temperature. Between 200 and 220 nm the MCD spectra are less reliable. Absorption spectra were measured on a Perkin-Elmer Hitachi 200 spectrophotometer. Solvents (Merck Uvasol) were dried and used without further purification.

Acknowledgment. Thanks are due to Mr. J. van der Helm for the preparation of some of the complexes and to Mr. A. Terpstra for measuring some of the absorption spectra.

Registry No. $Cr(CO)_5PCl_3$, 18461-41-1; $Cr(CO)_5PPh_3$, 14917-12-5; $Cr(CO)_5PMe_3$, 26555-09-9; $Cr(CO)_5$(thiazole), 55293-31-7; $Cr(CO)_5$py, 14740-77-3; $Cr(CO)_5$pyr, 66179-02-0; $Cr(CO)_5$(pyridazine), 54070-89-2; $Cr(CO)_5NMe_3$, 15228-26-9; $Cr(CO)_5$pip, 15710-39-1; $Mo(CO)_5$pip, 19456-57-6; $W(CO)_5$pip, 31082-68-5.

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Donor Properties of Metallomacrocyclic Tetrapyrrole Pigments with *sym*-Trinitrobenzene

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The interactions of metallo derivatives of macrocyclic tetrapyrrole pigments, pheophytin *a* (pheo), phthalocyanin (phth), and tetraphenylporphyrin (TPP) with *sym*-trinitrobenzene (TNB) have been studied with use of spectroscopic methods. These macrocyles form 1:1 molecular complexes with the acceptor. The association constants (K) for the interactions follow the decreasing order of binding as pheo > phth > TPP. The divalent metal ions influence the values of K for the various metallo TPP derivatives, and the relative order of stabilities decrease as Co > Cu ≈ VO > Ni > Zn. The stereochemistry of M(TPP) and the electronic configuration of the metal ions are shown to contribute to the magnitudes of K. The acceptor strongly quenches the fluorescence of the metallo macrocycles, and the quenching constant decreases as pheo > phth > TPP. The formation of exciplexes is postulated on the basis of the rate of bimolecular quenching constants and solvent effects.

Studies on molecular complexes of natural and synthetic tetrapyrrole pigments with diverse organic molecules have received considerable attention in the past few years.[1-5] In principle, the tetrapyrrole pigments can function both as a donor and an acceptor.[6] Introduction of metal ions can alter this behavior depending on their oxidation states and coordination numbers. In an earlier study involving porphyrins and various acceptors, it has been suggested that charge-transfer forces contribute to a small extent to the binding strength of these complexes.[7] We have been interested in the molecular complexation of macrocyclic systems in general, and the present study is directed toward the ability of tetrapyrrole pigments to form molecular complexes with a π acceptor, *sym*-trinitrobenzene (TNB), and the functional role of metal ions in the binding characteristics. The major objective is to elucidate the mode and site of interaction between donor and acceptor so that the additional knowledge of properties and functions of bioanalogues, chlorophyll, and heme might be gained.

The tetrapyrrole pigments chosen for the study are pheophytins *a* (pheo), phthalocyanin (phth), and 5,10,15,20-tetraphenylporphyrin (TPP) as their Zn(II) derivatives. The different macrocycles provide a range of sizes and chromophores; TPP is a N_4 chromophore with four benzene rings at the 5, 10, 15, and 20 positions, phth is a N_8 chromophore with four benzene rings fused to the pyrrole moieties, and pheo is a N_4 chromophore with an additional cyclopentanone ring in the tetrapyrrole skeleton (Figure 1). The TPP derivatives of the different divalent metal ions VO, Co, Ni, Cu, Zn, Cd, and Pd are chosen for study to define the functional role of these in the donor capacity of the pigments. Electronic absorption spectral methods have been used to evaluate the binding constants and associated thermodynamic properties. Emission data are also used to probe into the possible formation of exciplexes in these systems. The ^{1}H NMR measurements are valuable in ascertaining the site of interaction in these complexes. The ESR data are useful in assessing the axial perturbation on complexation. The results of these studies are informative in arriving at the nature of the stabilization forces and the relative orientations of the donor and acceptor.

