Registry No. 1, 26093-63-0; *cis*-**2**, 81554-06-5; *trans*-**2**, 81571-95-1; *cis*-**3**, 67217-63-4; *trans*-**3**, 67217-62-3; *cis*-**4**, 81554-07-6; *trans*-**4**, 81554-08-7; *cis*-**5**, 81554-09-8; *trans*-**5**, 81554-10-1; **6**, 16831-15-5; *cis*-**7**, 16831-12-2; *trans*-**7**, 16831-13-3; **8**, 76928-53-5; **9**, 81554-11-2; **10**, 81554-12-3; **11**, 81554-13-4; *cis*-**12**, 81554-14-5; *trans*-**12**, 81554-15-6; **13**, 81554-16-7; **14**, 81554-17-8; **15**, 81554-18-9; 2-methyl-1,5-pentanediol, 42856-62-2; *cis*-2-ethyl-3-methyltetrahydrofuran, 73435-16-2; *trans*-2-ethyl-3-methyltetrahydrofuran, 73435-17-3; 3-methyl-1,5-hexanediol, 4089-71-8; *cis*-2-ethyl-4-methyltetrahydrofuran, 73435-18-4; *trans*-2-ethyl-4-methyltetrahydrofuran, 73435-19-5; *cis*-2-(hydroxymethyl)-5-methyltetrahydropyran brosylate, 81554-19-0; 2,3-dimethyl-1,5-pentanediol, 81554-20-3; 2-(carbomethoxy)-5-methyl-3,4-dihydro-2*H*-pyran, 81554-21-4; methacrolein, 78-85-3; methyl acrylate, 96-33-3; ethynyl bromide, 593-61-3; 2-ethoxy-5-methyltetrahydropyran, 81554-22-5; 2-ethoxy-5-methyl-3,4-dihydro-2*H*-pyran, 2397-94-6; 2-chloro-5-methyltetrahydropyran, 81554-23-6; 2-chloro-4-methyltetrahydropyran, 79543-42-3; 3,4-dihydro-2*H*-pyran-2-methanol, 3749-36-8; 3,4-dihydro-2*H*-pyran-2-carboxylic acid sodium salt, 16698-52-5; 2-methyl-3,4-dihydro-2*H*-pyran, 13039-50-4; 2-chloro-6-methyltetrahydropyran, 81554-24-7; vinyl bromide, 593-60-2; *trans*-2-(carbomethoxy)-6-methyltetrahydropyran, 16831-11-1; 2-chlorotetrahydropyran, 3136-02-5; 3-methyl-3,4-dihydro-2*H*-pyran, 15990-72-4.

Porphyrins with Multiple Crown Ether Voids: Novel Systems for Cation Complexation Studies

V. Thanabal and V. Krishnan*

Contribution from the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India.

Received June 10, 1981

Abstract: Porphyrins appended with crown ether, benzo-15-crown-5, at the methine positions have been synthesized and characterized. The fully and partially substituted porphyrins and their metallo (Co, Cu, and Zn) derivatives describe one or more ether cavities in the periphery that are capable of recognizing spherical cations. The ability of these macrocycles to complex cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, and NH_4^+) is investigated by use of visible, ^1H NMR, ESR, and emission spectral studies. The tetrasubstituted crown porphyrin (TCP) exhibits very high selectivity for K^+. The cations (K^+, Ba^{2+}, and NH_4^+) that require two crown ether cavities for complexation promote dimerization of the porphyrins. The ESR study of the cation-induced porphyrin dimers reveals axial symmetry with the porphyrin planes separated by ~4.2 Å. This distance increases from the fully substituted to partially substituted porphyrins. The cations (K^+, Ba^{2+}, and NH_4^+) quench efficiently the fluorescence of the free base porphyrins and their metallo derivatives. The quenching process is attributed to the steric geometry of the dimers.

There has been considerable research interest in the synthesis of porphyrins with different substitutents in the periphery in view of their utility as models to mimic several biofunctions such as heme oxygenation, cytochrome activity, and photosynthetic electron transport. The design of model compounds depends on the judicious choice of the nature of the substituent and the peripheral position being substituted. Thus, covalently linked porphyrin dimers,[1] sterically crowded porphyrins,[2] and porphyrins appended with organic moieties with acceptor functionalities[3] have been studied to elucidate molecular mechanisms involved in energy transfers, reversible oxygenations, and light-induced electron transport, respectively. We have been interested in the macrocyclic compounds to model carriers for specific cation (Na^+/K^+) transport across biomembranes. Molecular entities endowed with cavities that are capable of recognizing spherical cations containing a central fluorescent porphyrin group form attractive systems to study the movement of cations during transport. The novel cavity-bearing porphyrins can be used with advantage as ionophores, and the ionophoric behavior monitored by the change in fluorescence may also be correlated with properties like the inhibition of oxidative phosphorylation in the respirating mitochondrial systems.

A majority of the synthesized porphyrins normally have substituents in pyrrole units containing paraffinic,[4] ether,[5] and/or amide[1d] linkages. Here, we report the preparation and characterization of porphyrins functionalized at the methine positions with macrocyclic polyethers as first examples of porphyrins with multiple host sites. These sites offer an opportunity to study cation complexation behavior of the porphyrin macrocycle.

Experimental Section

All solvents and reagents used in the synthesis work were of reagent grade quality. The solvents for spectroscopic work were purified and distilled prior to use. The spectrometers employed in the present study are the same as described in the earlier work.[6]

Benzo-15-crown-5 was synthesized according to Pederson[7] and was then converted into an 4′-aldehyde by using the method described in literature.[8] The 4′-aldehyde crown ether (50 mmol) and pyrrole (50 mmol) in propionic acid (300 mL) were refluxed for 45 min. The mixture was worked up in a manner similar to the one employed for the

---

(1) (a) Schwarf, F. P.; Gouterman, M.; Mulijiani, Z.; Dolphin, D. H. *Bioinorg. Chem.* **1972**, *2*, 1. (b) Collman, J. P.; Elliott, C. M.; Halbert, T. R.; Tovrog, B. S. *Proc. Nat. Acad. Sci. U. S. A.* **1977**, *74*, 18. (c) Kagen, N. E.; Mauzerall, D.; Merrifield, R. B. *J. Am. Chem. Soc.* **1977**, *99*, 5484. (d) Chang, C. K.; KuO, M.-S.; Wang, C.-B. *J. Heterocycl. Chem.* **1977**, *14*, 943. (e) Ogoshi,; Sugimoto, H.; Yoshida, Z. *Tetrahedron Lett.* **1977**, 169. (f) Anton, J. A.; Loach, P. A.; Govindjee. *Photochem. Photobiol.* **1978**, *28*, 235. (g) Collman, J. P.; Denisevich, P.; Konai, Y.; Marroco, M.; Koval, C.; Anson, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 6027.

(2) (a) Collman, J. P.; Gagne, R. R.; Halbert, T. R.; Marchon, J.-C.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 7868. (b) Almog, J.; Baldwin, J. E.; Dye, R. L.; Peter, M. *Ibid.* **1975**, *97*, 226. (c) Almog, J.; Badwin, J. E.; Huff, J. *Ibid.* **1975**, *97*, 227. (d) Molinaro, F. S.; Little, R. G.; Ibers, J. A. *Ibid.* **1977**, *99*, 5628. (e) Goff, H. *Ibid.* **1980**, *102*, 3252. (f) Collman, J. P.; Brauman, J. J.; Doxsee, K. M.; Halbert, T. R.; Bunnenberg, E.; Linder, R. E.; La Mar, G. N.; Del Gaudio, J.; Lang, G.; Spartalian, K. *Ibid.* **1980**, *102*, 4182.

