Optical and magnetic resonance studies of the interaction of metallo tetraphenylporphyrins with nitrobenzofuroxan

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Metallo tetraphenylporphyrins form 1:1 molecular complexes with 4,6-dinitrobenzofuroxan. The molecular association is described in terms of $\pi - \pi$ interaction with porphyrins functioning as donors. The association constants and thermodynamic parameters have been evaluated using optical absorption and ^{1}H nmr spectral methods. Based on the binding constants, the donor ability of various metalloporphyrins can be arranged in the following order: Pd(II) > Co(II) > Cu(II) > Ni(II) ~ VO(IV) ~ 2H > Zn(II). Electron paramagnetic resonance studies of the complexes reveal that the π-complexation results in changes in the electronic structure of the central metal ions which are reflected in the changes in the M$-$N σ bonding. The dipolar contribution to the acceptor proton chemical shifts in the CoTPP complex has been partitioned from ring current contributions using the shifts observed in the ZnTPP complex. The shifts, along with the line broadening ratios observed for the CoTPP complex, are used to arrive at the possible solution structures of the complexes.

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Les métallotétraphénylporphyrines forment des complexes moléculaires 1:1 avec le dinitro-4,6 benzofuroxane. On décrit l'association moléculaire en fonction des interactions $\pi - \pi$ avec les porphyrines agissant comme donneurs. On a évalué les constantes d'association et les paramètres thermodynamiques en faisant appel à l'absorption optique et à la rmn du ^{1}H. En se basant sur les constantes de liaison, on peut établir la capacité des diverses métalloporphyrines en tant que donneur dans l'ordre suivant: Pd(II) > Co(II) > Cu(II) > Ni(II) ~ VO(IV) ~ 2H > Zn(II). Les études de rpe des complexes révèlent que la complexation π est due à des changements dans la structure électronique de l'ion métallique central qui se réflète dans les variations de la liaison σ M$-$N. On a partagé la contribution dipolaire aux déplacements chimiques de l'accepteur de proton dans le complexe CoTPP, à partir du courant de cycle, en utilisant les déplacements observés dans le complexe ZnTPP. On a utilisé les déplacements chimiques ainsi que le taux d'élargissement des raies observé dans le complexe CoTPP pour arriver à déterminer les structures possibles des complexes.

[Traduit par le journal]

Introduction

The molecular interactions of porphyrins with neutral organic molecules is either donor$-$acceptor type or coordinative, depending on the functional groups present in the organic molecules. Nitroaromatics essentially function as π-acceptors and form donor$-$acceptor complexes with porphyrins (1). Among the nitroaromatics, the most widely used acceptor is sym. trinitrobenzene (TNB). Earlier we employed TNB as an acceptor and investigated the donor properties of tetraphenylporphyrin, phthalocyanin, pheophytin, and their metallo derivatives (2). 4,6-Dinitrobenzofuroxan is another member of the nitroaromatics and an examination of its structure reveals two canonical forms indicating planar structure of the compound. (Fig. 1). This bears a close resemblance to the structure of TNB. It is known that nitrobenzofuroxans form highly coloured complexes with aromatic donors exhibiting charge transfer bands in the visible region (3). The π-acceptor behaviour of benzofuroxans towards Co(II) derivatives of *meso*-porphyrin IX dimethyl ester and etioporphyrin has earlier been reported (4). In our continuing interest in the study of donor ability of porphyrins and their metallo derivatives with various acceptors, we chose to investigate the acceptor behaviour of 4,6-dinitrobenzofuroxan (BFO) in the expectation that near coplanarity of BFO may promote plane$-$plane overlap with the donor, thereby contributing significantly to the stability of the complexes. Moreover, such a study would make a comparative study with the TNB complexes more meaningful and help to delineate any specific site interaction that may prevail in the complexes.

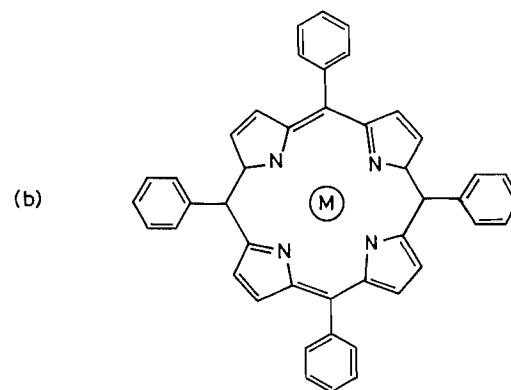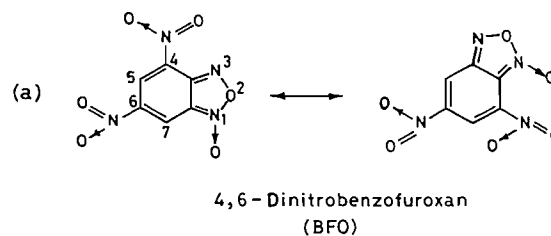The various donor porphyrins employed in the study are

FIG. 1. (a) Different canonical forms of 4,6-dinitrobenzofuroxan. (b) chemical structure of metallo porphyrin.

