

Metal ions in molecular association of porphyrins

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Abstract. Molecular association of porphyrins and their metal derivatives has been recognized as one of the important properties for many of their biological functions. The association is classified into (i) self-aggregation, (ii) intermolecular association and (iii) intramolecular association. The presence of metal ions in the porphyrin cavity is shown to alter the magnitudes of binding constants and thermodynamic parameters of complexation. The interaction between the porphyrin unit and the acceptor is described in terms of π - π interaction. The manifestation of charge transfer states both in the ground and excited states of these complexes is shown to influence the rates of excited state electron transfer reactions. Owing to paucity of crystal structure data, the time-averaged geometries of many of these complexes have been derived from magnetic resonance data.

Keywords. Metalloporphyrins; molecular association; charge transfer states; intramolecular interactions; intermolecular interactions; porphyrins.

1. Introduction

The widespread occurrence of porphyrins and their metal derivatives in many proteins and enzymes has stimulated considerable interest in the chemistry of these molecules. Metalloporphyrins lead to specific reactivity of hemoglobin, hemecytochromes and many oxidising enzymes. The available structural studies on a few heme proteins indicate strong evidence for the ubiquitous nature of molecular interactions between porphyrin π system and certain aromatic residues (Antonini and Brunni 1971; Abbot and Piafson 1974). This association of porphyrins with other aromatic molecules is of importance because of their involvement in redox catalysis (Castro *et al* 1977; Mannasen and Barllan 1970; Hill *et al* 1970; Dickerson 1972), their utility as models in the study of aromatic residue-porphyrin interaction in heme proteins, light-induced electron transfer in photosynthesis (Bradley and Calvin 1955; Seely 1966; Norris *et al* 1974; Sauer 1979; Clayton 1980) and herbicidal activity (Boon 1965). Moreover, many biological redox reactions are catalysed by metalloporphyrins and so an understanding of the role of charge transfer (σ) in these complexes is paramount. Much of the research in metalloporphyrins not only stems from their biological relevance but also arises from the search for new semiconductors, superconductors and conducting molecular crystals (Hoffman *et al* 1979, 1983). We present here a review of our work on the molecular complexation behaviour of porphyrins (both inter and intramolecular), the influence of metal ions on the stability of such complexes and the importance of structures of these complexes in explaining their stabilities and reactivities. First we will examine the work that has been carried out on the complexation behaviour of naturally occurring porphyrins.

The important features of the porphyrins are: (a) they are endowed with a cyclic

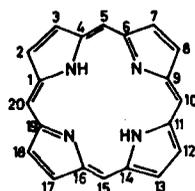
π -aromatic system, (b) they exhibit ampholyte character *i.e.* they can be successively reduced and oxidised with ease to form mono anion, dianion, monocation and dication respectively, (c) they exhibit unique coordination chemistry *i.e.* the metal derivatives assume interesting stereochemistries and (d) they function both as a π -donor and π -acceptor towards diverse neutral organic molecules. Many of the biological functions involving porphyrins can be traced to either one or more of these features. Central to the understanding of these biological reactions is the relative ability of the porphyrins to associate among themselves and reversibly bind other neutral molecules (substrates) either for enzyme function or for substrate activation or for molecular conduction. It becomes essential then to define such associated products in terms of their stereochemistry and the nature of forces that govern the stabilisation of these products. The strength of association, equilibrium structure, stability and life-time of these complexes are different from system to system. Many factors, however, contribute to the strength of association and they are: the nature of the state of interacting molecules, geometry of the molecules under study, the media in which they are studied, temperature and others. The origin of these interactions has been discussed widely and has been the subject of considerable theoretical debate. Morakuma (1979) in an effort to arrive at the stabilising energy of these molecular systems, has partitioned the total energy of the system into various contributions: (a) electrostatic (b) polarization (c) exchange repulsion (d) charge transfer (e) coupling (f) electron correlation and (g) dispersion energies. The relative energies of these interactions often depend on the magnitudes of intermolecular separation and geometries of the associated molecules. The latter is of considerable importance since activation of molecules bound to the porphyrin or its metal derivatives critically depend on the position of contact and its orientation. A knowledge of these features becomes essential in the interpretation of enzyme function and also for the design of biomimetic models at the molecular level. Delineation of these features have been attempted at different levels. The electronic states of the porphyrins form the first level while the experimental demonstration of the existence of the molecular association followed by the structural elucidation of these complexes constitute the other levels.

2. Electronic structure of porphyrins

Porphyrins are tetrapyrrole pigments endowed with a number of peripheral positions available for substitution with other organic groups. A few porphyrins which occur in biological environments along with the synthetic ones are listed in table 1. The naturally occurring porphyrins are devoid of meso-substitution and carry propionic acid side chains. As shown below, the substituent groups do not alter the optical and emission properties of the porphyrinic core; however they induce considerable solvation effects and solubility characteristics.

Several theoretical treatments are available to describe the electronic structure of the porphyrins (Zerner and Gouterman 1960; Zerner *et al* 1966; Gouterman 1978; Dedieu *et al* 1982). The choice of the geometries becomes an important factor in such calculations. Somewhat idealised geometries with a four-fold symmetry (D_{4h}) have been used in these descriptions. A four-orbital model provides a comprehensive picture to explain many optical absorption and emission properties of the porphyrins. Considerations of π -electron calculations indicate that (a) in metalloporphyrins (D_{4h})

Table-1. Chemical structures of porphyrins.



