

Coordination aggregation of mesoaryl substituted porphyrins

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Abstract. Synthesis of the free-base *tetrakis* (3'-nitro/aminophenyl), (H_2 TNP/ H_2 TAP) has been accomplished and its coordination behaviour towards Mg(II), Co(II), Zn(II) and Ag(II) ions is investigated. Optical and magnetic resonance properties of the metal derivatives MTNP and MTAP reveal that the aminoporphyrins exist as aggregates in solution. The aggregation is promoted by the coordination of the peripheral amino groups to neighbouring metalloporphyrins. Possible structures of aggregated species are proposed from the model studies.

Keywords. Metalloporphyrins; axial coordination; coordinated aggregates.

1. Introduction

The extensive occurrence of aggregated porphyrinoid molecules in biological systems has spurred a great deal of research activity. The design and syntheses of biomimetic models involving more than one porphyrin unit has attracted wide attention. The strategy adopted to obtain these systems lies in the proper choice of substituents and metal ions that promote dimerisation/oligomerization of porphyrins in solution. The presence of potentially ligating substituents such as sulphanato, carboxylato and dimethyl amino groups at the aryl positions of 5, 12, 15, 20-tetraphenylporphyrins (TPP) enhances the association property of the porphyrins (Pasternack *et al* 1973; Ojadi *et al* 1985; Koehorst *et al* 1988). The metalloporphyrins involving divalent metal ions that exhibit the least tendency to associate with solvent molecules predominantly exist as oligomers in solution. On the other hand, the metal (II) ions that easily form 5 or 6 coordinated species with solvent molecules are essentially monomeric in nature. Abraham *et al* (1977, 1978) have shown that the extent of aggregation of metal derivatives of deuteroporphyrin IX dimethylester is related to the strength of the porphyrin-metal interaction in the case of zinc, cadmium and palladium porphyrins.

An interesting approach to achieve oligomerization of tetraphenylporphyrin in solution is to have ligating substituents (of the aryl group) at specific orientation with strongly coordinating metal ions in the porphyrin cavity. Model building studies have suggested that substitution of the donor groups at the meta positions of the phenyl groups of TPP favours formation of aggregates. Here, we report the studies on coordination behaviour of 5, 10, 15, 20-tetra (3-aminophenyl) porphyrin (H_2 TAP) and the corresponding nitro derivative, (H_2 TNP), which is the precursor of H_2 TAP (figure 1). A comparison of the coordinating abilities of H_2 TAP and H_2 TNP towards the metal(II) ions (Co, Ni, Cu and Zn) clearly brings forth the importance of axial ligation in the aggregate formation.

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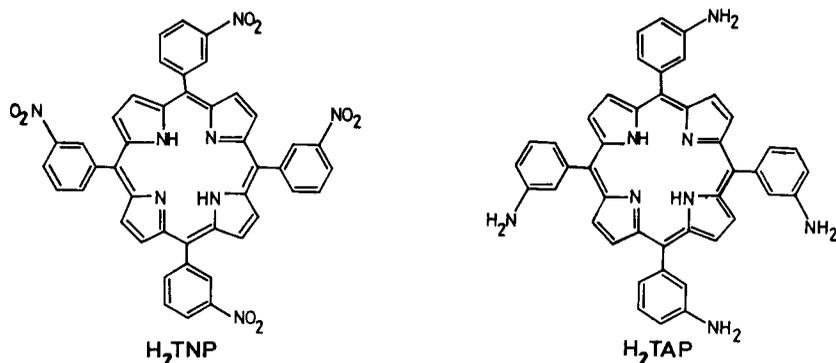


Figure 1. Structures of the free-base porphyrins *tetrakis* (3'-nitrophenyl) porphyrin, H_2TNP and *tetrakis* (3'-aminophenyl) porphyrin, H_2TAP .