(3) (a) Tabushi, I.; Koga, N.; Yanagita, S. *Tetrahedron Lett.* **1979**, 257. (b) Ganesh, K. N.; Sanders, J. K. M. *J. Chem. Soc., Chem. Commun.* **1980**, 1129. (c) Kong, J. L. Y.; Loach, P. A. *J. Heterocycl. Chem.* **1980**, *17*, 737. (d) Moore, A. L.; Dirks, G.; Gust, D.; Moore, J. A. *Photochem. Photobiol.* **1980**, *32*, 691.

(4) Pain, J. B., III; Dolphin, D. *Can. J. Chem.* **1978**, *56*, 1710.

(5) Chang, C. K. *J. Am. Chem. Soc.* **1979**, *99*, 2819.

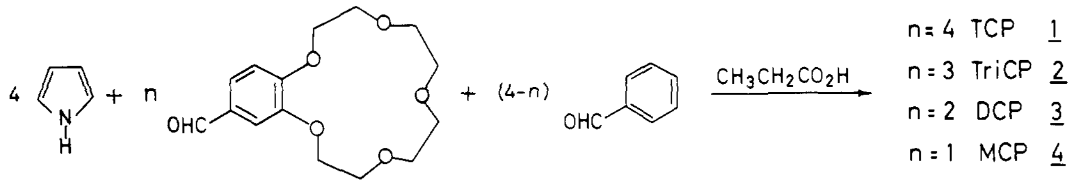
(6) (a) Malini, R.; Krishnan, V. *J. Phys. Chem.* **1980**, *84*, 551. (b) Chandrashekar, T. K.; Krishnan, V. *Inorg. Chem.*, in press.

(7) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7017.

(8) Hyde, E. M.; Shaw, B. C.; Shepherd, I. *J. Chem. Soc., Dalton Trans.* **1978**, 1696. The synthesized 4′-aldehyde of benzo-15-crown-5 has mp 79–81 °C.

0002-7863/82/1504-3643$01.25/0

Scheme I



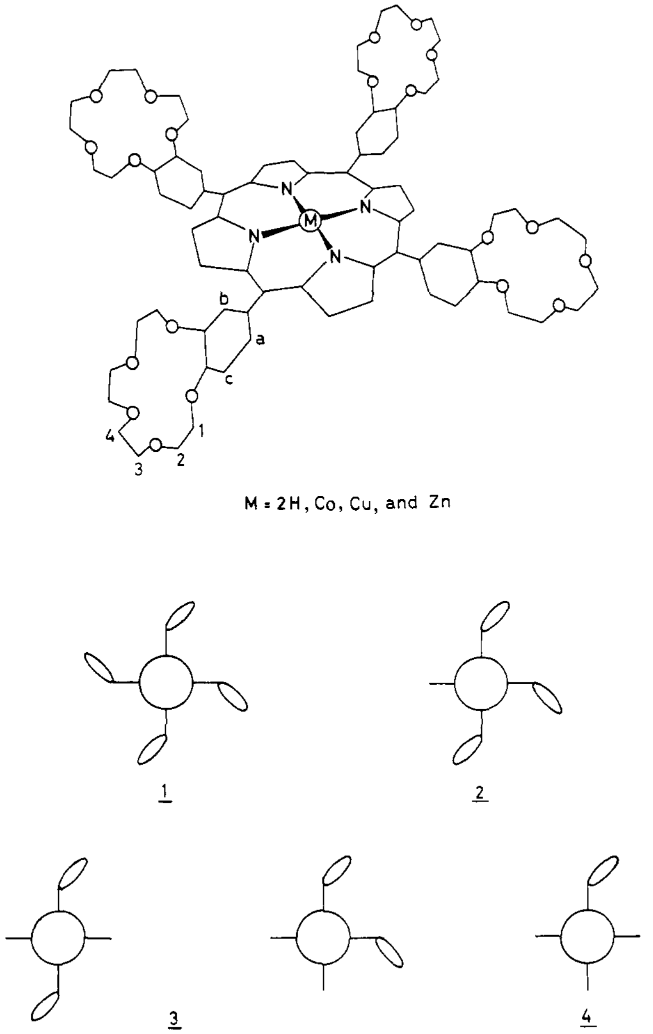


Figure 1. Structure of tetrakis(benzo-15-crown-5)porphyrin. The partially substituted porphyrins are shown. The full circle represents the porphyrin (N_4) plane, while the ellipse and line denote the substituents benzo-15-crown-5 cavity and phenyl ring in the methine positions, respectively. The possible isomers are also indicated.

synthesis of TPP.[9] The crude product, $\alpha,\beta,\gamma,\delta$-tetrakis(benzo-15-crown-5)porphyrin, TCP,[10] was purified by column chromatography (basic alumina) with $CHCl_3$–THF–CH_3OH solvent mixture as the eluant (Figure 1).

A similar procedure was adopted for the synthesis of TriCP, DCP, and MCP, where different mole proportions of the 4′-aldehyde crown ether and benzaldehyde were used (Scheme I). We experienced considerable difficulty in the separation of desired products, especially in the preparation of partially substituted ones, owing to the concomitant formation of TPP and all other substituted products during a particular reaction. Separation and purification of the desired products have been achieved by column chromatography. It has not yet been possible to separate the two isomers in the case of DCP, and the product obtained is a mixture of isomers. The chlorin contamination in the synthesized porphyrins is found to be negligible.

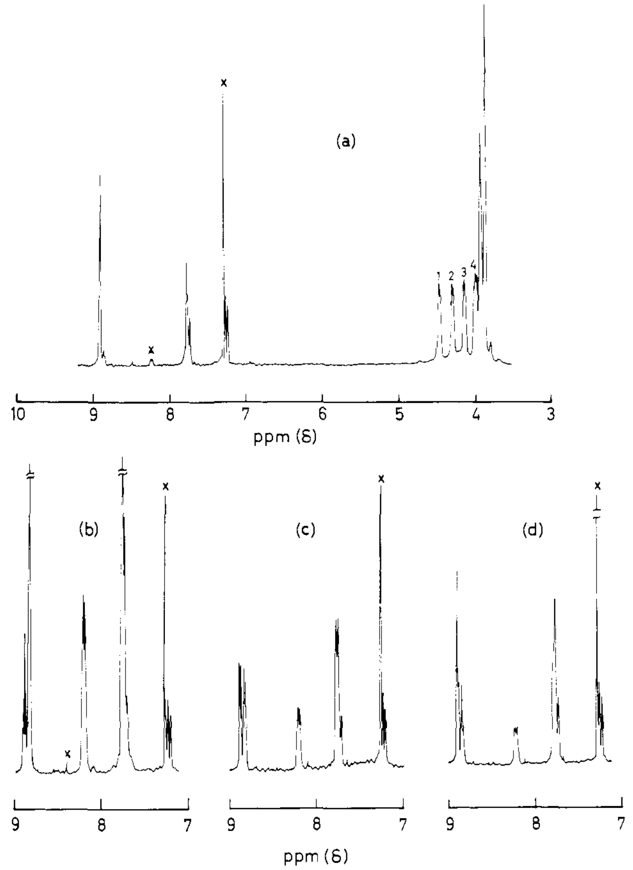


Figure 2. The ^1H NMR spectra of (a) TCP, (b) MCP, (c) DCP, and (d) TriCP in C^2HCl_3. The impurity and solvent resonances are marked × in the spectra.

The metalation reactions of these free base porphyrins, **1**, **2**, **3**, and **4** (Figure 1), were carried out by using the established procedures.[11] The progress of these reactions was monitored spectrophotometrically.