PORPHYRIN	2	3	5	7	8	10	12	13	15	17	18	20
Etioporphyrin - I	Me	Et	H	Me	E	H	Me	Et	H	Me	Et	H
Octaethylporphyrin	Et	Et	H	Et	Et	H	Et	Et	H	Et	Et	H
Mesoporphyrin - IX	Me	Et	H	Me	Et	H	Me	P	H	P	Me	H
Hematoporphyrin - IX	Me	OH CH.Me	H	Me	OH CH.Me	H	Me	P	H	P	Me	H
Protoporphyrin - IX	Me	V	H	Me	V	H	Me	P	H	P	Me	H
Uroporphyrin - I	A	P	H	A	P	H	A	P	H	A	P	H
Tetraphenylporphyrin	H	H	Ar	H	H	Ar	H	H	Ar	H	H	Ar
Coproporphyrin - I	Me	P	H	Me	P	H	Me	P	H	P	Me	H

Me = Methyl
Et = Ethyl
V = Vinyl
P = $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$
A = $\text{CH}_2\text{CO}_2\text{H}$
Ar = C_6H_5

the highest two occupied π -orbitals (a_{1u} and a_{2u}) are nearly degenerate and (b) the lowest unoccupied ($e_g\pi^*$) orbitals are degenerate. The optical absorption spectra of the porphyrins are characterised by an intense Soret absorption ($S_0 \rightarrow S_2$ transition) around 400 nm and Q bands (π - π transitions) in the region 500–650 nm. The relative intensities of the latter bands are often diagnostic of the nature of the substituents in the peripheral positions. It has been shown that the substituents do not alter the symmetry of the highest occupied and lowest unoccupied orbitals, though a marginal change in energies of these orbitals has been observed. Thus, the biologically active porphyrins exhibit absorption bands not too different from that of the synthetic ones e.g. 5,10,15,20 tetraphenyl porphyrin (TPP) and octaethyl porphyrin (OEP). For this reason, many studies utilise these porphyrins as biomimetic models.

The presence of metal ions in these porphyrins, however, induces considerable change in the geometries of the porphyrins and their orbital energies. Moreover, the perturbation of metal d electrons in the N_4 chromophore field alters the electronic structures of the porphyrins. Some of these features are listed in figure 1. It follows then, that the orbital energies and the stereochemistries can, in fact, dictate the electron donor and acceptor capacities of the metalloporphyrins. Moreover, the metal ions in the metalloporphyrins can themselves function as acceptors or donors towards other organic molecules. Thus, by changing the nature of metal ions in the porphyrin derivatives, it is possible to modulate the acceptor/donor properties of the porphyrins. It is for this reason, perhaps, the biological system chooses a few metal ions for their functional characteristics. Since the porphyrins are highly σ -donating bases and very weak π -acids, they increase the electron density on the metal ions typically, iron which leads to specific activity of hemoglobin and cytochromes. The porphyrins being extended π -system exhibit tendency to aggregate among themselves especially in solution. The solid state structures of a few porphyrins (Hoard 1975; Scheidt 1979) reveal that stacking of the porphyrin planes occur, though the interplanar separations are just above the van der Waal distances. The stability of the aggregated species is derived from incipient π - π interactions.

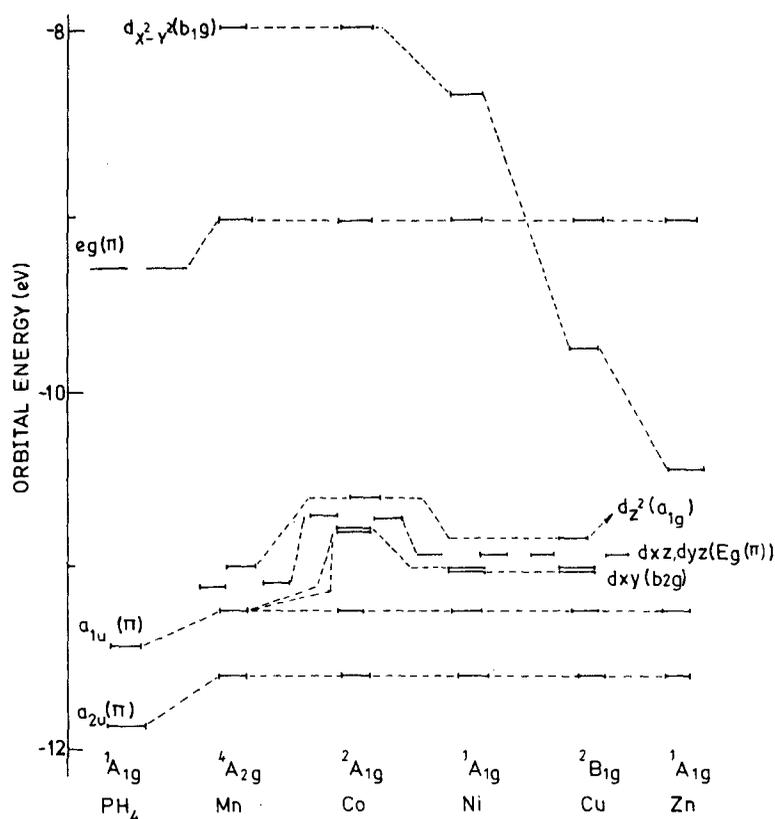


Figure 1. The energy levels of highest occupied and lowest unoccupied molecular orbitals of porphyrin dication and a few divalent metalloporphyrins. From Zerner and Gouterman (1960).

It is convenient to divide the molecular complexes formed by the porphyrins and their metal derivatives into two groups: intermolecular and intramolecular complexes. The intermolecular complexes can be further grouped to self-aggregated species and complexes formed between porphyrins and other neutral organic entities. The spectral features and the methods that have been used to characterise these species are different. A description of some of these features is given below.