2. Experimental

All the solvents and chemicals used in this section have been purified. The syntheses of *tetrakis* (3'-nitrophenyl)porphyrin (H_2TNP) and *tetrakis*(3'-aminophenyl) porphyrin (H_2TAP) have been accomplished according to the procedure described in the literature (Bettelheim *et al* 1986).

2.1 Preparation of metallated (Cu, Co, Ag and Zn) derivatives of *tetrakis* (3'-nitrophenyl)porphyrin (MTNP) and *tetrakis* (3'-aminophenyl)porphyrin (MTAP)

The metallation of the free-base porphyrins was carried out using the appropriate metal carrier in a mixture of solvents or in a pure solvent. The various metal carriers used and the solvents employed are given below:

| Metal carrier | Solvent employed |
|-----------------------------|-------------------|
| $MgClO_4 \cdot 6H_2O$ | C_5H_5N |
| $CoBr_2 \cdot 6H_2O$ | DMF |
| $NiCl_2 \cdot 6H_2O$ | DMF |
| $Cu(CH_3COO)_2 \cdot 4H_2O$ | $CHCl_3 : CH_3OH$ |
| $Zn(CH_3COO)_2 \cdot 4H_2O$ | $CHCl_3 : CH_3OH$ |
| $Ag(CH_3COO)_2$ | CH_3COOH |

A typical procedure for the metallation of the free-base porphyrin is given below.

To a solution of $CHCl_3 \cdot CH_3OH$ (1:1, v/v) containing 20 mg of H_2TNP was added 50 mg of $Cu(CH_3COO)_2 \cdot 4H_2O$. The solvent was removed under reduced pressure and the residue was taken in a minimum amount of dichloromethane and chromatographed on a basic alumina column using dichloromethane as the eluent. The eluate was evaporated to yield CuTAP as dark violet crystals. Yield: 90% (based on H_2TNP).

2.2 Methods

Protonation studies: The optical absorption spectral method was employed to follow the protonation equilibria of H_2TNP and H_2TAP (Corwin *et al* 1968; Meotner and

Adler 1975). A known concentration of trifluoroacetic acid in CHCl_3 ; CH_3OH (1:1, v/v) of 1 mM mixture was added to 1 ml of the porphyrin stock solution (10^{-4} M) and the mixture made up to 10 ml in a standard flask. The concentration of the acid was measured on a pH-meter. The solutions were equilibrated at 298 K before the measurements.

Acid demetallation studies on a few metal derivatives of H_2TAP were carried out using fluorescence spectroscopy. Determination of the acid stability of ZnTAP and MgTAP was made by following the decrease in intensity of the fluorescence bands. In a typical procedure the concentration of the metalloporphyrin was held at $10 \mu\text{M}$ and the pH of the solutions was varied from 3.0 to 1.0.

3. Results and discussion

The free-base nitro- and aminoporphyrins, H_2TNP and H_2TAP , and their metal derivatives are crystalline in nature. The nitro derivatives are found to be easily soluble in non-polar solvents, whilst the corresponding amino derivatives are relatively less soluble in non-polar solvents. Hence, methanol or DMSO was used as solvent throughout in this study.

The optical absorption spectra of *tetrakis* (3'-nitrophenyl) porphyrin and *tetrakis* (3'-aminophenyl) porphyrin were recorded in methanol at 298 K and the data are shown in table 1. The coordinative interactions of metal derivatives of H_2TNP with dimethylaminopyridine (DMAP) were studied. The choice of this base is dictated by its ease of coordination behaviour towards central metal ions in the porphyrins and its solubility.