Results and Discussion

Free Base Porphyrins. The ^1H NMR and optical spectral data of the free base porphyrins are highly characteristic and permit detailed structural elucidations. All of the proton resonances are suitably apportioned and assigned (Figure 2). The spectra in the high-field region are more complex due to a greater number of chemically nonequivalent ether fragments, and the four-spin AA′BB′ patterns of the ether protons are clearly discernible in all of the free bases. The occurrence of the well-separated signals arises from the ring current anisotropy of the porphyrin core, and this is further supported by the deshielding effect experienced by these protons relative to the free ether.[12] The complex multiplet structure is indicative of an all-gauche orientation of O–CH_2–CH_2–O fragments.

The origin of the four multiplets (1, 2, 3, and 4) observed in all the free base porphyrins is traced to the presence of nonequivalence of 1,1′ and 2,2′ ether protons brought forth by the

---

[9] Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsaroff, L. *J. Org. Chem.* **1967**, *32*, 476.

[10] For brevity the substituted porphyrins are abbreviated as TCP, **1**; TriCP, **2**; DCP, **3**; MCP, **4**; designating tetrakis-, tris-, bis-, and mono(benzo-15-crown-5)porphyrins. The phenyl rings form the other substituent in the partially substituted porphyrins (see Figure 1).

[11] Rothemund, P.; Menotti, A. R. *J. Am. Chem. Soc.* **1948**, *70*, 1808.

[12] (a) Live, D.; Chan, S. I. *J. Am. Chem. Soc.* **1976**, *98*, 3769. (b) Jayathirtha, Y.; Krishnan, V. *Indian J. Chem., Sect. A* **1979**, *18A*, 311.

substitution at the fourth position of the aromatic part of the ether. Support for this stems from (a) the mirror image relationship of 1,3 pair and 2,4 pair multiplet structures and (b) the close agreement in the difference in the chemical shifts between the 1 and 2 and 1′ and 2′ protons with that observed for the free crown ether.[13] It is reasonable to assign the high-field signals at δ 4.265 and 3.954 for the 1 and 2 protons and the resonances at δ 4.436 and 4.104 for the 1′ and 2′ protons in view of the fact that the 1′ and 2′ protons are influenced more by the inductive effect of the substituent at the fourth position of the aromatic part of the ether than the 1 and 2 protons. Resonance contributions are considered negligible, owing to the near perpendicularity of the aryl ring to the porphyrin core, as is observed for all the tetraaryl-substituted porphyrins.[14] The ring current anisotropy effect of the porphyrins diminishes as one traverses down the ether fragments, and this is clearly manifested in the observation of singlets for 3,3′ and 4,4′ protons.

The phenyl proton resonances of the fully and partially substituted prophyrins are clearly discernible. Though the expected doublet resonance of the c protons is seen clearly, the doublet of a is found to be merged with the singlet of b, owing to the equivalence of positions (both being ortho). The resonance signal at δ 8.30 is assigned to the ortho protons of the free aryl group(s) in the partially substituted porphyrins, while the meta and para protons resonate as a multiplet in a region where the a and b protons resonate. The positions of the proton resonances of the free aryl group(s) are essentially the same as those observed for TPP.[15] In principle, one would expect atropisomers to exist in view of the bulkiness of the ether substituents restricting the rotation of the aryl group. The apparent equivalence of ortho protons and absence of an ortho substituent seem to indicate the nonexistence of such isomers in the present study.

The pyrrole proton resonances are highly characteristic of the substituted products. In the fully substituted TCP, a singlet resonance (δ 8.878) was observed, while in the partially substituted TriCP and MCP, the pyrrole protons resonate as a multiplet. The structure of this multiplet exhibits a mirror image relationship, indicating the complementarity of the phenyl substituents in the products. In DCP, two isomers are possible. The pyrrole protons in the adjacent cis- and opposite trans-substituted isomers should resonate as AB multiplets. However, the ^{1}H NMR spectrum of the synthesised DCP shows a multiplet structure indicating the presence of both isomers in the product.

All of the free base porphyrins exhibit a singlet for N–H at δ −2.7. The position of this resonance remains unaltered, showing the absence of any interaction.

The visible absorption spectra of the synthesized porphyrins exhibit Soret and Q bands chracteristic of an etio type.[16] The emission spectra of the free base porphyrins show fluorescence maxima at 660 nm followed by weak emission at 720 nm.

The above-detailed observations are consistent with the formulation of a structure for the macrocycle in which a porphyrin cavity is surrounded by the receptor crown ether voids. The ability of this supramolecular entity (~25 Å in diameter)[17] to complex cations and organic substrates is then of interest to study.

The incorporation of transition-metal ions[18] in the porphyrin core results in the metalated derivatives with vacant crown ether cavities in the periphery for further cation complexation. The visible and emission spectral properties of these metalloporphyrins are not significantly different from MTPPs. There are no major changes in the proton resonance spectra of the different metalated derivatives.[19]

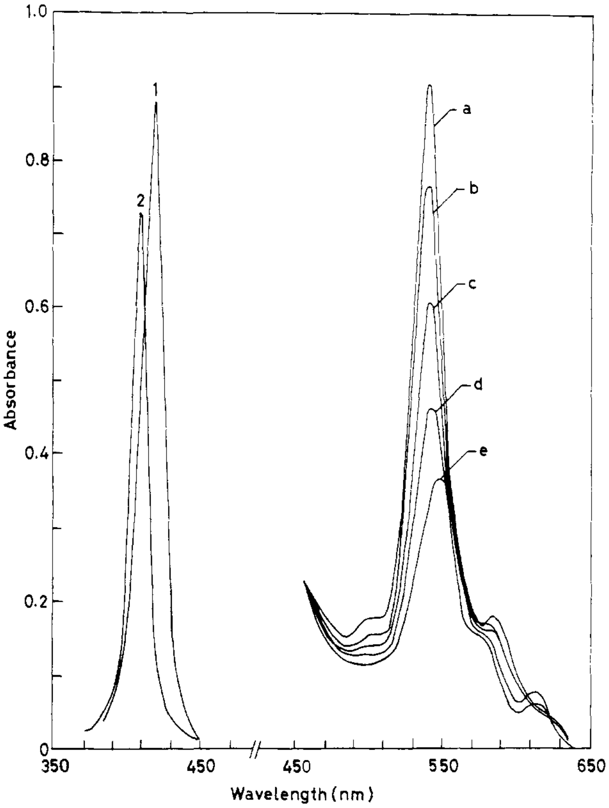


Figure 3. Visible absorption spectra of CuTCP in different solutions containing various concentrations of KCl in $CHCl_3$–CH_3OH (1:1): (1) CuTCP (2×10^{-6} M); (2) CuTCP + KCl (2×10^{-6} M + 4×10^{-4} M); (a) CuTCP (5×10^{-5} M). The various concentrations of KCl added to (a) are (b) 2×10^{-5} M, (c) 4×10^{-5} M, (d) 6×10^{-5} M, and (e) 1×10^{-4} M.

Table I. Soret Absorption (nm) of Crown Porphyrins and Their Cation Complexes

compound	free base	Zn	Cu
TCP	420	428	418
TCP + K^+	413	413	409
TCP + NH_4^+	414	414	409
TCP + Ba^{2+}	413	414	408
TriCP	419	427	416
TriCP + K^+	412	414	407
DCP[a]	419	426	
MCP[a]	418	424	

[a] The K^+ complexes of DCP and MCP and their metallo derivatives do not show any appreciable shift in the Soret region.