3. Aggregation phenomena

Aggregation is a general feature of molecules endowed with extended π -systems. Both synthetic and naturally occurring porphyrins have been shown to form aggregated species. The extent of aggregation is limited by the nature of organic groups in the peripheral positions, concentration factors and the nature of solvent in which they are dissolved. It has been possible to study the aggregation features both by optical and magnetic resonance spectral methods. The optical absorption method has been used with advantage to determine the extent of aggregation and it is found that dimeric forms dominate in solution (Pasternack *et al* 1972; Das and Plane 1975; Das 1975;

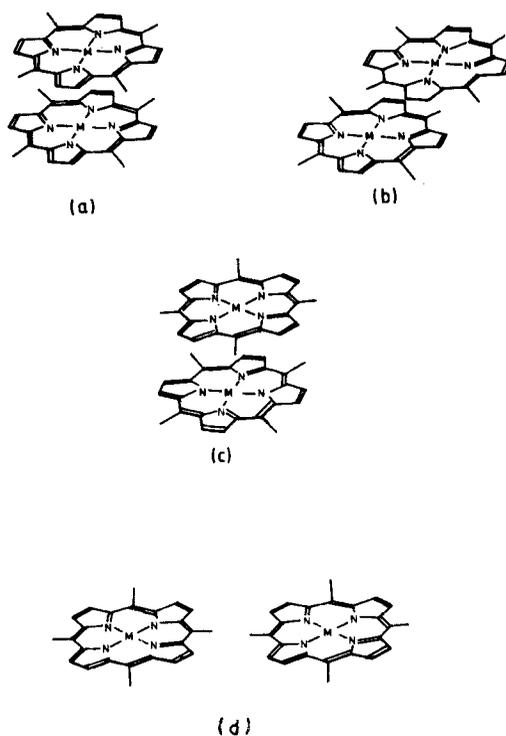


Figure 2. Possible geometries of porphyrin dimers (a) stacked (b) displaced (c) eclipsed and (d) linear.

White 1978). The dimerisation constant is found to be fairly high in the order of 10^5 to 10^6 . Addition of polar solvents seems to shift the equilibrium to monomer side. Despite the demonstration of the existence of aggregated species, no structural details are, however, available. In this connection it may be worthy to consider the magnetic resonance data. The $^1\text{H NMR}$ data of free-base coproporphyrins, mesoporphyrin, protoporphyrin and deuteroporphyrin IX dimethyl esters show a large dependence of the proton chemical shifts on increasing concentration of these porphyrins in solution (Abraham *et al* 1966; Janson and Katz 1972). The non-equivalence of proton resonances in concentrated solutions is taken as an evidence for the presence of aggregated species (Abraham *et al* 1973; Abraham and Swinton 1968; Doughty and Dwiggin 1969). Although the NMR method has provided the possible sites of the molecules in the monomer for the formation of aggregated species, the information obtained cannot unambiguously determine the extent of aggregation (dimer or higher order aggregates). The electron spin magnetic resonance data of Cu(II) porphyrin, however, has been interpreted in terms of a dimer (Blumberg and Peisach 1965). Aside, there has been no report concerning the structure of the dimers in solution. Several forms of dimer are possible (figure 2). Theoretical calculations on the energies of such dimers seem to indicate that face to face eclipsed configuration of the dimer is energetically more favoured than the rest (Lucia *et al* 1970; Sudhindra and Fuhrhop 1981; Tatsumi and Hoffmann 1981). The structural report on covalently-linked bisporphyrins has shown edge-edge overlap (Collman *et al* 1981) geometry while

noncovalently-linked crown porphyrin dimers have eclipsed geometries (Thanabal and Krishnan 1982a, b). A discussion of these aspects is dealt with under intramolecular association.

4. Intermolecular association

The electronic structure of the free-base porphyrins and their geometries are favourably poised to form numerous molecular complexes with various organic molecules. Most of the studies are directed towards the establishment of π - π interaction as a major source of stabilisation of molecular complexes formed between the porphyrin and other organic molecules. The enumeration of the nature of interactions has been the subject of many investigations. A few are directed towards the evaluation of binding constants and thermodynamic factors while others lay emphasis on the determination of structures of the molecular complexes. We shall critically examine some of these effects. Generally, optical absorption methods have been employed to evaluate binding constants while probes into the possible structures in solution are being made using magnetic resonance methods.

In a system containing an electron acceptor (A) and a donor (B) in equilibrium $A + D \rightleftharpoons AD$, the equilibrium constant (K) can be written as

$$K = [AD]/[A][D]. \quad (1)$$

Several methods are available in literature (Foster 1969) to evaluate the magnitudes of K . The value of K represents the binding constant of the two molecules in the associated state and the determination of K values at different temperatures essentially yields enthalpy (ΔH) and entropy change (ΔS) for the complexation process. In view of the very weak interactions that prevail in the associated state, it is anticipated that the values of K , ΔH and ΔS are small in magnitude. Evaluation of such parameters becomes an important component in determining the nature of forces that hold A and B in the associated state. The next question that arises is the manner in which the structure of the associated molecules is going to affect the magnitudes of these parameters. It has been suggested (Malini and Krishnan 1980) that in molecular complexing systems, the K values as determined represent the total stability (provided the concentration effects are taken care of) of the complex with respect to dissociation and the ΔH and ΔS values signify packing and orientation effects of the donors and acceptors in the complexes respectively. Thus, compatibility in sizes of the donor and acceptor, the planarity of the molecules and the symmetries of the orbitals (of donor and acceptor) for efficient overlap contribute to the magnitudes of the thermodynamic parameters. The strength of the complexes is related to the position of π absorption band and its intensity (Murrell 1959, 1961).