A perusal of the table brings forth the following points: (1) free-base porphyrins, H_2TNP and H_2TAP exhibit normal etio type of spectra (Gouterman 1969). (2) The

Table 1. Optical absorption data of *tetrakis* (3'-nitrophenyl) porphyrin (H_2TNP) and *tetrakis* (3'-aminophenyl) porphyrin (H_2TAP) and their metal(II) derivatives in methanol at 298 K.

| Porphyrin | Optical absorption bands λ in nm (log ϵ) |
|--------------------------------|---|
| H_2TNP | 420(5.65); 515(4.20), 550(3.90), 590(3.70), 650(3.50) |
| MgTNP | 423(5.30); 563(4.30), 605(4.10) |
| CoTNP | 419(5.30); 530(4.43) |
| $\text{CoTNP} + \text{DMAP}^a$ | 418, 438; 560, 600 |
| NiTNP | 420 (5.21); 531(4.30) |
| CuTNP | 414(5.48); 538(4.38), 620(4.04) |
| ZnTNP | 430(5.60); 560(4.38), 600(4.05) |
| $\text{ZnTNP} + \text{DMAP}^a$ | 435; 566, 606 |
| AgTAP | 423(5.39); 539(4.30) |
| H_2TAP | 420(5.63); 515(4.14), 550(3.80) 590(3.70); 650(3.50) |
| MgTAP | 423(5.35); 563(4.40), 603(4.00) |
| CoTAP | 429(5.28); 558(4.41), 600(4.05) |
| NiTAP | 420(5.24); 530(4.30), 620(4.10) |
| CuTAP | 418(5.45); 540(4.35), 640(4.03) |
| ZnTAP | 423(5.67); 550(4.35), 640(4.03) |
| AgTAP | 428(5.29); 542(4.20) |

^aSpectral data on addition of N, N'-dimethylaminopyridine (10 mM).

Soret band of metal derivatives of H₂TAP are generally red-shifted relative to the corresponding derivatives of H₂TNP, the exception being Mg(II) and Ni(II) derivatives. The Soret band of ZnTAP occurs at 423 nm while in the corresponding derivative of nitroporphyrin, ZnTNP, the band appears at 430 nm without any loss in intensity. (3) The visible absorption bands of the metal derivatives of H₂TAP show interesting changes relative to the bands observed for the corresponding derivatives of H₂TNP. Thus ZnTAP, CoTAP and NiTAP reveal bands in the red region at 640 nm, 600 nm and 620 nm respectively, relative to the band observed for ZnTNP, CoTNP and NiTNP at 600 nm, 530 nm, and 531 nm respectively. (4) Addition of the base dimethylaminopyridine (DMAP) to the metal nitroporphyrin derivatives, ZnTNP and CoTNP, shifts the absorption band to the red region. The spectrum obtained on addition of a base is very similar to that observed for the metal derivatives of aminoporphyrins, ZnTAP and CoTAP.

These observations suggest that the presence of a nitro or amino group in the 3-position of the meso aryl groups of the porphyrins does not cause any change in the absorption spectra of the free-base porphyrins. This is anticipated in view of the fact that mesoaryl groups are oriented perpendicular to the porphyrin plane and thereby make conjugative effects negligible (Hoard 1975). The shifts of the visible bands observed for MTAP relative to that observed for MTNP indicate that MTAPs possibly exist as coordinated aggregates in solution. This is also evidenced from the fact that addition of a base to MTNPs shifts the absorption bands to the red region. The appearance of a band at 606 nm is characteristic of the species [ZnTPP(L)] (Nappa and Valentine 1978; Kolling 1981; Bhyrappa and Krishnan 1993), where L is a neutral ligand. The red-shifted Soret band (438 nm) and visible absorption band (at 600 nm) on addition of a base to CoTNP indicate the possible formation of Co(III) porphyrin (Ellis *et al* 1980). Interestingly, NiTAP exhibits a visible band at 620 nm. It is believed that this band could arise from either penta- or hexacoordinated porphyrins. The existence of coordinated metal derivatives of aminoporphyrins is clearly seen from the optical data.