Cation Complexation. Addition of Na^+, Mg^{2+}, and Ca^{2+} to free base porphyrins and to their metallo derivatives in $CHCl_3$–CH_3OH (1:1) solvent mixture does not produce any appreciable changes in the visible absorption spectra of the macrocycles. However, marked changes are observed when K^+, NH_4^+, and Ba^{2+} ions are added to the macrocyclic porphyrins **1** and **2**. It is found that increasing addition of K^+, NH_4^+, and Ba^{2+} ions causes (a) reduction in intensity, (b) broadening, and (c) red shift (~10 nm) of the Q bands of **1** and **2** (Figure 3). These pronounced spectral changes can be interpreted by the specific complexation behavior of the macrocycles. It is known that K^+, NH_4^+, and Ba^{2+} ions form complexes with benzo-15-crown-5 in 1:2 (cation:ether)

---

(13) The observed difference in the chemical shift of the 1 and 2 protons and the 1′ and 2′ protons are δ 0.332 and 0.226, respectively. See ref 12.

(14) Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: New York, 1975; Chapter 8.

(15) Scheer, H.; Katz, J. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 10.

(16) Gouterman, M. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 1.

(17) CPK models were constructed. The distance of TCP from end to end is ~25 Å, assuming ether oxygens are coplanar with phenyl rings. The latter are perpendicular to the porphyrin plane. The *M* is 1375. Such molecules are termed "supra" molecules in accordance with Kotzyba-Hilbert, F.; Lehn, J. M.; Vierling, P. *Tetrahedron Lett.* **1980**, 941.

(18) The metal ion incorporation proceeds smoothly, and the reaction is completed within 1 h. It is observed that the appended crown ether moieties do not offer any steric hindrance in the metal incorporation reactions.

(19) The dipolar proton shifts observed in the Co(II) derivatives of TCP and TriCP are found to be much larger than those of the corresponding CoTPP/ZnTPP. The incremental hyperfine shifts for CoTCP relative to ZnTCP are pyrrole δ 7.143, *o*-H δ 5.144, and *m*-H δ 2.332.

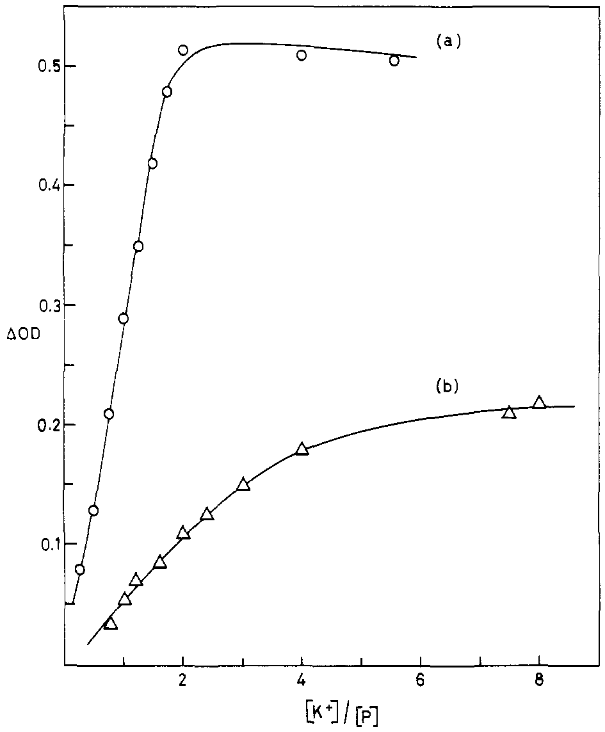


Figure 4. Plot of the decrease in optical density (ΔOD) vs. the ratio of cation to crown porphyrin concentrations ($[K^+]/[P]$) for (a) ZnTCP-K^+ interaction and (b) ZnTriCP-K^+ interaction.

stoichiometry while Na^+, Mg^{2+}, and Ca^{2+} form only 1:1 complexes.[20] Presuming that the appended crown ethers exhibit similar complexation behavior, two modes of cation encapsulation by **1** can be visualized. In case 1, the macrocycle can bind two cations, the cations being held by two adjacent crown ethers, leading to a stoichiometry of 1:2 (porphyrin macrocycle:cation), while in the alternate case (Case 2), four cations can be encapsulated by eight crown ether cavities from two macrocycles, each contributing four peripheral ether moieties, resulting in the formation of a 2:4 (porphyrin macrocycle–cation) complex. In either of these two modes, the overall stoichiometry of the cations to the binding system remains the same. However, the latter case implies dimerization of the macrocycle induced by the complexing behavior of the specific cations. The experimentally observed broadening, the red shift of the Q bands, and blue-shifted Soret absorption of the macrocycle in the K^+, NH_4^+, and Ba^{2+} ion complexation studies (Table I) are in accordance with the formulation of a dimer in these systems.[21] On the other hand, binding the cations with two peripheral crown ethers would not lead to major changes in the visible spectra, since the alignment of transition dipoles of the porphyrin chromophore remains unaltered in such complexation.

The decrease in intensity of the Q bands of the metallomacrocycles on successive addition of cations is depicted in a representative case in Figure 4. The stability of the dimer-K^+ complex is composed of a K^+–crown ether binding constant and a dimerization constant. The overall reaction can be represented as

$$2P + 4K^+ \rightarrow P_2(K^+)_4 \qquad (1)$$

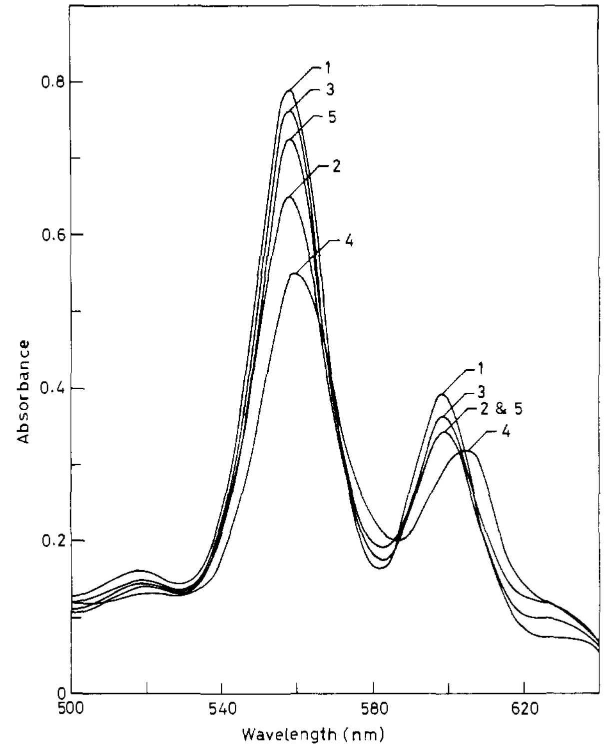


Figure 5. The visible absorption spectra of solutions containing (1) ZnTCP (5×10^{-5} M), (2) ZnTCP + NH_4ClO_4 (5×10^{-5} M + 6×10^{-3} M), (3)(2) + NaCl (3×10^{-3} M), (4)(1) + $Ba(Cl_2)$ (5×10^{-5} M + 6×10^{-3} M), and (5)(4) + NaCl (3×10^{-3} M) in $CHCl_3$-CH_3OH (1:9).

It is realized that (1) can either proceed through a prior dimer formation followed by cation complexation or a cation preferring two crown ether moieties from two independent porphyrins, thereby initiating the formation of a dimer. It is unlikely for a dimer to exist before the addition of a cation, especially in 10^{-5} M solutions, since the tetraaryl-substituted porphyrins predominantly exist as monomers unlike protoporphyrins.[22] We believe that the first addition of K^+ initiates dimer formation, providing sites for further complexation of K^+ by the peripheral ethers until it reaches a saturation of available sites. It is interesting to note that the saturation is reached even at 10^{-5} M concentrations of the cation. Viewed from the concentration exponents of (1), the stability of the dimer-K^+ complex is found to be 10^{23} L^5 mol^{-5}, which is several orders of magnitude greater than that observed from the K^+–crown ether interaction alone.[23] A possible reason for this high value is due to the dimerization of the macrocycle brought about by the K^+ ions rather than any electronic effects induced by the porphyrin on the crown ether oxygens. It is difficult to apportion the overall stability of the dimer-K^+ complex into the individual contributions arising from the stability constant of the K^+–crown ether complex and dimerization constant of the porphyrin.

