

### Solid State Spectral Properties of Related Six-coordinate Magnesium Tetraphenylporphyrin Complexes

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The electronic spectra of *in vivo* chlorophyll molecules are generally shifted to the red region compared to those observed for corresponding species in organic solvents [1]. Two main mechanisms have been proposed for this red shift – (1) chlorophyll–ligand–chlorophyll aggregation and (2) chlorophyll–protein interactions. However, the relevance of these mechanisms to the *in vivo* red shifts is still not well understood and further studies of *in vitro* systems and model magnesium complexes are required in order to resolve this issue [2].

One approach is to consider the effect of axial ligation to four-coordinated, planar magnesium entities. *In vitro* studies indicate that chlorophyll molecules tend to aggregate into dimers and oligomers [3]. In oligomeric chlorophyll species axial bonding produces both five- and six-coordinated Mg centres. From equilibrium studies [4] it can be ascertained that the visible absorption maxima of six-coordinated chlorophyll molecules are red shifted with respect to those of five-coordinated entities. Consequently, Katz has suggested that six-coordinated chlorophyll–bifunctional ligand adducts are suitable model compounds for chlorophyll molecules in reaction centres of photosynthetic systems and that the red-shift of these adducts is related to the distance between the nucleophilic centres of the axial ligands [2].

Although many physical studies of six-coordinated chlorophyll molecules have been carried out the structural basis of the red-shift is unknown as no crystal structure of such entities has been reported. However a related six-coordinated structure, Mg(octaethylporphyrin)(pyridine)<sub>2</sub>, has been determined [5] and the relevance of magnesium porphyrin structures to chlorophyll has again been highlighted in another recent paper [6]. We have recently reported the crystal structures of three related six-coordinated MgTPP complexes, MgTPP(1-MeIm)<sub>2</sub>, MgTPP(4-pic)<sub>2</sub> and MgTPP(pip)<sub>2</sub> (TPP = tetraphenylporphyrin, 1-MeIm = 1-methylimidazole, 4-pic = 4-picoline, pip = piperidine) [7], which, as shown earlier [5], have the axial ligands weakly bound to Mg at comparatively large distances. We report here results from electronic spectral studies of Nujol

and KBr-disc, solid-state samples of these complexes which indicate that the magnitudes of the red-shifts for these six-coordinated entities correlate with the Mg–N (axial ligand) bond distance structural feature.

### Experimental

(TPP)H<sub>2</sub> was prepared from pyrrole and benzaldehyde and purified according to the method of Barnett and coworkers [8]. Mg(II) was inserted into (TPP)H<sub>2</sub> using MgCl<sub>2</sub>·6H<sub>2</sub>O [9] and the crystalline MgTPP product was then heated in pure nitrogenous ligand. Crystalline MgTPP(1-MeIm)<sub>2</sub> was obtained from a solution of acetone and 1-methylimidazole, while MgTPP(4-pic)<sub>2</sub> and MgTPP(pip)<sub>2</sub> were crystallised from chloroform-nitrogenous ligand solutions. Electronic spectra were recorded on a Cary spectrophotometer by grinding the crystals with KBr to form a disc and using another KBr disc as a reference. In addition electronic spectra of the complexes were obtained as Nujol mulls using a Varian Superscan 3 UV-visible spectrophotometer.

### Results and Discussion

The electronic spectra of the crystalline MgTPP complexes as KBr disc and Nujol mulls show variable band intensities (Figs. 1 and 2). This is partly due to the effect of fluorescent emission which produces negative regions in some spectra especially at about 615 nm. However in addition details of the spectral