Experimental Section

The Zn(II) derivative of pheo, phth, and TPP were prepared according to the published methods.[8-10] TPP was obtained from Aldrich Chemicals and the metal derivatives were synthesized and purified as described elsewhere.[9] TNB was obtained from BDH and crystallized twice from benzene (mp 122 °C). The solvents were purified and distilled and purged with pure dry nitrogen before use. The visible absorption spectral method has been used for the determination of association constants. The sample handling and other details concerning the spectrometers used are the same as described earlier.[11] The concentration of the metallo macrocycles was held constant (10^{-5} M), and that of TNB was varied (10^{-4}–10^{-1} M). A Perkin-Elmer MPF 44A spectrometer was used for fluorescence measurements. The ESR spectra were recorded on a Varian E109 ESR spectrometer using toluene glasses.

Results and Discussion

The visible absorption spectra of the metallomacrocycles exhibit well-defined intense absorption bands, the position of which depends on the nature of the metal ion and the macrocycle. Addition of TNB lowers the intensities of these bands, indicating the formation of molecular complexes. More than

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Table I. Stability and Thermodynamic Parameters of Metallomacrocyclic Interaction with *sym*-Trinitrobenzene

complex	solvent	temp, °C	K, dm^{-3} mol^{-1}	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J deg^{-1} mol^{-1}
Zn(pheo)TNB	ether	25.0	261 ± 8.0	6.30 ± 0.6	24.90 ± 2.0
		14.5	277 ± 10.0		
		9.5	303 ± 10.0		
	CCl_4	25.0	40 ± 3.0		
	$CHCl_3$	25.0	20 ± 2.1		
Zn(phth)TNB	THF	25.0	180 ± 7.0	6.90 ± 0.6	19.80 ± 2.3
		13.0	197 ± 6.0		
		5.5	220 ± 9.0		
	acetone[a]	25.0	10.0		
Zn(TPP)TNB	ether	25.0	103 ± 7.0		
	$CHCl_3$	25.0	0.50 ± 0.05	120.0 ± 17.0	406.0 ± 61
		14.5	10.80 ± 0.50		
		5.5	14.50 ± 0.90		
	nitrobenzene[b]	25.0	0.6		
Co(TPP)TNB	$CHCl_3$	25.0	86.0 ± 2.0	14.0 ± 1.0	10.0 ± 1.0
		13.0	107.0 ± 2.0		
		5.5	128.0 ± 2.5		
Cu(TPP)TNB	$CHCl_3$	25.0	45.0 ± 2.0	20.0 ± 1.0	34.5 ± 1.0
		14.5	61.0 ± 1.5		
		5.0	81.0 ± 2.0		
Ni(TPP)TNB	$CHCl_3$	25.0	17.0 ± 0.8	30.0 ± 2.0	80.0 ± 5.0
		14.5	24.0 ± 1.2		
		5.0	41.0 ± 1.1		
Cd(TPP)TNB	ether	25.0	126.0 ± 3.0	13.0 ± 1.0	3.3 ± 0.5
		14.0	166.0 ± 4.0		
		5.0	184.0 ± 3.0		
VO(TPP)TNB	$CHCl_3$	25.0	46.0 ± 1.5		
Pd(TPP)TNB	$CHCl_3$	25.0	118.0 ± 3.0		

[a] Cartin, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2021. [b] Gouterman, M.; Stevenson, P. E., Stevenson, J. *J. Chem. Phys.* **1964**, *37*, 2266.