The high selectivity for K^+ by ZnTCP is shown by the higher magnitude of the stability constant of the dimer-K^+ complex. The cation competition experiments provide additional support for this. It is observed that K^+ ions ($\sim 10^{-5}$ M) in the presence of a large excess of Na^+ ions ($\sim 10^{-2}$ M) produce perceptible charges in the visible spectrum of ZnTCP ($\sim 10^{-5}$ M) in alcohol, thereby allowing possible detection and estimation of K^+ ions at such low concentrations. Interestingly, an evidence for the lower stability of the NH_4^+ or Ba^{2+} complex is seen by the disaggregation brought about by the addition of Na^+ ions to the solutions containing the

---

(20) Kent Dalley, N. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M., Christiansen, J. J., Eds.; Academic Press: New York, 1978; Chapter 4.

(21) The blue shift of the Soret absorption in the dimers can be ascribed to purely excitonic interaction. (a) Blumberg, W. E.; Peisach, J. *J. Biol. Chem.* **1965**, *240*, 870. (b) Pasternack, R. F.; Huber, P. R.; Boyd, P.; Engasser, G.; Framcesconi, L.; Gibbs, E.; Fasella, P.; Cerio Venturo, G.; de C. Hinds, L. *J. Am. Chem. Soc.* **1972**, *94*, 451. (c) Das, R. R.; Plane, R. A. *J. Inorg. Nucl. Chem.* **1975**, *37*, 147. (d) Das, R. R., *J. Inorg. Nucl. Chem.* **1975**, *37*, 153. (e) White, W. E.; Plane, R. A. *Bioinorg. Chem.* **1974**, *4*, 21. For a comprehensive review, see: (f) White, W. I. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Chapter 7.

(22) The free base porphyrins TPP and ZnTPP do not dimerize in solution due to steric factors. However, tetracarboxylic acid (TPPC) and tetrasulfonic acid ($TPPS_4$) derivatives of Ni(II) and Cu(II) dimerize in aqueous solutions. The tetrapositive pyridinium and methylpyridinium porphyrin derivatives of Cu(II), Ni(II), and Zn(II) complexes do not aggregate.

(23) The benzo-15-crown-5-K^+ complex has a stability constant of $\sim 10^2$ L mol^{-1}. Frensdorff, H. K. *J. Am. Chem. Soc.* **1971**, *93*, 600.

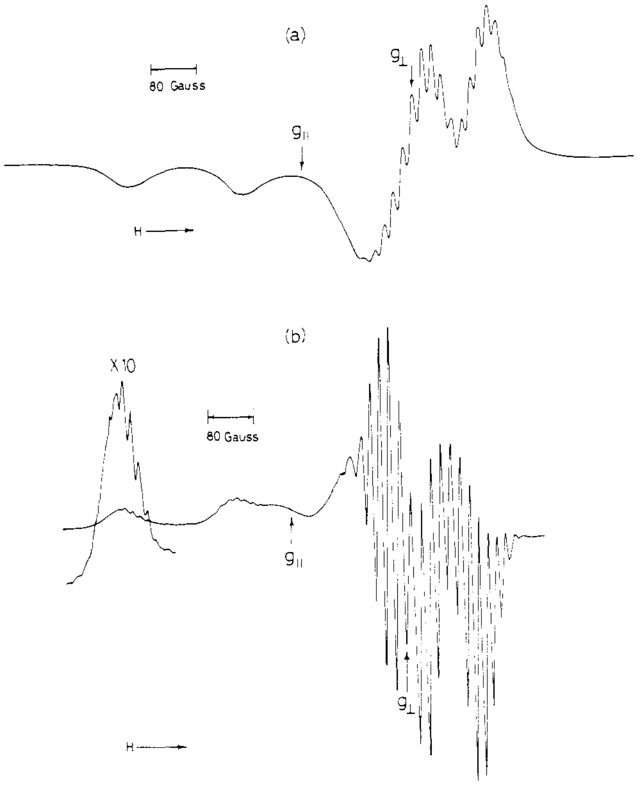


Figure 6. ESR spectra of (a) CuTCP and (b) CuTCP-Na^+ complex in $CHCl_3$-MeOH (1:1) glass.

dimer formed by NH_4^+ and Ba^{2+} ions (Figure 5).

Among the partially substituted porphyrins, the cation-induced dimer formation, as observed by the changes in the visible spectra, is noticeable only in ZnTriCP, though in principle ZnDCP and ZnMCP are also capable of forming a dimer. The K^+ complexation of ZnTriCP shows that attainment of saturation requires relatively higher concentration of K^+ compared to ZnTCP. This is reflected in the lower order of stability ($\sim 10^{16}$ L^4 mol^{-4}).

ESR Spectroscopy. The choice of Cu(II) and Co(II) in the porphyrin cavity provides an ESR probe to study the cation complexation by these macrocycles. The ESR spectra of the Cu porphyrins **1**, **2**, **3**, and **4** are typical of CuTPP. Addition of Na^+ ions to these porphyrins exhibits well-defined spectra compared to those of cation-free porphyrins (Figure 6). A possible reason for this is that the introduction of Na^+ into peripheral crown ether cavities prevents any likely aggregation of the macrocycle[24] due to strong repulsion among the two macrocycles induced by four Na^+ ions on the periphery of each of the macrocycle. The ESR parameters are, however, not affected by the Na^+ complexation.[25]

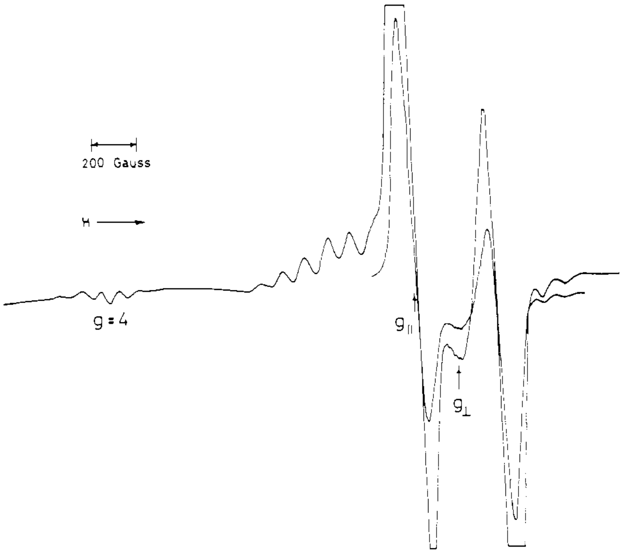


Figure 7. ESR spectrum of CuTCP-K^+ in $CHCl_3$-CH_3OH (1:1) glass. The half-field spectrum is shown.