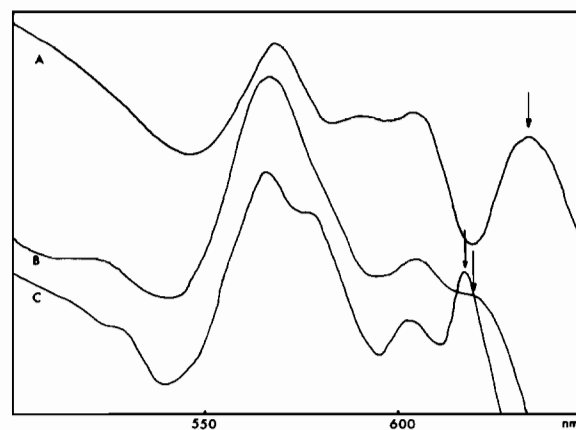


Fig. 1. KBr disc electronic spectra of A: MgTPP(1-MeIm)<sub>2</sub>, B: MgTPP(4-pic)<sub>2</sub> and C: MgTPP(pip)<sub>2</sub>. The arrows indicate the positions of the Q<sub>0</sub> bands.

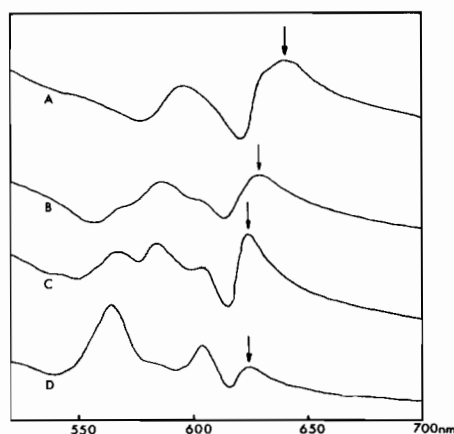


Fig. 2. Nujol mull electronic spectra of A: MgTPP(1-MeIm)<sub>2</sub>, B: MgTPP(4-pic)<sub>2</sub>, C: MgTPP(pip)<sub>2</sub> and D: MgTPP(pip)<sub>2</sub> with a larger amount of nujol. The arrows indicate the positions of the Q<sub>0</sub> bands.

absorptions indicate that a variable degree of decomposition to corresponding five-coordinated species occurs in all cases. Generally, three or four distinct bands are observed in the visible region. From information available from equilibrium studies [10], the positions of these bands correspond to those of five- and six-coordinated MgTPP complexes. This suggests that grinding of the crystals decomposes them partially, through the loss of axial ligand. Such an effect is consistent with the presence of very weak axial binding in the six-coordinate crystalline complexes [7]. Forming a mull with Nujol apparently also facilitates this decomposition as the spectral intensities of the five-coordinate species increase with an increase of Nujol concentration (see Fig. 2).

The Q<sub>0</sub> and Q<sub>1</sub> visible bands for the five-coordinated complexes may be clearly identified for the KBr disc samples (Table I). Values for these bands are closely similar to those observed in the solution state (Table I). Also the values for all three

complexes are essentially identical, indicating that the electronic properties of five-coordinated MgTPP (ligand) complexes are not affected by the nature of the axial nitrogenous ligand.

By contrast, the positions of the bands for the six-coordinated MgTPP(ligand)<sub>2</sub> species vary significantly from one complex to another and with the state of aggregation and preparation of solid sample. Fluorescent emission also occurs around 615 nm, particularly for solid-state samples, making assignments of Q<sub>0</sub> values somewhat uncertain in those cases. Values that have been assigned to the Q<sub>0</sub> and Q<sub>1</sub> bands are given in Table I. Although the peak positions for the Q<sub>0</sub> bands of each six-coordinate species in Nujol mull, KBr disc and in solution are different, the order for their red-shifts remains the same; MgTPP(1-MeIm)<sub>2</sub> > MgTPP(4-pic)<sub>2</sub> > MgTPP(pip)<sub>2</sub>. This order correlates with the Mg–N (axial ligand) bond lengths of these complexes in an inverse sense (Table I). The KBr disc values for the Q<sub>1</sub> band show the same trend. (The value listed for MgTPP(1-MeIm)<sub>2</sub> is the 1-MeIm solution value – see discussion of solvent effects below). The shorter the Mg–N distance the greater is the magnitude of the red-shift.