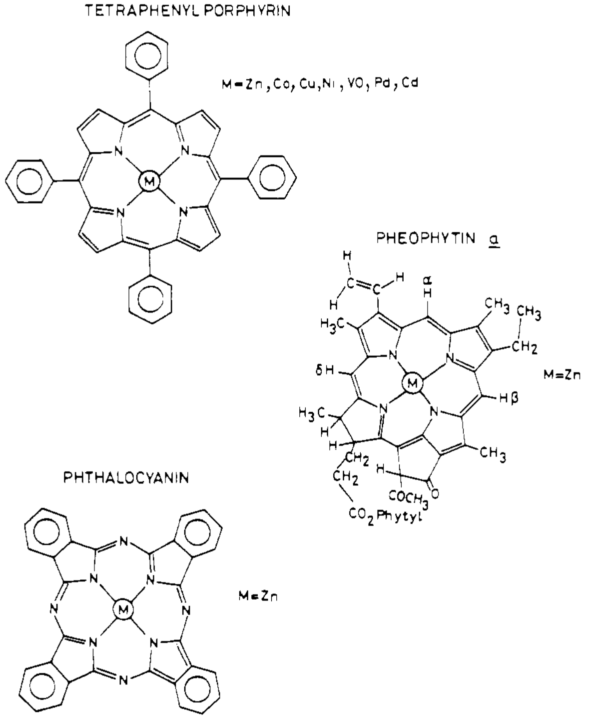

Figure 1. Structure of the metallomacrocycles.

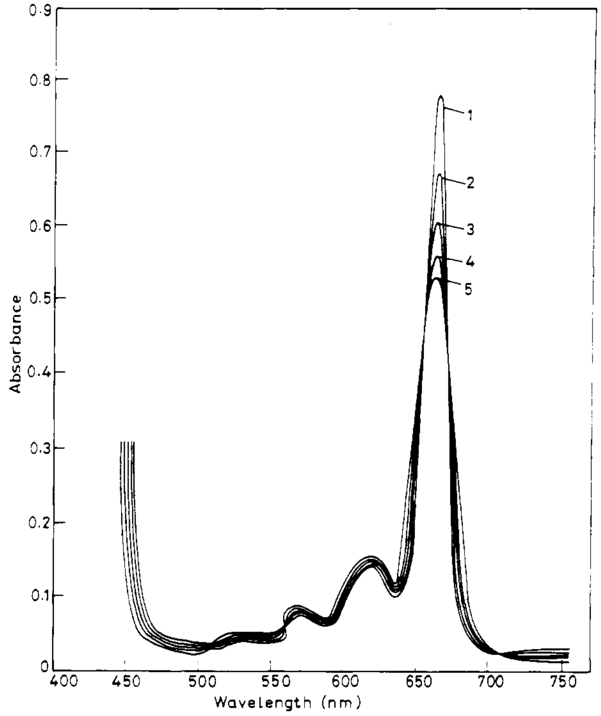

Figure 2. Visible absorption spectra of ether solutions of (1) Zn(pheo) (1×10^{-5} M) containing the following concentrations of TNB at 25 °C: (2) 1.2×10^{-3} M; (3) 5.8×10^{-3} M; (4) 1.0×10^{-2} M; (5) 4.9×10^{-2} M.

one isobestic point are observed in the absorption spectra of the solutions containing metallomacrocycles and different amounts of TNB (Figure 2). The binding constants, K, were evaluated with use of expression of Nash[12] (eq 1) where C_A

$$\frac{1}{C_A} = \frac{d^\circ}{d^\circ - d}[(K - K\epsilon_{DA}/\epsilon_D) - K]$$

is the concentration of the free acceptor, d° is the optical density of the pure donor, d is the total optical density of the complex and the donor, and ϵ_{DA} and ϵ_D are the molar extinction coefficients of the complex and the donor, respectively. The values of K are real and relatively free from errors and checked with use of Deranleau's saturation factor criteria.[13] The linear nature of the plot $1/C_A$ vs. $d^\circ/d^\circ - d$ (Figure 3) supports 1:1

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(12) Nash, C. *J. Phys. Chem.* **1960**, *64*, 950.

(13) Deranleau, D. A. *J. Am. Chem. Soc.* **1969**, *91*, 4044.