5,10,15,20-tetraphenylporphyrin (TPP) and its metallo VO(II), Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) derivatives. Besides employing the optical absorption method for the evaluation of

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association constants and thermodynamic parameters, the use of the ^{1}H nmr method is exploited for the determination of binding constants of BFO with ZnTPP and CoTPP's. The choice of ZnTPP as a donor is to apportion the ring current contributions to the proton chemical shifts of BFO in the CoTPP complex to evaluate the dipolar shifts. The esr measurements, coupled with the magnitude of the dipolar shifts and line broadening effects in the paramagnetic TPP's, are useful in arriving at the possible solution structures of the molecular complexes. The paramagnetic resonance parameters of the complexes provide information regarding the manner in which the $\pi-\pi$ interaction is transmitted through the metal−porphyrin bonding framework.

Experimental

The donor porphyrin (TPP) was procured from Aldrich, USA. The metal derivatives of TPP have been prepared according to the published procedures (5). 4,6-Dinitrobenzofuroxan was prepared from the nitration reaction of nitrosobenzene (6). It was crystallized twice from acetic acid, mp 172°C. All the solvents employed in the study were distilled before use. The preparation of solutions and all manipulations were carried out in dim light under a blanket of nitrogen. The spectra of the solutions were recorded immediately after mixing.

The optical absorption method employed for the evaluation of association constants involves the measurements of absorbance of the Q bands of porphyrin and its derivatives in the solvent CH_2Cl_2 on increasing addition of BFO. The concentration of the donor porphyrins is held constant ($\sim 10^{-5}\ M$) and the range of concentration of BFO employed is 1.0×10^{-4} to $2.0 \times 10^{-2}\ M$. The spectrometer used was the same as described previously (2).

The ^{1}H nmr spectra were recorded on a WH-Bruker 270 MHz FT instrument using $CDCl_3$ as a solvent and TMS as an internal standard. The nmr titration experiment was performed as follows. To a constant volume of $CDCl_3$ solution of BFO ($1 \times 10^{-2}\ M$ varying amounts of ZnTPP/CoTPP in $CDCl_3$ were added, and the ^{1}H nmr spectra recorded, the temperature of measurement being 27°C. The shifts are with respect to TMS and the accuracy of the shifts lies in the range $\pm 0.005\ \delta$. In both the optical and ^{1}H nmr experiments, the spectra of several sets of solutions were recorded to check reproducibility of the data obtained.

Electron spin resonance measurements of the solutions containing the donors and acceptors were recorded on a Varian E 109 esr spectrometer using toluene as the solvent. The spectra reported are at a temperature of 100 K. The field strength was calibrated using an nmr probe.

Results

BFO in CH_2Cl_2 exhibits well-defined intense absorption bands at 422 mm (log ϵ = 2.87), 333 nm (log ϵ = 2.77), 276 nm (log ϵ = 3.14), 261 nm (log ϵ = 3.11), and 233 nm (log ϵ = 2.96). Addition of increasing amounts of BFO to the donor porphyrins in CH_2Cl_2 causes a progressive decrease in the absorbance of Q bands in the region 500 to 600 nm (Fig. 2). Association constants were evaluated using the method of Nash (7). A typical plot of C_A^{-1} versus $d^0 (d^0 - d)^{-1}$ where C_A, d^0, and d denote the concentration of BFO, the absorbance value of the pure donor, and the absorbance value of the donor in presence of acceptor respectively, is shown in Fig. 3. The linearity of the plots suggests that the complexes formed are of 1:1 stoichiometry. The absorbance measurements taken at different temperatures permit the evaluation of thermodynamic parameters. The values of K and related parameters obtained in the present study are given in Table 1. The reliability of the K values is tested using Deranleau's saturation factor criterion (8). This is defined as the ratio of the concentration of the
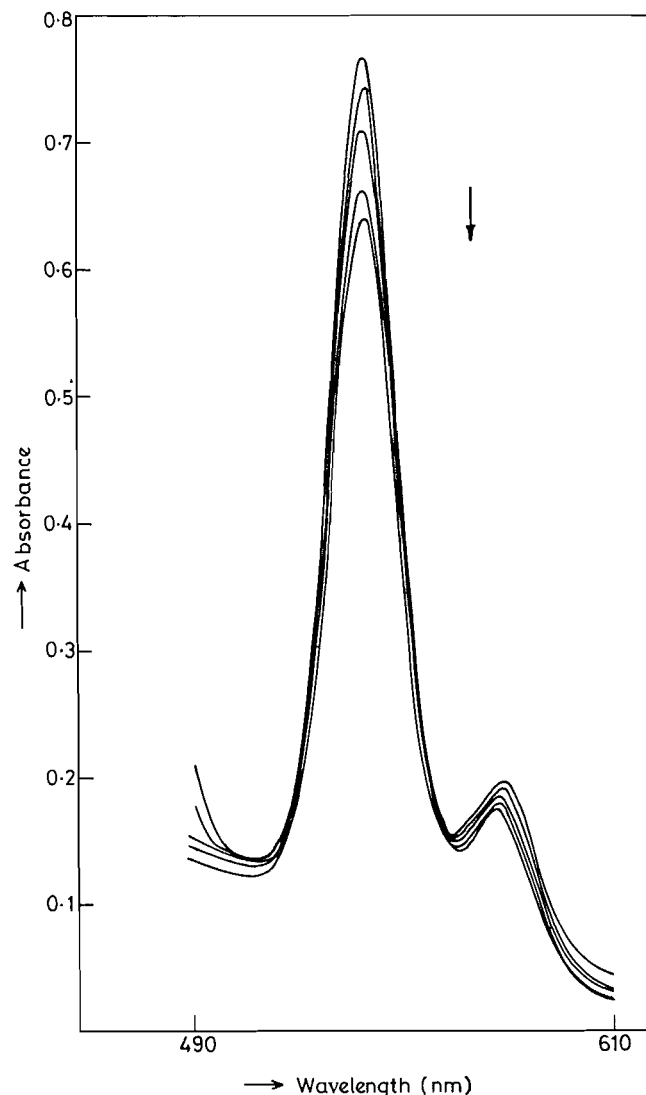

