

U.V-Visible Spectral Analysis of Synthesized *Meso*-Tetraphenyl Porphin(TPP) and Some of its Metal Complexes.

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Abstract

This work investigated the effect of the central metal atom on the U.V-Visible spectra of metalloporphyrins, with correlations made between the ligand and the various metal derivatives. The porphyrin ligand, meso-tetraphenylporphin, was synthesized by direct reaction between pyrrole ring and benzaldehyde, and the metal complexes from the acetate of the divalent metal. Solubility tests of the ligand and the complexes were carried out. They were found to be soluble in many organic solvents such as chloroform, dichloromethane, benzene and pyridine, with the extent of solubility varying from one complex to the other. Solutions of $10^{-6} \text{ mol dm}^{-3}$ of the tetraphenyl porphin and its Mn(II), Cu(II), Ni(II), Co(II), Zn(II), Mg(II) and Hg(II) complexes were prepared and scanned over frequency range of 300-700nm using λ -3 Perkin-Elmer U.V/Visible spectrophotometer. The U.V/Visible properties of the meso-tetraphenylporphin complexes were found to depend on the central metal atom. The differences were quite definite which may probably be attributed to whether or not a d-metal orbital is available for covalent bonding. Those metals such as Mn, Co, Ni and Cu which have such orbitals have spectra which are shifted to the blue region and characterized by a low intensity first band, while metals in which covalent bonding is limited to s and p orbitals of the metal, such as Mg and Hg, have spectra which are shifted to the red region and which are characterized by a much more intense first vibrational band.

Introduction

Porphin is the parent molecule of all porphyrins. They are an interesting group of molecules from almost any chemical and physicochemical point of view. They are highly coloured compounds and absorb radiation in the visible and ultraviolet regions of the spectrum and exhibit a brilliant luminescence. Some are used as industrial catalysts and photo-sensitizer (Kozyrev, et al, 1996). They are physiologically important when they occur as certain iron or magnesium complexes. Iron porphyrin or heme compounds are the prosthetic or active groups of a number of heme proteins, which serve in general for oxygen transport and oxidative respiration. e.g haemoglobin catalase, peroxidase, and the cytochromes (Meunier, et al, 1994)

The green pigments of plant cells active in photosynthesis, that is, chlorophylls, are magnesium dihydroporphyrins. Vitamin B12 is a reduced porphyrin-like derivative containing the metal cobalt (Pandey et al, 1996). Bacteriochlorins, which have anti-tumor activities, are porphyrin derivatives (Pandey et al, 1994).

Porphyrins are starting materials for the synthesis of other important compounds. In 1993, the first crystallographic determination of an isoporphyrin perchlorate salt, which detailed the significant structural consequences of the porphyrin tautomerisation, was reported (Barkigia, et al, 1993). It had earlier been proposed that metalloisoporphyrins are one of the intermediates in trifluoroacetoxylation reaction of metalloporphyrins to afford metallo-mesotrifluoroacetoxyphyrins (Barnett et al, 1973).

Porphyrins are most often prepared by the assembly of mono-pyrrolic subunits. Reported synthesis where porphyrins have been obtained directly from monopyrrolyl intermediates

include reaction of pyrrole itself with certain aldehydes to give α , β , γ and δ -tetra substituted porphins, e.g. the reaction of pyrrole with benzaldehydes give α , β , γ , δ -tetra phenyl porphins (Final, 1987; Nguyen, et al, 1994; Nguyen, et al 1996).

Porphins and their metal derivatives possess as one of their most striking physical properties a series of well-defined and intense absorption bands in the visible region of the spectrum. These spectra have not only been of practical use in the characterization and analysis of porphin compounds, but have also been the subject of many theoretical discussions and interpretations.

The aim of this work is to study the structure and properties of porphyrins especially in connection with the spectra analyses, which permit an evaluation of the effect of the central metal substituent on the porphyrin spectra.

Experimentals

Materials

Reagents: Pyrrole, Benzaldehyde, Propanoic acid, Copper(II) acetate, Manganese(II) acetate, Zinc acetate, Magnesium acetate, Nickel(II) acetate, Cobalt(II) acetate, Glacial ethanoic acid.