It would be fruitful at this stage to examine the different systems that have been studied and the results obtained thereof. Naturally occurring porphyrins form the first choice of study owing to their relevance in biological systems and their enhanced solubility in polar solvents. Mauzerall (1965) in his studies on coproporphyrins was able to characterise a few molecular complexes formed between the porphyrins and certain aromatic molecules and suggested that ionic and dispersion forces and in some cases π interactions contribute significantly to the stabilisation. The ability of the biomolecules, hemin and hematoporphyrin to function both as a n and π donor was

demonstrated by Cann (1967) and Slifkin (1971). These studies essentially delineate the existence of molecular complexes; however, no structural information is available. The importance of molecular complex as an intermediate in certain biological reactions comes from the observation of increased denaturation of myoglobin by urea (Cann 1969) and enhanced rate of Zn(II) insertion into myoglobin in the presence of aromatic compounds (Cann 1965). In an effort to simulate the cyt P. 450 function of steroid hydroxylation, Hill *et al* (1973a) carried out an interesting study of the interaction of the Co(II), Fe(III), Ag(II) and Ni(II) derivatives of mesoporphyrin IX dimethyl ester with various steroids to find the possible site of location of the steroid over the porphyrin centre. This study constitutes the first experimental probe into solution structures of porphyrin complexes. The advantageous use of $^1\text{H NMR}$ and ESR methods have been exploited to arrive at the solution structures. Such studies reveal a family of structures for the complexes owing to randomization of molecules in solution and no specific interaction is discernible. However, they are able to point out the dominance of porphyrin ring interaction with steroids. The fruitfulness of such a study is borne out in the demonstration that metal ions do take part in binding (besides the porphyrin ring) especially in the interaction of caffeine and imidazole with porphyrins (Barry *et al* 1973).

Investigations on naturally occurring porphyrins and biologically important molecules, however, have certain limitations especially in view of their restricted solubility of these molecules in a range of non-polar solvents. Thus, use of organic molecules which essentially function as π -acceptors has been sought to delineate the structures and factors contributing to the stability of these complexes. The various acceptors that have been used are shown in figure 3. The studies utilising these acceptors

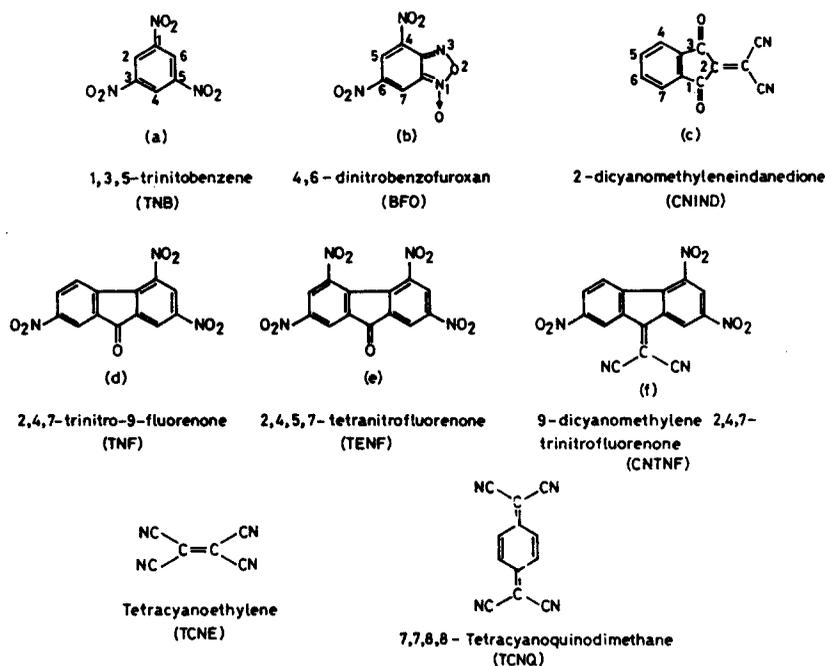


Figure 3. Chemical structures of various organic acceptors.

have yielded a wealth of information concerning the structures, factors contributing to the stabilities of the molecular complexes and the possible nature of interaction. Firstly, we will examine the interaction of some of these acceptors with naturally occurring porphyrins. Studies on the molecular complexes formed between mesoporphyrin IX dimethyl ester derivatives of Co(II) and Ni(II) with TNF and other nitroarenes deserve mention (Barry *et al* 1973; Hill *et al* 1967, 1973b). The use of Co(II) porphyrin as a donor served as a dipolar probe in the ^1H NMR measurements to locate the protons of the acceptor molecule over the porphyrin core. Though they were able to arrive at the possible structures of the complexes, no unique structure has emerged from these studies. The absence of an unique structure in solution is probably due to the large size of the acceptor employed (TNF) which completely overlaps with the porphyrin core. Under these circumstances it would be difficult to perceive any preferential shielding and deshielding effects of the proton resonances of the acceptor (La Mar and Walker 1978). All the complexes thus far investigated presupposes 1:1 stoichiometry of the donor and acceptor and in a few cases this has been confirmed by optical and ^1H NMR methods. Only one structural report is available in literature (Grigg *et al* 1978). This relates to the 1:2 complex formed between Ni(II) derivative of etioporphyrin and tetranitrofluorenone (figure 4). It can be seen that fluorenone and porphyrin rings are approximately planar and the fluorenone ring is positioned in a fashion that its carbonyl group is nearest to the porphyrin plane at 2.97 Å. The Ni(II) atom is situated at 3.39 Å from the mean plane of the fluorenone ring. This preliminary report is of importance especially with respect to the so far observed 1:1 stoichiometry in solution and the possibility of weak interaction between ketocarbonyl on Ni(II) ion. As we would see later such interactions have not been detected in solution (Chandrashekar and Krishnan 1982).