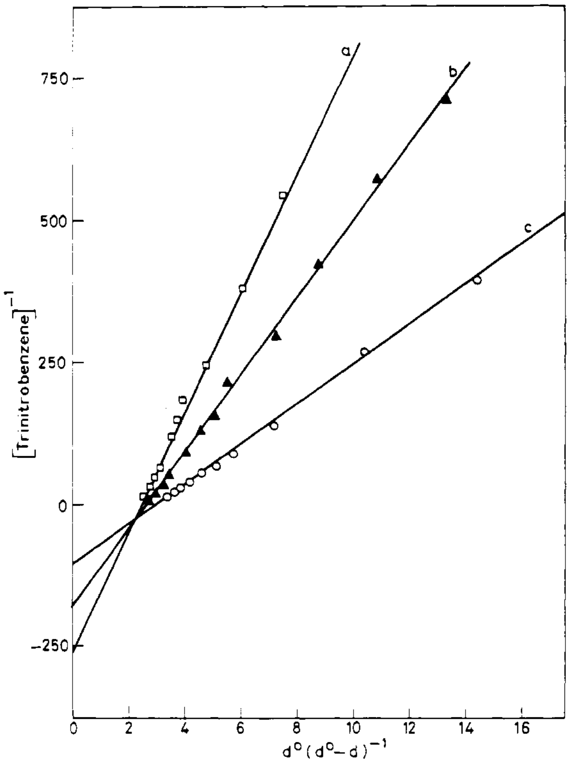

Figure 3. Plot of $1/C_A$ vs. $d°(d° - d)^{-1}$ for (a) Zn(pheo), (b) Zn(phth), and (c) ZnTPP interaction with TNB at 25 °C.

stoichiometry of the complexes. It is interesting to note that, though the macrocycles contain more than one π system for complexation, only 1:1 complexes are formed. The K values and the other thermodynamic parameters for Zn(II) derivatives of different macrocycles are given in Table I.

An inspection of the Table I reveals that the values of K, within the limits of uncertainity, decrease with ring size of the macrocycle as pheo > phth > TPP. The interesting gradation in the K values is fortuitous, and it will be difficult to explain this except to state that the large value for pheo implies stronger interaction in the ground state relative to other macrocycles. A possible explanation that this can arise from the partial removal of an electron from a π orbital of pheo to a π^* orbital of TNB in the formation of an electron donor–acceptor complex leading to an electron-deficient pheo which is stabilized by conjugation with the electron-rich centers (keto >C=O of the cyclopentanone ring) appears reasonable. The K value of Zn(pheo) is about 3 times that of metal-free pheo, indicating the role of metal ion in the enhanced stability of the complex.[14]

The role of solvents in governing the magnitude of K in the interaction of the metallomacrocycles with TNB is shown in Table I. It is worthy to note that there is no aggregation of the donor or acceptor species in solution under the experimental conditions employed in the present study. The values of K in different solvents vary as $Et_2O > CCl_4 > CHCl_3$ while the polarity as reflected in the dielectric constant values follow the order $CHCl_3 > Et_2O > CCl_4$. The above finding is in contrast to the normally observed trend that the poorest ionizing solvent gives rise to the highest values of K for association between neutral donor and acceptor. The dependency of K on the nature of the solvent can either arise from the donor or acceptor behavior of the solvent with the interacting molecules or from the ability of the solvent to participate in hydrogen bonding with the component molecules.[15] Though it is difficult to quantify these interactions, it seems probable that these effects are significant in contributing to the values of K.

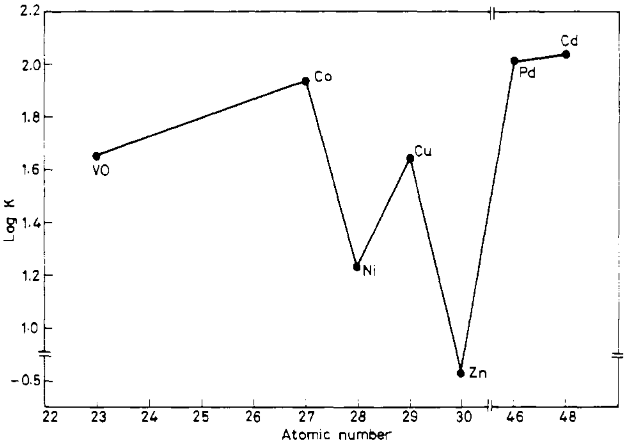

Figure 4. Plot of log K vs. the atomic number of the metals in the metallo TPP derivatives.