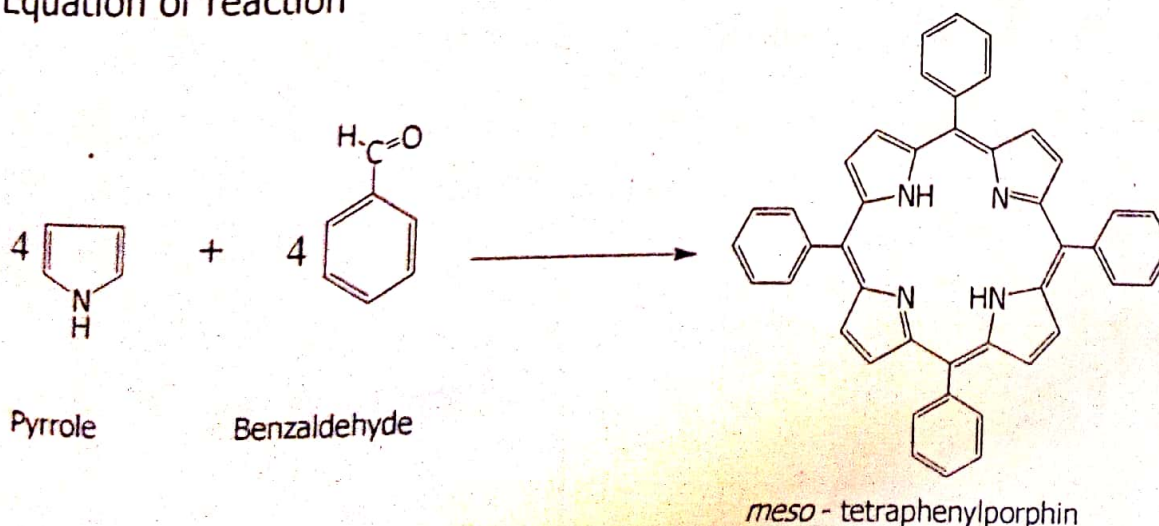
Solvents: Chloroform, Dichloromethane, Benzene, Carbon tetrachloride, Xylene, Propanone, Methanol, Ethanoic acid, 1,4-dioxan, Ether, Diethyether.

All reagents and solvents were analytical grade, manufactured by BDH, England, and no further purifications were made.

Methods

The *meso*-tetraphenylporphin ligand was synthesized by adding simultaneously 0.1 mole of benzaldehyde and 0.1 mole of pyrrole to 300cm³ of propanoic acid and the mixture refluxed for 1 hour on a water bath before being allowed to cool and stand for about 6 hours. The mixture was then filtered by suction and the crude product washed with water and then with methanol (Lee, et al 1995). A shining blue crystals of the *meso*-tetraphenyl porphin was obtained.

Equation of reaction

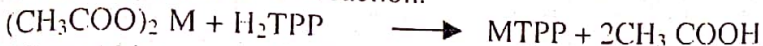


The metal complexes (metalloporphyrins) were synthesized by dissolving 500mg of the *meso*-tetraphenylporphin ligand in 50cm³ of chloroform and the solution added to 200mg of

the respective metal ethanoate dissolved in 50cm³ glacial ethanoic acid. The mixture was then heated to reflux for 1 hour. The crude product was obtained after filtration by suction (Alder and Longo, 1969; Xie and Smith, 1992).

Ethanoates of the following divalent metals were used: manganese, copper, nickel, cobalt, and zinc, magnesium and mercury.

General equation of the reaction:



Where M is the metal of interest and TPP is tetraphenylporphin.

The solubility tests of the prepared tetraphenylporphin ligand and those of its metal complexes in various organic solvents were carried out using chloroform, dichloromethane, carbon tetrachloride, benzene, acetone, acetic acid, ether and pyridine. The results obtained are shown in Table 1.

Solutions of 10⁻⁶mol dm⁻³ of the tetraphenylporphin ligand and its metal complexes in chloroform were prepared and scanned over frequency range of 300-700nm using λ -3 Perkin Elmer U.V/Visible spectrophotometer. Correlations were made between various absorption band positions obtained. The results obtained are given in Table 2 and 3.

Results And Discussions

% Yield

The yield obtained for ligand was greater than 50%, while those of most of the complexes were greater than 60%.

Solubility Test

Table 1 shows the results of the solubility tests of the ligand and the metal complexes in various organic solvents. It was found that the *meso*-tetraphenylporphin ligand and its metal derivatives are soluble in many organic solvents such as chloroform, dichloromethane, benzene and pyridine but less soluble in others such as carbon tetrachloride, acetone, acetic acid and ether. Changes in the solubility between the ligand and its metal complexes in various solvents is an indication that complexation had taken place.

Table 1: Solubility Tests of Meso-Tetraphenylporphin and Some of its Metal Complexes.