Several synthetic porphyrins, TPP, substituted TPP, OEP and their metal derivatives have been employed as donors. The usage of these porphyrins has certain advantages in that they are relatively more soluble in a range of organic solvents than the naturally occurring porphyrins, a variety of substitutions is possible to delineate the effect of substituents on the molecular complexation characteristics and the influence of metal ions on the stability of these complexes could easily be studied. We shall now illustrate some of these aspects here. One of the desired objectives of the studies on molecular complexation of porphyrins is to determine any preferred orientation of the acceptor and donor in the associated species. The choice of small size acceptors (smaller in size relative to the size of porphyrin donor) is well suited for this kind of investigation. The

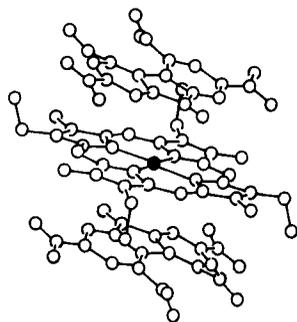


Figure 4. Structure of Ni(II) porphyrin-TNF complex. From Grigg *et al* (1978).

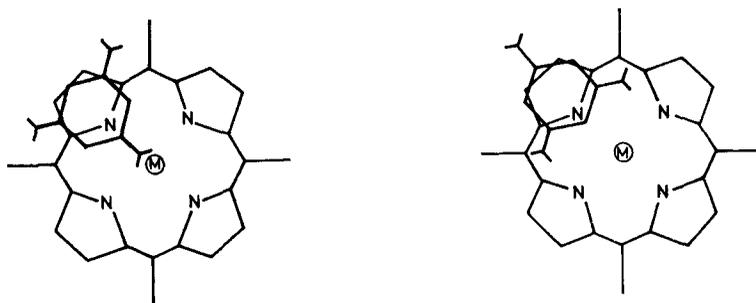


Figure 5. Possible geometries of porphyrin-TNB complex.

studies of La Mar *et al* (1974) and that of Fulton and La Mar (1976) are worthy of mention here. Based on the $^1\text{H NMR}$ results of Co(II) and Ni(II) porphyrin interaction with TNB, they were able to arrive at a possible structure of the molecular complex (figure 5). Moreover, it was pointed out that π -complexation of porphyrin with TNB alters σ binding framework of the porphyrin. Such changes brought out by the charge donation from the π -level of metalloporphyrin would in fact be accompanied with small changes in the orbital energies of these metal ions. An ESR study of these complexes involving metalloporphyrins (or spin-free metal ions) has revealed interesting features (Walker 1973, 1974; Hiroshiyoki and Iwaizumi 1980). Of particular interest is the manner in which the hyperfine tensors of the metalloporphyrins change on complexation with Lewis bases and aromatic π -acceptors. For example, it has been shown that axial ligation of the metal ion results in an increase in g values and decreases in $|A|$ values while the formation of a molecular complex leads to decrease in g values and increase in $|A|$ values. These changes have been useful in arriving at the M-N σ covalency as a consequence of π -donation to an acceptor. As we shall see later an increase in covalency factor relative to uncomplexed metalloporphyrin can be related to the electron affinity of the acceptor. Besides this, ESR study has been particularly helpful in the characterisation of charge-separated species [Co(III) TPP-TCNE] and TCNE^- and Co(III) TPP-TCNQ $^-$ (Wayland and Mohajer 1973; Konishi *et al* 1980). The interesting aspect being the formation of these species originates from molecular complexes in which donor porphyrin and acceptor exist in associated state.

A detailed description of molecular complexes formed by different metalloporphyrins (MTPPS) with diverse organic molecules is given in the work of Chandrashekar and Krishnan (1981, 1982, 1984a, b). The dominant theme in these studies is to relate the binding constants and thermodynamic parameters of complexation with the nature of metal ions, stereochemistries of the donor metalloporphyrins, ring size and electron affinity of the acceptors.

Interestingly, in all these systems, the donor function essentially rests with the porphyrin π manifold. The variation of metal ions in the porphyrin cavity results in the increased binding constants and for the interaction of any acceptor (TNB, TNF, TENF, BFO) with MTPPS, the binding constant varies as $\text{Co}^{2+} > \text{Cu}^{2+} > \text{VO}^{2+} > \text{Ni}^{2+} > 2\text{H} > \text{Mn}^{3+} > \text{Zn}^{2+}$. In a given group, however, the following order of stabilities holds good: $\text{Pd}^{2+} > \text{Ni}^{2+}$; $\text{Cd}^{2+} > \text{Zn}^{2+}$. This order of stabilities is quite different from that of Irving-Williams series proposed for coordinatively interacting systems. In order to find what parameters of the metal ions are responsible for this stability sequence, the

authors have examined the redox potential data, electronic configuration of metal ions and stereochemistries of the MTPPs. The first oxidation potentials of MTPPs signify the energy of the highest occupied molecular orbital (HOMO) and thus any π -donation is expected to originate from this level. The oxidation potential data of MTPPs follow the order: CoTPP > NiTPP > VOTPP ~ TPP ~ CuTPP ~ ZnTPP (Felton 1978). This order, however, is not coincident with the observed order of stabilities. Since the binding constants only represent the stability with respect to dissociation, more appropriate parameters would be either the σ transition energy or the enthalpy change of complexation. As has been pointed out earlier (Gouterman and Stevenson 1962) the σ band in these molecular complexing systems could not be located with certainty owing to the intense bands of porphyrin π systems in the visible region. It is estimated that the position of γ_{σ} would be 15000–14000 cm^{-1} and it is not yet known with certainty the manner in which the position of this band is altered on changing the metal ions. The ΔH values for the interaction of various MTPPs with acceptors reveal not much change in any given order. Typically of ZnTPP interaction with acceptors, the K values are found to be much smaller, though the magnitudes of ΔH are much higher. A possible reason for this is attributed to the near-planarity of ZnTPP relative to other MTPPs. This brings in the importance of stereochemistries in governing the observed stability sequences.