The ΔH and ΔS values of Zn(pheo *a*) and Zn(phth) are almost the same within the limits of experimental error and is significantly different in ZnTPP. It is reasonable to presume that the factors contributing to ΔH and ΔS values in the molecular complexing system originate from the ability of two interacting molecules to pack with one another efficiently and orientation effects (leading to maximum overlap), respectively. The large decrease in ΔH and ΔS values in ZnTPP indicates an efficient packing of the molecules in the complex. Attempts to crystallize the complexes have so far not been successful.

The data presented in Table I afford an opportunity to relate the effect of the nature of the metal ion in the cavity on the stabilities of the molecular complexes formed with TNB.

The association constants of the different metallomacrocycles follow the order Co > Cu ≈ VO > Ni > Zn for the first-row transition series and the relative stabilities follow Cd > Zn and Pd > Ni in a given group (Figure 4). The order of stabilities, however, differs from those of the Irving–Williams series, and this departure can be ascribed to the noncoordinative but yet specific interaction in the molecular complexes. The important factors that govern the magnitude of association constants are the stereochemistry of the metallomacrocycle and the intrinsic nature of the metal ions.

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 values of K, if there exists no specific site interaction. In the plane to plane overlap, the stabilizing contribution of delocalized π bonding to the energy of the porphinato core is maximized by a conformation of D_{4h} symmetry. Any deviation from the planarity would then affect adversely the magnitude of K. It is seen that in the case of Ni, Cu, and Pd there is S_4 ruffling of the molecule departing the geometry from the ideal planarity which almost satisfies the requirement of D_{2d} symmetry, while Zn(II) is positioned in the plane of the porphyrin core.[16,17] However, the value of K is the least for the Zn(II), indicating that the electronic configuration of the metal ion plays an important role in governing the magnitude of K (vide infra). The low-spin

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(14) Larry, J. R.; Vanwinkle, Q. *J. Phys. Chem.* **1969**, *73*, 570. The metal-free pheophytin–TNB association in ether has a value of 81 dm^{-3} mol^{-1}. The binding constant for the Mg^{II} pheo–TNB complex (228 dm^{-3} mol^{-1}) is slightly lower than that observed for the Zn(pheo)–TNB interaction.

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(16) (a) Smith, K. M. In "Stereochemistry of Porphyrins and Metalloporphyrins"; Elsevier: New York, 1975. (b) Dolphin, D. In "Porphyrin Stereochemistry"; Academic Press: New York, 1978; Vol. III.

(17) Scheidt, W. R.; Kastner, M. E.; Hatano, K. *Inorg. Chem.* **1978**, *17*, 706.

Table II. ESR Parameters of Metal-TPP Complexes of *sym*-Trinitrobenzene in Toluene Glasses

complex	$g_\parallel$	$g_\perp$	$10^3A_\perp$, cm^{-1}	$10^3A_\parallel$, cm^{-1}	$10^3A_\perp^N$, cm^{-1}	$10^3A_\parallel^N$, cm^{-1}
CoTPP[a]	1.798	3.322	31.5	19.7		
Co(TPP)TNB	1.713	3.148	36.54	24.50		
CuTPP	2.185	2.047	3.15	20.81	1.57	1.47
Cu(TPP)TNB	2.180	2.037	3.23	20.77	1.61	1.52
VO(TPP)	1.968	1.997	5.76	16.43		
VO(TPP)TNB	1.966	1.995	5.89	16.17		

[a] The values are for polycrystalline CoTPP in H_2TPP from: Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235.