Table II. Data on the Cation-Induced Dimers of Copper(II) Porphyrins[a]

compound	$g_\parallel$	$g_\perp$	$A_\parallel^{Cu}$, 10^4 cm^{-1}	$D_\parallel$, G	$D_\perp$, G	R, Å
$[CuTCP]_2(K^+)_4$	2.190	2.060	102.250	380	380	4.309[b] 4.226[c]
$[CuTCP]_2(NH_4^+)_4$	2.187	2.050	102.110	376	374	4.324[b] 4.241[c]
$[CuTriCP]_2(K^+)_3$	2.176	2.048	101.596	372	368	4.331[b] 4.263[c]
$[CuTriCP]_2(NH_4^+)_3$[d]		2.056			344	4.365[c]
$[CuDCP]_2(K^+)_2$	2.181	2.064	101.783	366	356	4.357[b] 4.321[c]
CuMCP-K^+[e]	2.181	2.044	205.690			

[a] The cations employed are K^+, NH_4^+, and Ba^{2+}. The addition of Ba^{2+} ions to CuTCP and CuTriCP results in the dimers as seen by the two strong lines in the perpendicular region. However, the interplanar distances in these dimers could not be calculated, due to the preponderance of CuTCP and CuTriCP lines. [b,c] Values of interplanar distances calculated from parallel (*b*) and perpendicular (*c*) regions of the spectra. [d] Evaluation of parameters in the parallel region could not be carried out because of the overlap of pure CuTriCP lines. [e] The ESR parameters are the same as those observed for CuMCP.

Dramatic changes in the ESR spectra of copper(II) porphyrin macrocycles are observed by the addition of K^+ ions (Figure 7). The four parallel lines of the Cu(II) ($I = {}^3/_2$) are decomposed into two sets, each set being split into seven lines. In addition to this, two strong perpendicular transitions, without nitrogen hyperfine splitting, are observed in the $g = 2$ region. This is typical of a triplet state with axial symmetry. The hyperfine structure indicates the presence of two equivalent Cu(II) nuclei. Strong support for the existence of an axial dimer stems from the appearence of a half-field spectrum with seven lines of equal spacing of 75 G. The signals are isotropic and the hyperfine coupling constants in both the $g = 2$ and $g = 4$ regions were found to be one-half of the coupling constants observed for the monomeric copper(II) porphyrin.

The well-resolved ESR spectra of the cation induced dimers permit evaluation of ESR parameters (Table II). The similarity in g and A values of the dimer with those of the cation-free copper(II) porphyrin suggests that the two Cu(II) are in the plane of the porphyrin core. The zero-field splitting parameter, D, calculated both in parallel and perpendicular regions was used to compute the distance between the two Cu(II) nuclei in the dimer, making use of the expression developed by Chasteen and Belford[26] (Table II). The observed Cu–Cu distance of ~4.20 Å is in agreement with the reported values of the covalently linked dimers[1g] as well as those derived from radical dimerization,[27] indicating coaxial symmetry rather than displaced geometry for the dimer. A reasonable structure for the dimer consistent with the observed Cu–Cu separation is possible at this stage (Figure 8). The approach of two Cu(II) nuclei is induced by the binding of the peripheral crown ethers to the K^+ ions. Sandwiching the four K^+ ions by eight crown ether moieties, one from each of the

---

(24) Normally the ESR spectra of pure MTPPs (10^{-3} M in toluene glass) are not not-so-well resolved. However, the addition of acceptors improves the quality of the spectra; this has been attributed to possible disaggregation of MTPPs. Walker, F. Ann. *J. Magn. Reson.* **1974**, *15*, 201.

(25) The $g_\parallel$ and $g_\perp$ values for the Na^+ complexes of CuTCP, Cu-TriCP, CuDCP, and CuMCP are 2.183 ± 0.003 and 2.045 ± 0.005. These are the same as those observed for the pure Cu(II) complexes of the substituted porphyrins. There are no significant differences in the $A_\parallel^{Cu}$ $A_\perp^{Cu}$, and $A_\perp^{N}$ values (2.04×10^{-4}, 32×10^{-4}, and 16.2×10^{-4}) in going from the pure copper porphyrins to the Na^+ complexes.

(26) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* **1970**, *9*, 169.

(27) Mengersen, C.; Subramanian, J.; Fuhrhop, J.-H. *Mol. Phys.* **1976**, *32*, 893.

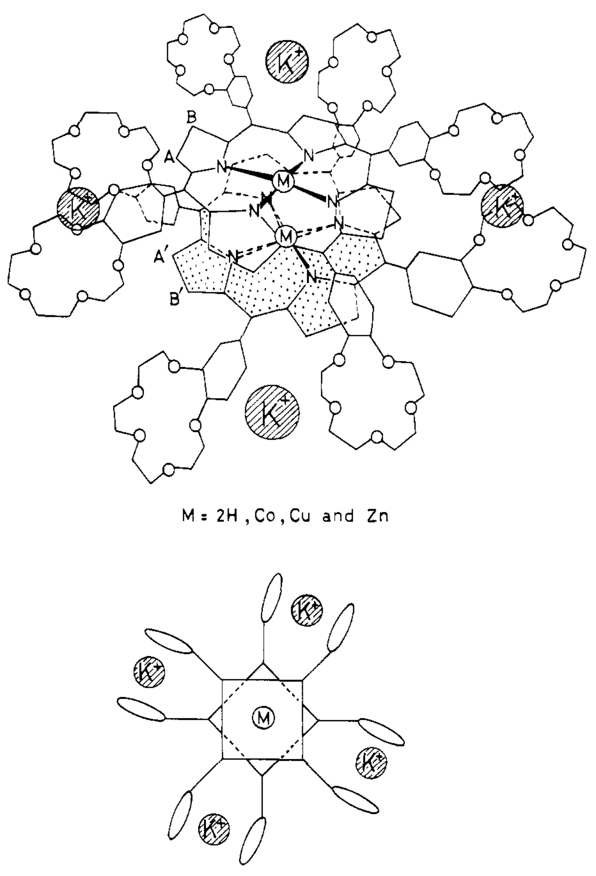


Figure 8. A possible structure for the K^+-induced dimer of MTCP. The complexed K^+ ions are shown. Rotation of the porphyrin planes in the dimer is depicted in the bottom of the figure.

porphyrin macrocycle complexing a K^+ ion, would be sterically favored if one of the macrocycles is rotated by ~45° with respect to the other, such that the K^+ ions are held laterally by the crown ether cavities. This rotation still retains the coaxial symmetry of the dimer. In the X-ray structure of KI (benzo-15-crown-5)$_2$, the two ether moieties are separated by ~3.8 Å and the plane of the ether oxygens is collinear with the aryl part.[28] Presuming that a similar situation exists in the K^+ complex of the dimer, the constructed CPK models of the dimer structure reasonably fit into the Cu–Cu separation of ~4.2 Å. The counter anions, Cl^- and CNS^-, in these dimers are isotropically distributed around the macrocycle without any interaction with the central Cu(II) ion, either in the bridging position or in the axial positions, as evidenced from the small magnitude of J(Cu–Cu) and J_{d-d} values.

Interestingly, the tri- and disubstituted porphyrins of Cu(II) also form dimers when complexed with K^+ ions, with the retainment of axial symmetry. In view of the unsymmetrical substitution in $[CuTriCP]_2(K^+)_3$ and $[CuDCP]_2(K^+)_2$, one would expect a displaced geometry. However, the results obtained here indicate the tendency for high levels of organization in these systems. The Cu–Cu separation increases in these dimers from TCP to DCP, indicating inefficient packing by the partially substituted porphyrins. This is further evidenced by the appearance of signals arising from both the monomer and dimer in CuDCP and the absence of half-field spectrum in the $[CuMCP]_2(K^+)$.

The ESR spectra of the cation-induced dimers of cobalt(II) porphyrin macrocycles are often plagued with Co^{II}–O_2 lines. We have not been able to obtain a good Co(II) dimer spectrum, although strong indication to its formation is clearly demonstrated in the visible spectral studies.

NMR Spectroscopy. Although the proton resonances of the free bases and their metallo derivatives are assignable, the ^1H NMR spectra show a large dependency on the nature of the solvent, indicating greater solvent anisotropic effects. The cation complexation studies using the ^1H NMR method is thus limited to solubility factors. In the present study, we employed solvent mixtures, $CDCl_3$–CD_3CN (1:1), containing 0.1–0.2 mL of $(CD_3)_2SO$ to prevent precipitation of the complex, to record the ^1H NMR spectra.