The singlet emission spectra of a few representative metal derivatives of H₂TNP and H₂TAP in degassed methanol are shown in figure 2. The quantum yields were calculated and the results are given in table 2. It is noted that the relative quantum yields of H₂TNP and MTNP were lower than those observed for H₂TAP and MTAP. This is ascribed to the presence of nitro groups which can deactivate the excited singlet state of the porphyrin through fast intersystem crossing (isc). It is interesting to note that both the Q_{0,0}, Q_{10,0} bands of MgTAP are red-shifted relative to that observed for MgTNP and ZnTNP. Moreover, ZnTAP exhibits a single emission peak at 627 nm. A comparison of fluorescence spectrum of ZnTAP with that obtained for ZnTNP in presence of a base reveals the general red-shift of the emission peaks. This feature is similar to that observed in the optical absorption spectral data. It is known that aggregation of pigments generally shift both the optical absorption and emission band to red region (White and Plane 1974; Katz *et al* 1979) These observations seem to support the view of the existence of aggregated species of MTAPs in solution.

The ¹H NMR spectra of the nitro and amino derivatives of the free-base porphyrins and their metal complexes were recorded in DMSO-*d*₆. It is worthy of note that the nitroporphyrins exhibit well-defined ¹H NMR signals, while the spectra of the corresponding aminoporphyrins reveal relatively broad signals. The integrated intensities of the signals provide complete characterization of the porphyrins. The nature of 3-substitution

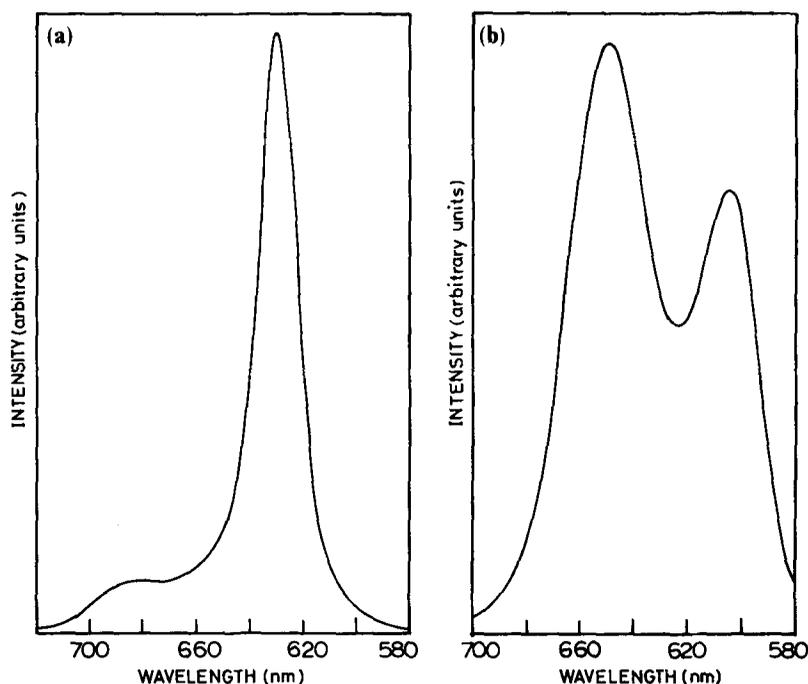


Figure 2. Fluorescence spectra of (a) ZnTAP and (b) ZnTNP in methanol. The excitation wavelength is at the Soret transition.

Table 2. The fluorescence data of *tetrakis* (3'-nitrophenyl) porphyrin (H_2 TNP) and *tetrakis* (3'-aminophenyl) porphyrin and their magnesium(II) and zinc(II) derivatives in methanol at 298 K.

| Porphyrin | Emission wavelength ^a (nm) | Quantum yield ^b |
|-----------------|--|----------------------------|
| H_2 TNP | 650, 715 | 0.20 |
| MgTNP | 604, 650 | 0.20 |
| ZnTNP | 606, 650 | 0.20 |
| ZnTNP + DMAP | 614, 665 | |
| H_2 TAP | 652, 712 | 0.80 |
| MgTAP | 620, 665 | 0.90 |
| ZnTAP | 625 | |

^aThe excitation wavelength is the Soret band with solutions having absorbance value of 0.10.