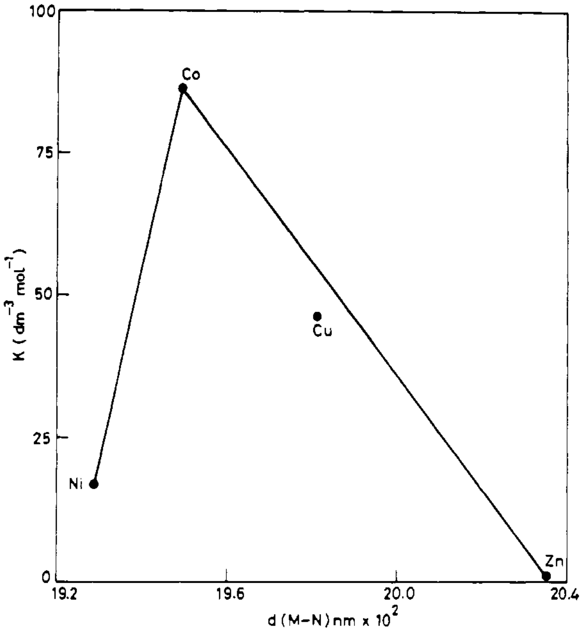

Figure 5. Plot of K vs. d(M–N), the metal–nitrogen distance for the various M(TPP)–TNB complexes.

Co^{II}TPP although S_4 ruffled, the metal ion is situated in the center of the porphinato core having quasi D_{4h} symmetry. In the case of VO(TPP) which is far removed from D_{4h} symmetry, an explanation is sought in terms of "d" orbital occupancy. The different geometries of M(TPP)'s can be rationalized in terms of M–N distances, and this is shown in the plot of d(M–N) vs. K (Figure 5). A maximum is observed for Co(II) among the first-row transition metals in accordance with the above reasoning.

The electronic configuration of the metal ions in a given geometry also contribute to the stability of the molecular complexation. The energies and the availability of the axially oriented d orbitals in the respective metal ions are also expected to contribute to the donating power of the macrocycle. The relative positioning of TNB over the donor M(TPP)'s can occur only in the axial direction and is expected to perturb an axially oriented metal d orbital. An explanation based on the occupancy and availability of axially oriented d orbitals in governing the values of K in spin-free M(TPP)'s appears reasonable. In the low-spin Co^{II}TPP, the odd electron is in the $^2a_{1g}$ (d_{z^2}) orbital which can easily sense any perturbation arising from the added TNB since it is in the plane of the incoming acceptor. In the doublet ground states of VO(TPP) and CuTPP the highest occupied molecular orbital is d_{xy} and $d_{x^2-y^2}$, respectively.[18] The ESR data presented in Table II implies an axial perturbation on complexation.

It is seen that there are significant changes in the g values for CoTPP as shown by Walker[19] and minor changes are observed for the TPP derivatives of Cu(II) and VO(II).

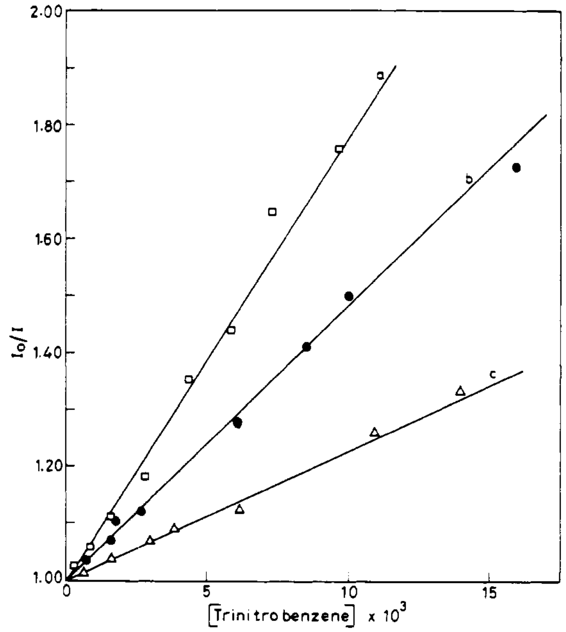

Figure 6. Stern–Volmer plots of Zn(II) derivatives of (a) pheo, (b) phth, and (c) TPP with TNB.