Ligand/complex	Chloroform	Dichloro- methane	Carbon tetra- chloride	Benzene	Acetone	Acetic acid	Ether	Pyri
TPP	VS	S	S	S	S	S	S	S
Mn(II)TPP	S	S	SS	S	S	S	SS	S
Cu(II)TPP	S	S	SS	S	I	SS	I	S
Ni(II)TPP	S	S	S	S	I	SS	SS	S
Co(II)TPP	S	S	SS	S	SS	VSS	S	V S
Zn(II)TPP	VS	S	SS	S	S	D	S	VS
Mg(II)TPP	VS	S	SS	SS	VSS	D	VSS	V S
Hg(II)TPP	VS	S	SS	SS	VSS	D	VSS	V S

VS = Very Soluble, S= Soluble, SS = Slightly Soluble,
VSS = Very Slightly Soluble, I = Insoluble, D = Decomposes.

Spectral Analysis

Tables 2 and 3 show the absorption band position of the *meso*-tetraphenylporphin and the metal complexes respectively. Four bands in the visible region and a soret band at 400nm is characteristic of the ligand while two bands in the visible region and the soret band is characteristic of the metal complexes. The soret band is characteristic of all conjugated detrapyrroles. Within the limit of the capacity of the instrument used the soret band, which is always about twenty times the intensity of the most intense of the other bands, runs out of the scale.

Table 2; Absorption Band Positions of TTP Ligand

Bands	I	II	III	IV
Position (λnm)	650 (2.5x10 ⁵)	590 (2.6x10 ⁵)	550 (3.6x10 ⁵)	520 (7.7x10 ⁵)

Table 3: Absorption Band Position of Metal Complexes of *Meso*-Tetraphenylporphin (TPP)

Complexes	Band position, λ(nm)	
	I	II
Mn(II)TPP	590 (2.7x10 ⁵)	520 (8.5x x10 ⁵)
Cu(II)TPP	595 (1.1x10 ⁵)	525 (9.55 x10 ⁵)
Ni(II)TPP	650 (2.2x10 ⁵)	520 (2.95 x10 ⁵)
Co(II)TPP	—	530 (2.95 x10 ⁵)
Zn(II)TPP	590 (1.2x10 ⁵)	550 (5.3 x10 ⁵)
Mg(II)TPP	660 (2.4x10 ⁵)	560 (3.6 x10 ⁵)
Hg(II)TPP	658 (1.7x10 ⁵)	562 (2.66 x10 ⁵)

The Molar Absorptivity (ε) is given in parenthesis

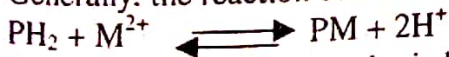
Note:

Bands I and II of the complexes corresponds to I and III of the ligand (Electronic transition).

Spectra arise because electron can be promoted form one energy level to another. Such electronic transitions are of higher energy, and in addition lower energy vibration and rotational transition always occur.

The d-orbitals are not all identical in energy, and in the transition elements that have partly filled d shell it is possible to promote electrons from one d level to another d level. This corresponds to a fairly small energy difference, and so light is absorbed in the visible region.

Generally, the reaction between free porphyrin base and divalent metal is:



Where PH₂ is the free porphyrin base and M²⁺ the divalent metal.

The two hydrogen atoms attached to the nitrogen atoms of the free porphyrin base is being replaced when the metal ion is complexed with the nitrogen atoms. Since the effect of the metal on the main porphyrin system is transmitted through the four nitrogen atoms to which the metal is attached, it is reasonable that correlations should exist between the kind of spectra given by a particular metalloporphyrin and the nature of the metal-to-nitrogen bonding. Although most of the divalent metalloporphyrins in this work have rather similar spectra, there were quite definite differences, which may probably be attributed to whether or not a d metal orbital is available for covalent bonding. Those metals, which have such an orbital, have spectra, which are shifted to the blue region and characterized by a low intensity first band. This can be seen with the transition metals, Mn, Co, Ni and Cu. The divalent metals in which covalent bonding is limited to s and p orbitals of the metal have spectra

which are shifted to the red compared to the d group, and which are characterized by a much more intense first vibrational band, as in Mg and Hg.

The vibrational fine structure in the electronic spectrum appeared according to the Herzberg-Teller mechanism and bands I and III, in the porphyrin ligand, were assigned to electronic transitions and II and IV to vibrations (Serchenko, 1969). The two bands of the metal complexes appear in the region of I and III of the porphyrin ligand indicating the disappearance of the vibrational bands (Table 2). Furthermore, the remaining bands shift slightly from that of the ligand depending on the metal.

Conclusion

The U.V/Visible absorption properties of the *meso*-tetraphenylporphyrin complexes depend on the central metal atom. The differences are quite definite and depend on the nature of the metal-to-nitrogen bond.

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