^bThe quantum yields were calculated on the basis of the unit quantum yield of the corresponding meso tetraphenylporphyrin analogues, H_2 TPP and MTPP.

in the mesoaryl group of the porphyrin is clearly seen from the complexity of the spectra in the region 8.60–8.80 δ and the appearance of a singlet around 9.10 δ . This signal has been assigned to ortho protons of the mesoaryl group. The deshielding of this

resonance seems to arise from the proximity of the *o* protons to the porphyrin ring current and also the nitro group (Abraham and Smith 1983; Martell *et al* 1986). The $^1\text{H NMR}$ spectra of Co(II) derivatives of H_2TNP and H_2TAP are diagnostic in arriving at the structure of these compounds. The spectrum of CoTNP reveals dipole induced shifts and this is clearly manifested in the upfield shift of the *o* protons (aryl) around 13.50δ . The line width of the pyrrole proton resonances is found to be 200 Hz. Addition of a base results in the deshielding of the proton resonances and decrease in line width. This is ascribed to the possible formation of hexacoordinated Co(II) and/or the presence of Co(III). A comparison of the $^1\text{H NMR}$ spectra of CoTAP with that obtained on addition of base to CoTNP reveals broad similarities. Though the spectra of these two cannot be overlapped, the general trend of decreasing line width and shielding effect of proton resonance signals are also seen. This suggests that the cobalt derivatives of aminoporphyrins exist possibly as coordinated aggregates, and cobalt ions are possibly in the oxidised state (Huet *et al* 1982).

The EPR spectra of the copper(II) and silver(II) derivatives of H_2TNP and H_2TAP have been recorded in DMSO at 133 K (figure 3). The EPR parameters have been calculated using the spin Hamiltonian described in literature (Manoharan and Rogers 1969) and are given in table 3. In order to compare the effects induced by axial coordination on the *g* and *A* values, an EPR spectrum was recorded on a solution containing CuTNP and a base (piperidine). The values of *g* tensors calculated for CuTNP and CuTAP are not significantly different indicating thereby that the nitro/amino substituents in the mesoaryl groups of the porphyrins do not alter the electronic features. Addition of a base to CuTNP results in the decrease of A_{11}^{Cu} values

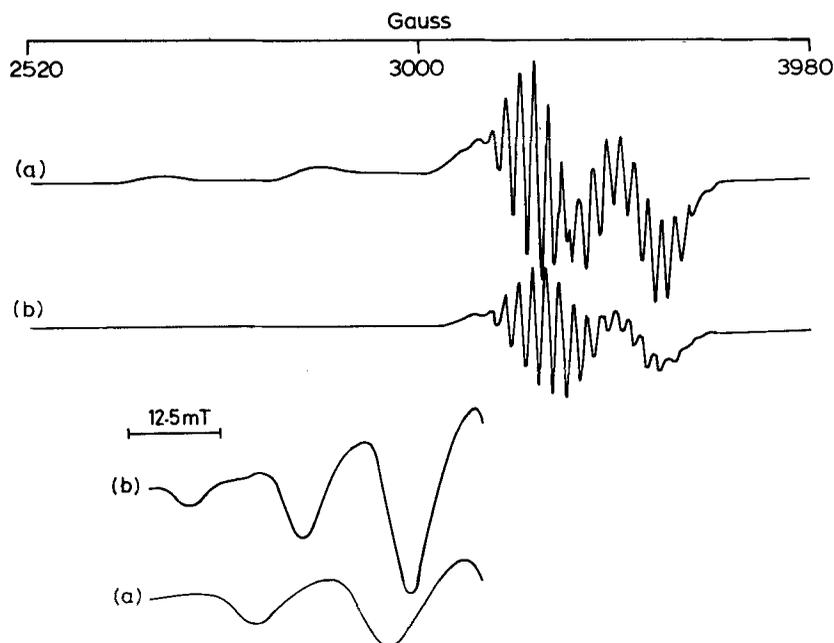


Figure 3. The EPR spectra of (a) CuTNP and (b) CuTAP in DMSO at 120 K. The expansions of the perpendicular components are shown in the lower portion of the figure.