Table III. Emission Data

complex	solvent	K_{SV}	$10^{-10}K_q^S$, dm^{-3} mol^{-1} s^{-1}
Zn(pheo)TNB	ether	77.10	7.70
Zn(phth)TNB	THF	42.10	4.21
Zn(TPP)TNB	ether	24.25	2.42
	1-butanol	104.7	10.47
	methanol	134.0	13.40
Cd(TPP)TNB	ether	112.0	11.20

Theoretical treatments of the g values in low-spin d^7 systems have shown that $g_\perp$ depends on the magnitude of separation of d_{z^2} and d_{xz} and d_{yz} orbitals.[20] This separation is in turn dependent upon the strength of the axial field. The odd electron in the d_{z^2} orbital of CoTPP therefore will sense more perturbation compared to that of VO(TPP)'s and CuTPP's. The slight decrease in $g_\parallel$ and $g_\perp$ values and increase in A values are in contrast to that observed in the interaction of M(TPP)'s with axially coordinating bases.[21] The present results can at best be described in terms of π-complex formation where the interaction is not specific. The π complexation would lead to a small change in the distribution of π electrons over M(TPP) and in turn affect the electronic levels of the central metal orbitals. This is clearly seen in the CuTPP–TNB interaction. The perturbance of electronic levels of copper is manifested in the slight decrease in the α^2 value[22]

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(18) Gouterman, M. In ref 16b.

(19) Walker, F. A. *J. Magn. Reson.* **1974**, *15*, 201.

(20) (a) Griffith, J. S. *Discuss Faraday Soc.* **1958**, *26*, 81. (b) Assour, J. M. *J. Chem. Phys.* **1965**, *43*, 2477.

(21) (a) Walker, F. A. *J. Am. Chem. Soc.* **1970**, *92*, 4235. (b) Yokoi, H.; Iwaizumi, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1489. (c) The g and A values increase and decrease on morpholine interaction with M(TPP)'s (unpublished observations from authors' laboratory).

accompanied by simultaneous increase in $A_{\parallel}^{N}$ and $A_{\perp}^{N}$ values. This signifies that the σ bonding (M–N) is slightly more covalent. The origin of this can be traced to either an increase in the π-electron density on nitrogens or an increase in the electronic charge on copper in the complex relative to CuTPP.[21b]

The emission studies of the macrocycles indicates that the TNB strongly quenches the fluorescence of the donor due to the possible formation of the exciplex. The Stern–Volmer plot corrected for ground-state complexation gave reasonably good straight lines at lower acceptor concentrations (Figure 6). The emission data presented in Table III indicate that the values of K_{sv} decreases as Zn(pheo) > Zn(phth) > ZnTPP. On the assumption that the lifetimes of M(TPP)'s are of the order of nanoseconds, the bimolecular quenching constants were calculated and they are of the order of the diffusion-controlled rate. Lopp et al.[23] have studied the quenching of excited-state metalloporphyrins with various electron-deficient nitro aromatics and concluded that the possible mechanism for quenching of the excited state of the donor include either the formation of the excited-state complex (exciplex) or electron transfer from donor to acceptor to form the radical ion. Since the values of K_q^s are of the order of the diffusion-controlled rate, quenching occurs through formation of a collision complex. The fact that K_{sv} changes only slightly on increasing the solvent polarity suggests formation of a exciplex with some polar character rather than a complete electron transfer as the quenching mechanism. Further, the acceptor concentration required to quench the porphyrin fluorescence is very much less than the concentration of the same acceptor required to decrease the optical density of the donor in the ground state, suggesting that the TNB forms an exciplex with donors strongly in the excited state rather than in the ground state.[24] The absence of any separate emission for the complex implies extremely fast radiationless deactivation of the exciplex possibly by intersystem crossing as observed for the TNB complex of anthracene.[25]

