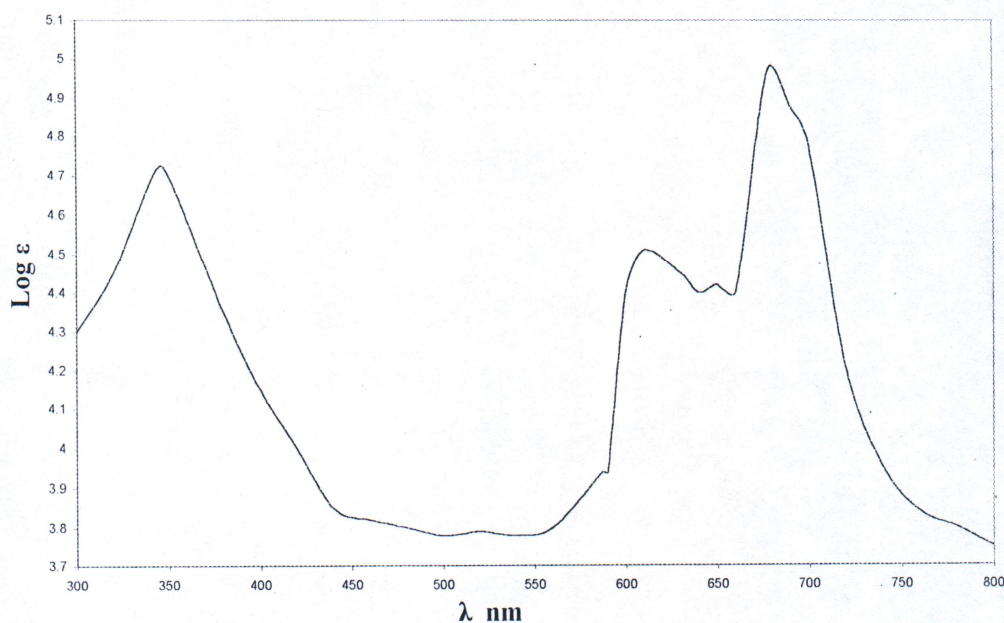


Fig 3: Electronic absorption spectrum of MgPc in Pyridine

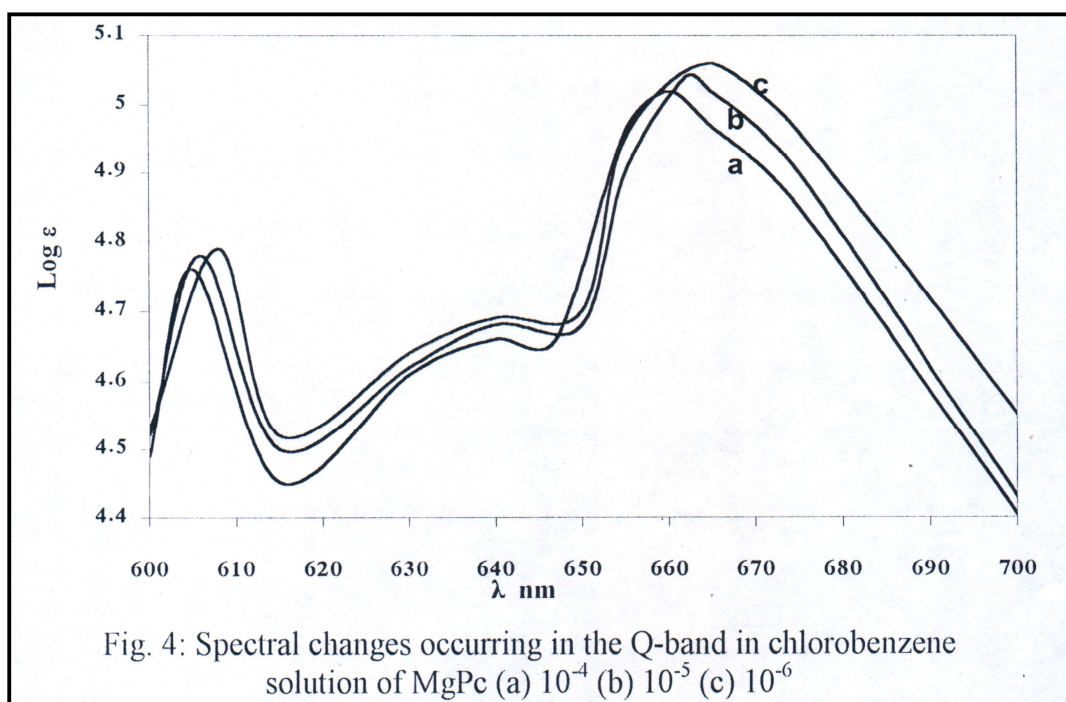
In Pyridine (Fig 3) Q - band shifted to higher wavelength compared to the DMF, DMSO and THE solutions, these effects may be explained by interactions between the Pyridine and the compound where a complex is formed by the axial coordination of pyridine molecules with the Center atom (Mg) of the Phthalocynine(8).

In Chlorobenzene a blue shift of the Q-band was observed. A solution of different concentration of MgPc in chlorobenzene (10^{-4} , 10^{-5} and 10^{-6} M) were prepared and the uv/visible spectra were recorded, the results shows that any increase in concentration results in a blue shift of the Q-band with some decrease in intensity (Fig. 4 and Table 2) these results may be attributed to the aggregation of phthalocyanine molecules(9, 10) and the aggregation increase with concentration.

The insolubility of MgPc in dilute H_2SO_4 and the decomposition in cone. H_2SO_4 did not allow us to obtain their uv / visible spectra in 112804 like other metallophthalocyanes such CuPc NiPc and CoPc.

Table (2): Electronic spectra data of MgPc in chlorobenzene at different concentration.

concentration	Q - band λ_{\max} nm (log e)	Other band	B - band
10^{-6}	665 (5.06)	608 (4.74)	347(4.1)
10^{-5}	662(5.01)	606 (4.78)	344 (4.02)
10^{-4}	660 (4.96)	605 (4.76)	340(3.9)





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