Table 3. EPR parameters of the metal derivatives of H₂TNP and H₂TAP in DMSO at 120 K.

| Porphyrin | g_{\parallel} | g_{\perp} | $A_{\parallel}^M \times 10^4$ (cm ⁻¹) | $A_{\perp}^M \times 10^4$ (cm ⁻¹) | $A_{\parallel}^N \times 10^4$ (cm ⁻¹) | $A_{\perp}^N \times 10^4$ (cm ⁻¹) |
|-----------------|-----------------|-------------|--|--|--|--|
| CuTNP | 2.17 | 2.03 | 194 | 32.5 | 15.2 | 21.3 |
| CuTNP + base | 2.17 | 2.03 | 185 | 32.5 | 15.2 | 21.3 |
| CuTAP | 2.17 | 2.02 | 185 | 32.4 | 15.1 | 20.1 |
| AgTNP | 2.11 | 2.01 | 47.2 | 24.7 | | |
| AgTAP | 2.12 | 2.02 | 47.6 | 24.7 | | |
| AgTNP + base | 2.11 | 2.01 | | | | |
| CoTNP | | | | | | |
| CoTAP | | | | | | |

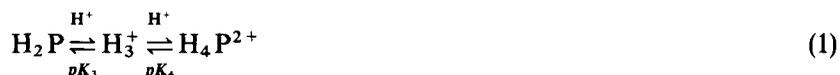
(Chandrasekhar and Krishnan 1981) whilst the other g and A tensors remain more or less unaffected. Axial coordination to Cu(II) in the porphyrins is known to alter the Cu–N σ bonding thereby decreasing the $A_{\parallel}^{\text{Cu}}$ values. A similar trend is observed in the $A_{\parallel}^{\text{Cu}}$ values of CuTAP. This seems to suggest that CuTAP may possibly exist as coordinated complexes in solution.

The EPR parameters of AgTNP and AgTAP do not show any appreciable changes. Moreover, addition of a base to AgTNP does not show any appreciable change in g and A tensors in contrast to that observed for Cu(II) porphyrins. This may be due to the fact that Ag(II) exhibits relatively less tendency to form axial coordination. It is worthy of mention here that the EPR spectrum of CoTNP in DMSO exhibits the formation of dioxygen adduct (Walker 1974). It is interesting to note that the EPR spectrum of CoTAP does not reveal any signals whilst in DMSO. It is believed that cobalt in CoTAP most probably exists in the Co(III) state and exhibits a spectrum indicating the formation of dioxygen adduct. It has not been possible to obtain valid proof for the existence of Co(III) from analytical methods.

Table 4. The protonation constants (pK_a values) of the free base porphyrins in a mixture of CHCl₃:CH₃OH (1:1, v/v) at 298 K and the acid stability constants of the Mg(II) and Zn(II) derivatives.

| Porphyrin | $pK_3 + pK_4$ | Acid stability constant (K) |
|--------------------|---------------|--------------------------------|
| H ₂ TNP | 1.61 | — |
| H ₂ TAP | 2.54 | — |
| H ₂ TPP | 2.49 | — |
| ZnTAP | — | 1.40×10^2 |
| MgTAP | — | 3.4×10^{-2} |
| ZnTPP | — | $3.0\text{--}3.4 \times 10$ |
| MgTPP | — | 3.00×10^{-4} |

The protonation process of the free-base porphyrin can be depicted as follows:



In the present study, it has not been possible to obtain distinct breaks in the Henderson plot characteristic of pK_3 and pK_4 . Hence, the values obtained are a combination of pK_3 and pK_4 ($pK_3 + pK_4$). It is worth noting that protonation leads to an optical absorption spectrum of a completely protonated species H_4P^{2+} . A comparison of the pK values obtained for H_2TPP (2.54) with those observed for H_2TPP (2.49) in the same solvent reveals that H_2TNP is difficult to protonate compared to H_2TAP and H_2TPP . This suggests that the presence of an electron-withdrawing nitro group diminishes the electron density on imino nitrogens. This could arise possibly from field effects or some other electronic effect rather than any conjugative effects. The pK values of H_2TPP indicate the relative ease of protonation of H_2TAP . This suggests that the amino group functions as the electron-donating group.