Addition of Na^+ ions to ZnTCP or ZnTriCP does not produce any perceptible changes in the NMR spectra whereas complexation with K^+ ions induces major spectral changes in both the high- and low-field regions (Figure 9). First, the complexity of the spectrum increases with the appearence of a greater number of multiplets. Although no detailed assignments of these multiplets are possible, an indication as to the restricted rotation of the OCH_2CH_2O groups of the ether is suggested. Secondly, a general downfield shift of the ether protons relative to the free ether exemplifies the effect of K^+ complexation.

It is interesting to note that the a and b protons of the aryl groups are shifted upfield and downfield, respectively, to about the same extent (δ ~0.58) in the dimer. A possible explanation for this differential shift is due to the lateral complexation of the K^+ ion by the crown ether moieties of the porphyrin macrocycle. Such complexation would position the b protons in a face-to-face orientation, thereby deshielding these protons from the porphyrin core, and dispose the a protons in the shielding zone. The c protons do not experience any such effects. Strong support for this assignment of these proton resonances stems from the weak 1,3 coupling effects (~2–3 Hz) experienced by the a and b protons.

More dramatic effects are observed in the low-field region where pyrrole protons resonate. The singlet resonance of ZnTCP is decomposed into two doublets on complexation with K^+ ion followed by an upfield shift of δ ~0.30. The shifts are in accordance with the formation of a dimer similar to that observed for a covalently linked cofacial dimer.[29] The appearance of two doublets suggests the presence of two sets of nonequivalent pyrrole protons in the dimer. It is recognized that a 45° rotation of one of the mcrocycles with respect to the other would orient the pyrrole protons in two different orientations. The A and A′ protons from each of the porphyrins constituting the dimer would be disposed nearer to the complexing crown ether moieties, while the B and B′ protons from each would be away from the ether moieties resulting in the differential shift. The ^1H NMR spectra of the $[CoTCP]_2(K^+)_4$ provide additional support for this, where an upfield shift of δ ~0.40–0.50 for the pyrrole protons is observed.

Emission Spectroscopy. The emission bands of the free base porphyrins and their Zn(II) derivatives are found to be slightly red-shifted relative to the TPP and ZnTPP. Addition of methanolic solutions of Na^+, Mg^{2+}, and Ca^{2+} to the solution of the free base porphyrins or their Zn(II) derivatives (5×10^{-5} M) in $CHCl_3$ does not purturb the emission behavior of the porphyrin.[30] However, addition of K^+ to these solutions leads to quenching of the macrocycle fluorescence. It is noticed that the concentration of K^+ required to quench the fluorescence intensity of ZnTCP or ZnTriCP is very much less than the concentration of the cation required to reduce the optical density of the porphyrin in the ground state. The results of the quenching studies are represented in the corrected Stern–Volmer plot (Figure 10).

A possible explanation for the observed quenching can be ascribed to the specific K^+ ion complexation behavior of these macrocycles. It was shown earlier that encapsulation of K^+ ions by the peripheral ether moieties leads to the formation of dimers with the porphyrins stacked plane to plane. Such an arrangement would promote weak incipient CT interactions. The singlet–singlet emission in the porphyrins and in their metal derivatives is governed by the efficiency of the intersystem crossing to the low-lying triplet excited states in these systems.[16] The ISC efficiency can be enhanced by favorable spin–orbit (SO) coupling and

---

(28) Mallinson, P. R.; Truter, M. R. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1818.

(29) The shifts observed for the pyrrole and phenyl protons in the dimers described in the present study are much larger than those reported in ref 1b.

(30) Even the addition of Cs^+ does not perturb the emission intensity of the ZnTCP or ZnTriCP, which shows the absence of any heavy atom effect.

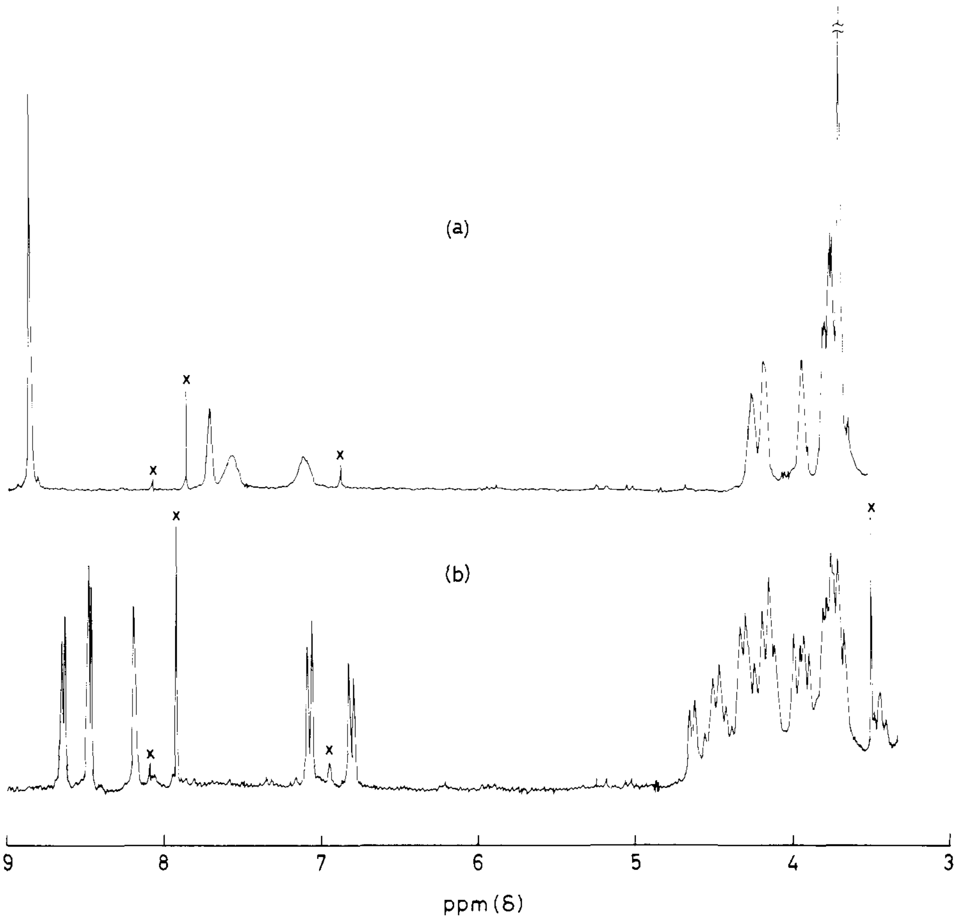


Figure 9. The ^{1}H NMR spectra of (a) ZnTCP and (b) ZnTCP–K$^+$ in the solvent mixture containing C^{2}HCl$_3$, C^{2}H$_3$CN, and (C^{2}H$_3$)$_2$SO. The impurity and solvent resonances are marked ×.