It is easy to recognize that an ideal planar geometry (D_{4h}) would satisfy the condition of maximum overlap with the acceptor molecules thereby enhancing the stability, if there exists no specific site interaction. Possibly this provides an explanation for higher ΔH values observed for ZnTPP interaction. Any deviation from the stipulated

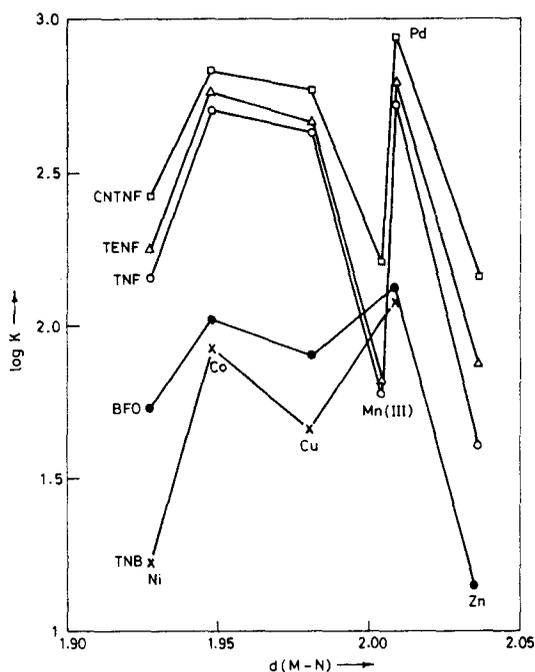


Figure 6. The dependence of stability constants of various complexes in solution of the M-N distance.

condition for the maximum overlap would immediately result in the lowered values of ΔH . In the case of transition metal derivatives of porphyrins [especially of VO(IV), Co(II), Cu(II), Ni(II) and others] there is an S_4 ruffling of the molecule departing from ideal planarity. A rough estimate of this departure could be depicted in terms of M-N distance (average). A plot of this parameter versus binding constant, however, showed no direct relation (figure 6). These arguments are rather too naive and a more reasonable approach would be to probe into d orbital energy levels of MTPPS and of their molecular complexes. Since, not much information about these aspects could be obtained from optical spectroscopy, the ESR data are worthy of consideration.

The detailed electronic energy levels are given in figure 1. Owing to the out-of-plane position of these metal ions, the d orbitals designation is as follows:

$$d_{x^2-y^2}; (b_1); d_{z^2}, (a_1); dxz, d_{yz}, (e); \text{ and } d_{xy}(b_2).$$

For the first row transition metal ions, the relative energies of these orbitals follow the order $a_1 > e > b_2$ which are nevertheless closely spaced. It can be recognized that an electron is in a_1 and b_2 orbitals for Co and VOTPP derivatives while a hole is present in b_1 in the case of CuTPP. Designating the orbital coefficients of b_1, a_1, e and b_2 as α, β, γ and δ , it is possible to estimate them from ESR hyperfine splittings. At this point we would like to seek how the magnitude of these coefficients varies on molecular complexation. Alternately one can approximate this by calculating 'unreduced energies' assuming the coefficients to be unity. This assumption should be followed with a caution that the coefficient should be multiplied by a factor 'orbital reduction factor'. Such a procedure when adopted for a series of analogous systems *viz.* molecular complexes formed by CuTPP with different π -acceptors of varying electron affinities, has given many useful information. The spin Hamiltonian for various systems is described in literature (Assour 1965; Manoharan and Rogers 1969) the covalency factor, α^2 can be calculated assuming that M-N bonds in MTPPS do not possess any in-plane or out-of-plane π bonding (Kivelson and Nieman 1961). The energies of the different orbitals calculated from g and A tensors for various CuTPP complexes are given in figure 7. It can be seen that $\Delta\alpha^2$, (change in covalency factor in the complex relative to CuTPP) varies linearly with the electron affinity of the acceptor. The decrease in α^2 value in the complexes indicates that M-N σ bond becomes more covalent. This can either arise from the increased electron density on nitrogens or an increase in the electronic charge on the copper in the complex relative to CuTPP. A similar observation has been made for VOTPP and CoTPP complexes.

The influence of solvents on the stabilities of these complexes has been investigated (Chandrashekar and Krishnan 1984a). It is demonstrated that solvents of high polarity decrease the binding constant values. Another point of interest emanating from these studies is the $^1\text{H NMR}$ study of BFO interaction with MTPPS (Chandrashekar and Krishnan 1984b). It has been found that though BFO is structurally related to TNB the possible site of location of BFO over the porphyrin is quite different from that of TNB in the molecular complex. The limiting proton chemical shifts experienced by different BFO protons are of the same magnitude indicating random positioning of BFO.