The Q<sub>0</sub> and Q<sub>1</sub> visible spectral bands of metalloporphyrins are associated with π–π\* transitions of the porphyrin ring. The result reported here suggests that the closest proximity of the 1-MeIm ligand perturbs the porphyrin π-electron system to the greatest extent and that this interaction leads to the largest red-shift. However all of the axial bond distances are long and the influence of the axial ligands on the porphyrin electronic transitions may need to be mediated through the axial bonds. This could occur through the involvement of the diffuse d orbitals of Mg in the metal–ligand bonding. It is noted that Zn, having filled, lower energy d orbitals, does not form six-coordinated porphyrin complexes [11].

TABLE I. Bond Distances and Electronic Data for MgTPPP(ligand)<sub>2</sub> Complexes.

Compound	Electronic Bands (nm)						Mg–N (axial) bond lengths (Å)
	KBr disc		Nujol Mull		CH <sub>2</sub> Cl <sub>2</sub> Solution <sup>b</sup>		
	Q <sub>0</sub>	Q <sub>1</sub>	Q <sub>0</sub>	Q <sub>1</sub>	Q <sub>0</sub>	Q <sub>1</sub>	
MgTPP(1-MeIm) <sub>2</sub>	634	591	640	<sup>a</sup>	627	583	2.297
MgTPP(1-MeIm)	604	566	<sup>a</sup>	<sup>a</sup>	603	563	
MgTPP(4-pic) <sub>2</sub>	621	585	629	<sup>a</sup>	623	577	2.386
MgTPP(4-pic)	604	565	<sup>a</sup>	<sup>a</sup>	603	563	
MgTPP(pip) <sub>2</sub>	619	576	624	<sup>a</sup>	620	576	2.419
MgTPP(pip)	604	565	<sup>a</sup>	<sup>a</sup>	603	563	

<sup>a</sup>Band not clearly resolved.

<sup>b</sup>Data from ref. 10, except for MgTPP (1-MeIm)<sub>2</sub> which are the values for MgTPP dissolved in pure ligand (see text).

A comparison of the  $Q_0$  band values for the Nujol mull, KBr disc and solution samples indicates the axial bond lengths in the latter two states are approximately the same but weakened. The values for Nujol mull samples, being higher, together with the lower intensity of five-coordinate bands, suggest the Mg–N (axial) bonds are least affected by this mode of preparation. KBr disc samples may be affected by pressure effects while for solutions, solvent interaction could weaken axial binding. It is of interest that for MgTPP(1-MeIm)<sub>2</sub> the  $Q_1$  value of 566 nm, reported for the CH<sub>2</sub>Cl<sub>2</sub> solution state [10], is significantly lower than that for the solid state and also significantly lower than the corresponding value of 583 nm observed for MgTPP dissolved in 1-MeIm (Table I) (the  $Q_0$  value is 629 compared with 627 nm). The 583 value fits the general trends shown in Table I better than 566 nm, indicating that the 1-MeIm solution species more closely resembles the one observed for the solid state and that solvent interactions are probably quite large for the CH<sub>2</sub>Cl<sub>2</sub> solution state (we find comparable values of 628 and 566 nm for CHCl<sub>3</sub> solution).

Thus solid state spectral studies have provided information on the effect of axial binding on electronic transitions in the visible region. Overall, the spectral and X-ray studies of MgTPP complexes indicate that the extent of Mg–axial ligand bonding determines the magnitudes of the red-shifts – the stronger the bonding the larger the red-shift. This agrees well with the suggestion made by Katz and coworkers regarding the red-shifts for six-coordinated chlorophyll–bifunctional ligand adducts [2]. It is possible that in natural systems the protein environment of chlorophyll facilitates

axial binding of the type established in particular for MgTPP(1-MeIm)<sub>2</sub>, and that observed red shifts are related, at least in part, to this kind of interaction.

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