Franck–Condon parameters. It is known that the SO coupling can be enhanced in the porphyrins either by halogen substitution in the periphery[31] by use of an external heavy atom.[32] It is worthwhile to consider the possibility of the existence of low-lying triplets in the dimers formed in the present study. In the synthesized covalently linked cofacial dimers, the singlet–singlet emission persists even though CT interactions between the porphyrin planes exist. We believe that the geometry of the dimer plays an important role in bringing about the effectiveness of spin–orbit coupling in the system, as was pointed out by Chandra and Lim[33] in naphthalene dimers. The steric configuration of the dimer, [ZnTCP]$_2$(K$^+$)$_4$, as proposed from our results requires an ~45° rotation of one of the porphyrins with respect to the other. This promotes σ (lone pair orbitals on N) $-\pi$ (π of the porphyrin manifold) interactions leading to the formation of triplet states, thereby enhancing the singlet–triplet transitions. The reasonableness of our belief is evidenced by the lack of such interactions in the cofacial dimers where the porphyrin planes are not displaced or rotated but stacked one over the other.[34]

It is realized that the K$^+$ ion is an effective quencher of the crown-porphyrin fluorescence, since a tenfold excess of K$^+$ is enough to quench completely the fluorescence of the porphyrin (1 × 10^{-5} M). The corrected S–V plot for the quenching of ZnTCP by K$^+$ is nonlinear and curves upward. The deviations from linearity are often explained in terms of collisional mechanisms where a certain fraction of the excited states are deactivated instantaneously by the quencher molecule through random collisions. The local distribution of the quencher molecules in the ordered system is described by the term V in the exponent $V[Q]$ introduced in the Stern–Volmer equation to correct for nonlinearity.[35] In the present studies, we suggest that the nonlinearity

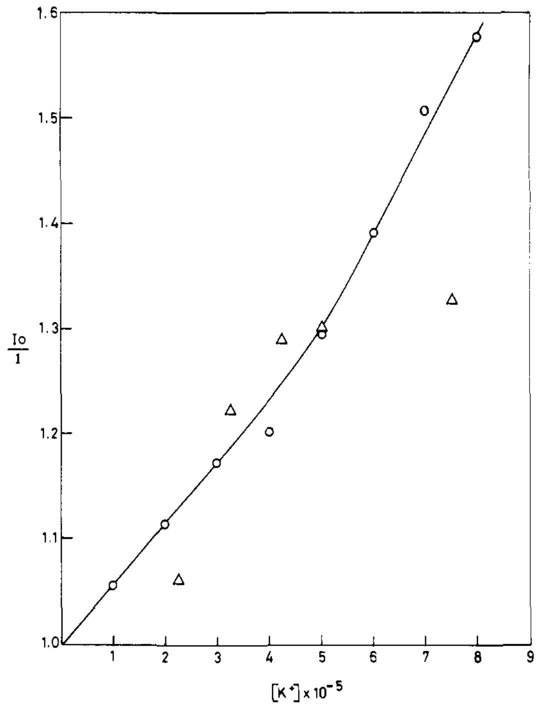


Figure 10. The corrected Stern–Volmer plot of ZnTCP (○) and ZnTriCP (△) with K$^+$ ions.

---

(31) Solovĕr, K. N.; Grady ushko, A. T.; Tsvirko, M. P. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1972**, *36*, 1107.

(32) (a) Egorova, G. D.; Mashenkov, V. A.; Solovĕr, K. N.; *Biofizika*, **1973**, *18*, 40. (b) Gradyushko, A. T.; Sevchenko, A. N.; Solovĕr, K. N.; Tsvirko, M. P. *Izv. Akad. Nauk SSSR, Ser. Fiz.* **1970**, *34*, 636.

(33) Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1977**, *45*, 79.

(34) The rotation of one of the porphyrin planes by ~45° would lead to effective coupling, resulting in $(\sigma\pi)(\pi\sigma^*)$ configurations, thereby enhancing the ISC efficiency.

arises from the dimer formation, which deactivates the singlet states of the monomer through an excimer formation.[36] The Stern–Volmer plot for the K^+ quenching of ZnTriCP deviates markedly from linearity. It is difficult to comprehend this behavior, though it is suggested that the compactness of the dimer with the retainment of geometry (as percieved for ZnTCP) may not strictly hold in ZnTriCP, since only three crown ethers of each of the porphyrins are involved in binding three K^+ ions.

Conclusion

Porphyrins containing peripheral molecular cavities have been synthesized. We examined the cation complexation behavior of these interesting macrocycles and derived a good deal of information about their solution structures.

The structures of the synthesized molecules are consistent with the formulation of supramolecular entities possessing a central cavity (described by four nitrogens) surrounded by one or more lateral circular voids (defined by five ether oxygens). These macrocycles are shown to complex cations. The sizes of the cations that are not compatible with the dimensions of the crown ether voids induce dimerization of the porphyrin. The dimer formation is thus specific for cations (K^+, NH_4^+, and Ba^{2+}) and primarily governed by the mismatch in sizes of the cation and ether voids. The dimerization leads to interesting changes in the visible, NMR, ESR, and emission spectral features. The magnitude of the blue shift in the Soret absorption $[MTCP]_2(K^+)_4$ complexes decreases in the order Zn > Cu > Co > 2H. It has been suggested that the magnitude of the blue shift in Soret absorption in the covalently linked porphyrins is related to the interplanar separation of the porphyrin planes. Relying on this premise, it is suggested that the dimer formed by Zn(II) should have an interplanar distance less than Cu(II) (~4.2 Å°).[37] Furthermore, the dimers reported here are unlike those formed by the addition of 1:1 electrolytes to either tetracarboxylated or tetrasulfonated porphyrins. This once again underlies the importance of the specificity displayed by the cations.

The emission properties of the cation complexation studies of these macrocycles lead to interesting results. The complete quenching of the fluorescence of ZnTCP by K^+ ions provides an interesting fluorescence probe for K^+ ions. These systems are of importance in the development of specific probes for K^+ ions. The biochemical significance of the free base crown porphyrins and their metal derivatives as ionophores was studied. Preliminary experiments have shown that these porphyrins are able to penetrate the membrane in the respirating rat liver mitochondria and capture intracellular K^+ ions. This was followed by a change in the fluorescence consequent to K^+ uptake. It is shown that the inhibition of oxidative phosphorylation depends on the nature of the metal ion at the central cavity as reflected in the respirative coefficient index values (unpublished work). The novel crown ether–porphyrin system described above should prove valuable as a highly selective K^+ ionophore and will be a potentially useful probe for the study of cation transport across biological membranes.

Acknowledgment. This work is being supported by a grant from the Department of Science and Technology, Government of India, New Delhi. One of the authors, VT, is thankful to the University Grants Commission, New Delhi and Department of Atomic Energy, Trombay, Bombay, for the fellowship.

Registry No. 1, 81294-37-3; **2**, 81294-38-4; *cis*-**3**, 81294-39-5; **4**, 81294-40-8; CuTCP, 81293-80-3; CuTriCP, 81293-81-4; *cis*-CuDCP, 81293-79-0; CuMCP, 81293-82-5; ZnTCP, 81315-54-0; ZnTriCP, 81293-83-6; CoTCP, 81293-84-7; CoTriCP, 81293-85-8; Na, 7440-23-5; K, 7440-09-7; NH_4^+, 14798-03-9; Ba, 7440-39-3; benzo-15-crown-5 4′-aldehyde, 60835-73-6; pyrrole, 109-97-7; benzaldehyde, 100-52-7; *trans*-**3**, 81294-41-9; *trans*-C_4DCP, 81293-86-9.

---

(35) Eftnik, M. R.; Ghiron, C. A. *J. Phys. Chem.* **1976**, *80*, 486.

(36) A possible scheme is

$$P \xrightarrow{h\nu} P^*$$

$$P^* + K^+ \rightarrow P^*\cdots K^+$$

(an encounter complex) deactivation step being $[{}^1P^*\cdots K^+\cdots {}^3P^*]$ leading to dark P_2K_4 (P = crown porphyrins).

(37) In tetrasulfofthalocyanines of Cu^{2+} and VO^{2+}, the relative ability of dimer formation is in the order $Cu^{2+} > 2H > VO^{2+} \sim Zn^{2+} > Co^{2+}$. See: Boyd, P. D. W.; Smith, T. D. *J. Chem. Soc., Dalton Trans.* **1972**, 839.