The ^{1}H NMR spectra of the diamagnetic Ni^{II}TPP and Zn^{II}TPP and paramagnetic Co^{II}TPP complexes have shown that the aryl proton resonances of TNB occur in a shielded region (δ 0.8–1.08) relative to the acceptor alone. It is seen that both pyrole and aryl protons of the M(TPP)'s are shifted upfield in the spin-free Co(II) case while an upfield shift (for pyrole protons) and a downfield shift (for aryl protons) are observed for Ni(II) and Zn(II) complexes. These observations are essentially in agreement with the earlier study[4,5] wherein a time-averaged structure for the complex was proposed in which TNB is positioned near the pyrrole moiety with one of its >NO_2 groups projected away from the metal ion. We tend to believe that a similar structure previals in the solution of these complexes, however, further work is necessary to explain the metal-dependent K values.

Acknowledgment. T.K.C. is thankful to the University Grants Commission, New Delhi, for the award of a fellowship.

Registry No. TNB, 99-35-4; Zn(pheo), 15739-11-4; Zn(phth), 14320-04-8; Zn(TPP), 14074-80-7; Co(TPP), 14172-90-8; Cu(TPP), 14172-91-9; Ni(TPP), 14172-92-0; Cd(TPP), 14977-07-2; VO(TPP), 14705-63-6; Pd(TPP), 14187-13-4.

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[22] The α^2 values is calculated with use of the procedure described by: Kivelson, D.; Neiman, R. *J. Chem. Phys.* **1961**, *35*, 149. The α^2 value (CuTPP–Cu(TPP)TNB) is –0.0097 and compares favorably with that of Cu(OEPO)TNB (see ref 21b).

[23] (a) Lopp, I. G.; Hendren, P. W.; Wides, P. D.; Whitten, D. G. *J. Am. Chem. Soc.* **1970**, *92*, 6440. (b) Whitten, D. G.; Lopp, I. G.; Wides, P. D. *Ibid.* **1968**, *90*, 7196.

[24] The ground-state complexation in all the cases contributes only to the extent of 20–25% while the percent quenched is in the order of 60–65%.

[25] Kleineraman, M.; Azarraga, L.; McGlynn, S. P. "Luminescence of Organic and Inorganic Systems"; Wiley: New York, 1962.

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Effect of Axial Interaction in High-Spin Iron(III) Porphyrins. Paramagnetic Anisotropy and Zero-Field Splitting in (Tetraphenylporphyrin)iron(III) Thiocyanate and Iodide

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Magnetic anisotropy measurements in the 80–300 K temperature range on the single crystals of high-spin (tetraphenylporphyrin)iron(III) thiocyanate and iodide are reported, and the data have been used to deduce the zero-field splitting parameter (D) of the ferric ion. The variation in D for the prophyrin series follows the sequence $D_{NCS} < D_{Cl} < D_{Br} < D_{I}$.

Introduction

(Tetraphenylporphyrin)iron(III) complexes, (TPP)FeX (X = NCS, Cl, Br, I) form a series of high-spin ($S = {}^5/_2$) synthetic iron(III) porphyrins which are very similar to natural heme systems.[1,2] The ferric ion is coordinated to the four pyrrole nitrogen atoms of the essentially planar porphyrin macroring, the halide ion occupying an axial position to give approximately square-pyramidal geometry around the iron(III) atom (Figure 1). The iron is however not coplanar with the porphinato core or with the four nitrogen atoms but is displaced (by ca. 0.4–0.6 Å) in the direction of the axial ligand. The ferric ion is thus under the influence of a crystal field generated by the basal porphyrin ring and the axial halide.

Table I. X-ray Structural Data for the (TPP)FeX Series

compd	Fe–N, Å	Fe–X, Å	Ct–M (Δ), Å
(TPP)Fe(NCS)	2.065	1.957	0.55
(TPP)FeCl	2.060	2.192	0.39
(TPP)FeBr	2.069	2.348	0.56
(TPP)FeI	2.066	2.554	0.53

We are currently investigating by single-crystal magnetic study the effect of variation of the apical ligand on the electronic ground-state properties of the ferric ion in the (TPP)FeX series.[3–6] There are several advantages in choosing the

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