Besides, the stabilities of these molecular complexes, the major question that has not been answered is the extent to which CT contributes to the stabilities. Different lines of arguments have to be pursued since there exists no separate γ_{CT} band in the spectra of these complexes. A linear relation of K values *vs* electron affinity of the acceptors (figure

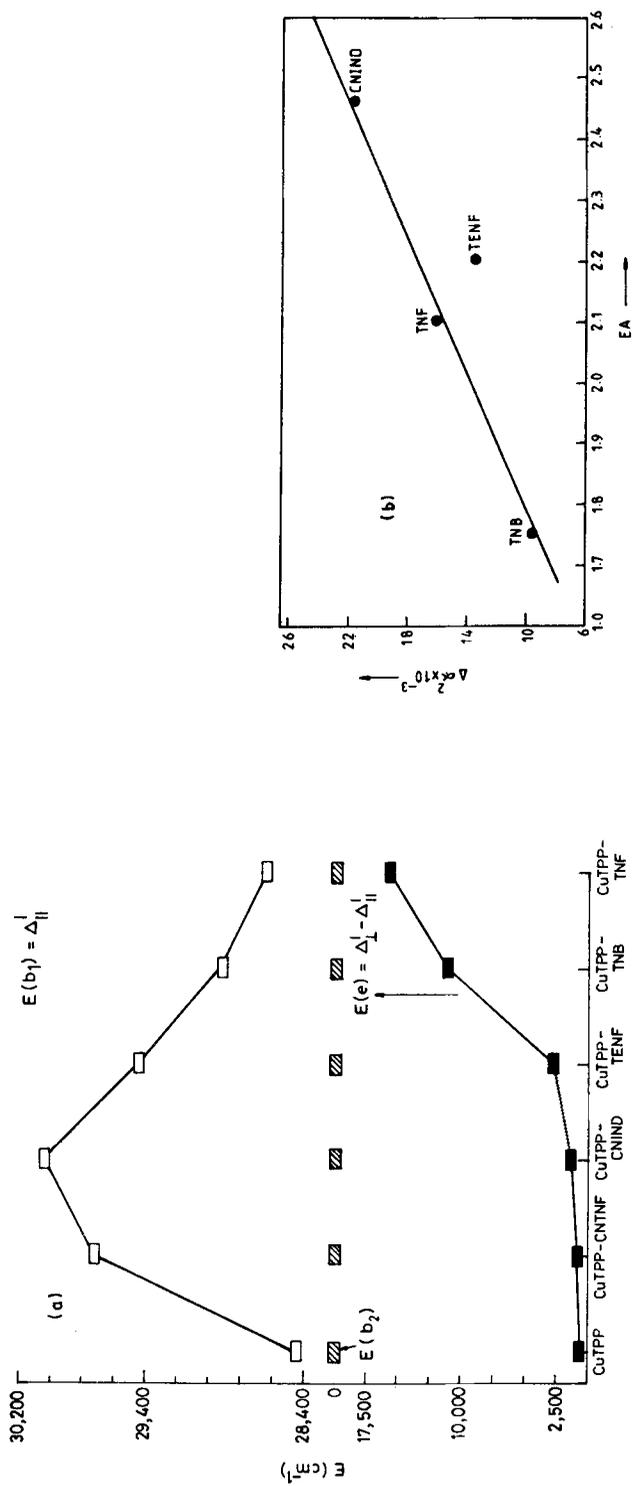


Figure 7. (a) Orbital energies of Cu(II) TPP complexes with various acceptors. (b) Linear dependence of Δx^2 with electron affinities of the selected acceptors.

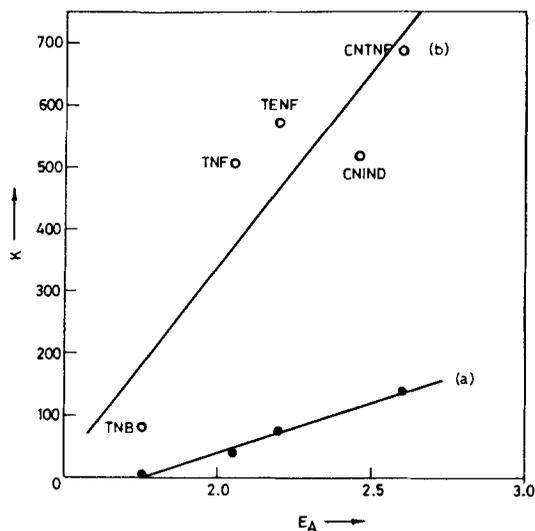


Figure 8. The dependence of stability constants of (a) Co(II) TPP and (b) ZnTPP complexes with various acceptors.

8) is not a sufficient condition to establish the π contribution to the stability. In this context the interaction of Cu(II), Fe(III), Co(II) and Ni(II) derivatives of uroporphyrins and other metal (II) porphyrin derivatives with phenanthrolines is of interest (Shelnutt 1981, 1983a, b, c). Raman difference spectroscopy has been used in these studies. The metal-dependent frequency shifts are shown to be a sensitive function of the substituents in the phenanthroline acceptor. These studies further point out that ΔH values found in these systems are similar to those observed for other π systems. These observations when interpreted in conjunction with the oxidation state-marker vibrations of metal porphyrin derivatives seem to indicate the existence of π interactions.