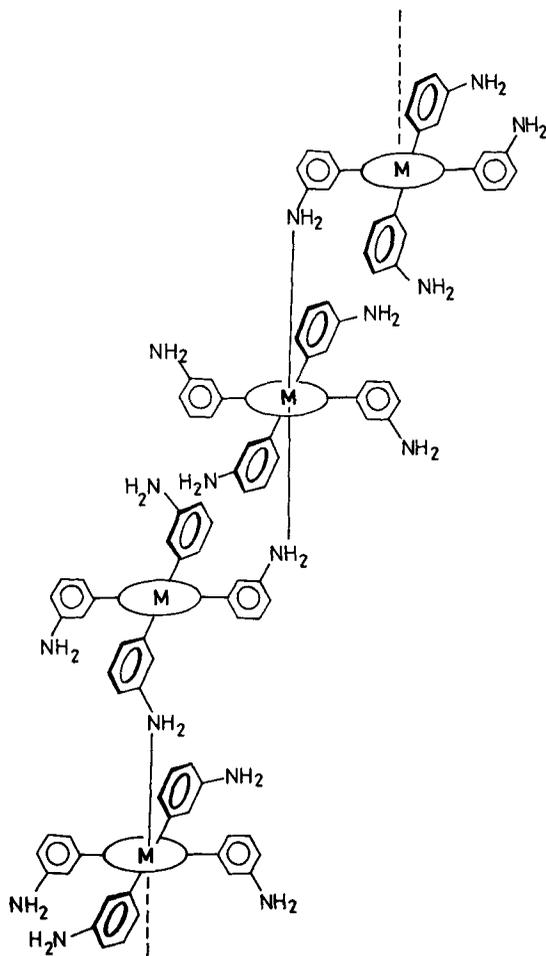


Figure 4. Proposed structure of coordinated aminoporphyrin metal derivatives.

The acid stabilities of MgTAP and ZnTAP have been measured using fluorescence spectral method. Henderson's plot has been employed to obtain acid stability constants (table 4). A comparison of these values with those observed for MgTPP and ZnTPP reveals that the aminoporphyrin derivatives of metal ions are very stable towards metallation. This suggests the existence of aggregated species in which metal ions are axially coordinated. The optical absorption, emission and magnetic resonance spectral properties of MTNP and MTAP support the view that the MTAPs exist in the aggregated form. The resistance CPK models have been constructed to arrive at plausible structures (figure 4). It is possible to have different orientations of amino groups in the four mesoaryl groups of the porphyrin. Any two adjacent mesoaryl amino groups can function as a bidentate ligand and/or one of the amino groups function as a monodentate axial ligand to the other metalloporphyrin and this can happen only if the metalloporphyrins are arranged in an off-set manner. This arrangement of porphyrins is energetically more favourable than the stacking of the macrocycles one above the other (Leighton *et al* 1988). It is easy to realise that the disposition of the amino group either in the ortho and para position of the mesoaryl entities does not result in the proper orientation for binding to the metal ion in the adjacent porphyrin molecules. The *o*-aminoporphyrin leads to steric hindrance while, in the *p*-aminoporphyrin, the amino group is situated too far away for metal coordination. The resulting structures bear a close resemblance to that proposed for chlorophyll aggregates where the keto carbonyl group functions as the donor for the magnesium of the neighbouring chlorophyll molecule.

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