It would be fruitful at this state to enquire whether π in the ground state of these complexes play any role in the excited states. It has been shown that nitroaromatics quench the singlet emission of Zn(II) derivatives of various porphyrin derivatives (Gouterman and Stevenson 1962; McCartin 1963; Whitten *et al* 1968; Lopp *et al* 1970; Chandrashekar and Krishnan 1981; Yamada *et al* 1983). These studies reveal that singlet quenching occurs through the formation of a collisional complex. The observation that the rate of bimolecular quenching is fairly independent of the polarity of the solvents suggests the formation of an exciplex rather than a complete electron transfer. This is in contrast to the observation of Seely (1969) and the work on the corresponding complexes of chlorophyll analogues (Droupadi and Krishnan 1984). The formation of exciplexes in the study seems to derive support from the following observations (a) the concentration of the acceptors required to quench the singlet emission of porphyrins is much less than the concentration of the same acceptor required to decrease the absorbance of the donor porphyrin in the ground state and (b) absence of separate emission band of the complex. The latter though recognized as a necessary condition for the existence of an exciplex, the absence of this can be interpreted in terms of fast radiationless deactivation of the exciplex possibly by

intersystem crossing as observed in the TNB complex of anthracene (Kleinerman *et al* 1962).

4. Intramolecular association

The phenomenon of intramolecular association described in this section is distinct from that of self-association in a sense that the organic group involved in the molecular association originates from one of the peripheral positions, within the system. A study of these systems has important bearing in heme and cytochrome function, and in the primary charge separation in photosynthesis. Of systems of our present interest are the porphyrins. These can be classified into two groups: (a) covalently-linked bisporphyrins where the porphyrin unit is attached covalently (either singly or doubly) to another porphyrin moiety and (b) sidearm porphyrins where a porphyrin entity is covalently attached to another organic group (which can either function as an acceptor or a donor) through one of its peripheral positions. The basic question is what are the conditions under which one can obtain 'folded' conformer or whether folding of either one of the porphyrins (in the case of bisporphyrins) or the organic group (in the case of side arm porphyrins) over the porphyrin plane is a natural consequence of the omnipresent incipient π interaction? Secondly, what special advantages can be derived in the case of folded conformer *vis-a-vis* open conformers? Several synthetic model compounds have been designed (Wasielowski 1982). It appears that π interaction is a prerequisite for the exhibition of many photophysical properties *viz.* light-induced electron transfer singlet-singlet energy transfer and others. Though one can visualise such π interactions in the doubly-linked bisporphyrins, it is difficult to conceive this in the singly-linked bisporphyrins where there exists no steric constraints. Jeyakumar and Krishnan (1983) have suggested novel ways of folding two porphyrins through promotion of intramolecular π interaction. Interaction of a π -acceptor, TNB, with the singly-linked bisporphyrins is shown to result in the cooperative binding of two porphyrin planes mediated by a TNB molecule (figure 9). Several interesting consequences result from such studies. This suggests that π interaction is one of the dominant factors that govern the stabilities and the natural tendency of two extended π systems linked covalently would lead to folding depending on the inter-chromophore separation. Turning our attention to side arm porphyrins, several interesting compounds have been reported. The basic objective of such a study is not as much to elucidate π interaction but then to study intramolecular energy and electron transport. A variety of porphyrins

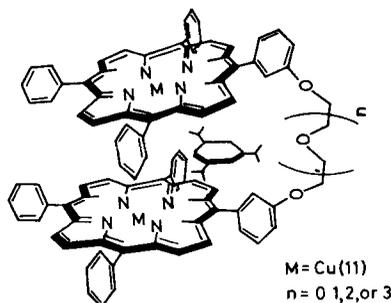
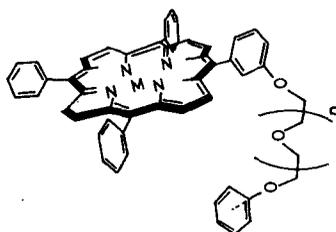


Figure 9. Chemical structure of covalently linked bisporphyrin complexes with TNB.



M = 2H, Co(II), Cu(II) and Zn(II)

Figure 10. Chemical structure of porphyrins endowed with podand side arm.

linked to quinones with methylene-ester groups (Kong *et al* 1982), methylene groups of variable length (Nishitani *et al* 1981), amides (Alan *et al* 1983; Siemiarczuk *et al* 1983) and porphyrins linked to mono and bisquinones and carotenoids (Moore *et al* 1980, 1982; Joshi *et al* 1982) have been reported. It is suggested in most of these compounds that intramolecular π is responsible for many of the observed interesting photo-physical properties. It is demonstrated that the natural tendency of porphyrins bearing an organic acceptor (figure 10) is to engage itself in the intramolecular π interaction (Bhaskar Maiya and Krishnan 1983). This interaction, however, is critically dependent on the distance parameter which separates the organic acceptor from the porphyrin unit. The manifestation of intramolecular π is also realized in a series of porphyrins appended with heterocyclic groups (Suriyanarayanan and Krishnan 1983). This has led to the increased singlet quantum yields indicating that the π interaction is possibly present in the excited states as well.

5. Conclusion

This review presents a coherent picture of interactions that prevail in the molecular complexes involving porphyrins and their metal derivatives. Special emphasis can be laid on the following. The presence of metal ions in the porphyrin core is recognized to promote π interaction, though more substantial evidence is necessary. The self-aggregation of porphyrins occur possibly through π interaction; however, the energetics of such processes has not been completely understood. The π interaction in the ground state seem to influence the excited-state properties. In a few cases it has been observed that π interaction modulate the rate of excited state electron transfers from the singlet-excited state of the porphyrins to an acceptor. The covalently-linked porphyrin systems offer viable models to demonstrate the existence of π interaction. The presence of these interactions is responsible for many interesting photophysical properties. It is hoped that in the near future many of these aspects would be understood in better terms especially in view of the tremendous importance the porphyrins bear in many biological reactions. Thus we expect this area of research to be continuing and a fruitful one.

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