FIG. 2. Visible spectrum of (a) ZnTPP ($5.6 \times 10^{-5}\ M$) containing increasing amounts of BFO in CH_2Cl_2 (3.9×10^{-4} to $5.5 \times 10^{-2}\ M$).
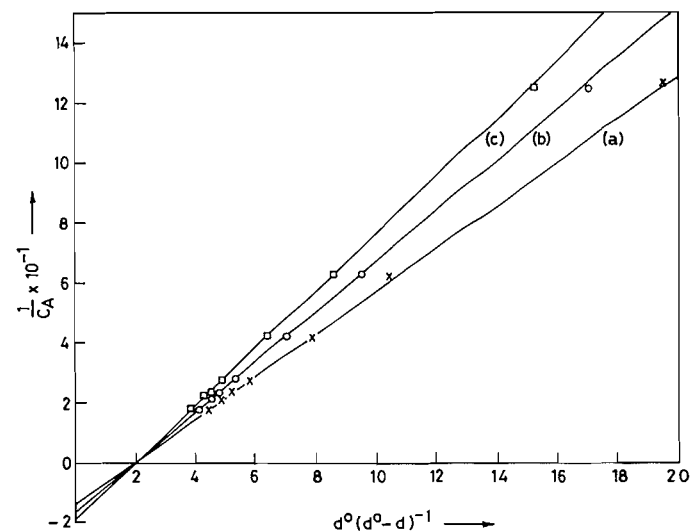

FIG. 3. Plots of $d^0 (d^0 - d)^{-1}$ versus $1/C$ for the interaction of ZnTPP with BFO at (a) 25°C; (b) 16°C; and (c) 9°C.

TABLE 1. Association constants and thermodynamic parameters for MTPP—BFO interaction in CH_2Cl_2

Complex	Temperature °C	K dm^3 mol^{-1}	$-\Delta H$ kJ mol^{-1}	ΔS J mol^{-1} deg^{-1}
VOTPP—BFO	25.0	53±7.0		
	17.0	67±11.0	16.20±2.5	−21.20±2.5
	8.0	79±12.0		
PdTPP—BFO	25.0	132±22.0		
	17.0	161±28.0	12.90±3.6	−2.92±9.5
	9.0	178±31.0		
CuTPP—BFO	25.0	77±10.0		
	17.0	101±12.0	18.90±2.5	−27.15±4.0
	9.0	119±13.0		
NiTPP—BFO	25.0	55±6.0		
	18.0	65±9.0	13.80±3.0	−13.20±5.0
	10.0	74±7.0		
H_2TPP—BFO	25.0	56±7.0		
	16.0	71±11.0	16.80±3.0	−22.90±40
	10.0	80±9.0		
CoTPP—BFO	25.0	105±12.0		
	16.0	114±15.0	8.70±2.0	9.20±3.0
	10.0	127±14.0		
ZnTPP—BFO	25.0	14.2±3.0		
	16.0	16.8±2.5	14.0±2.0	−25.10±4.5
	9.0	19.6±3.0		

complex to that of the acceptor and in the present study this is within the range of 0.2−0.8 for well-defined K values.

The ^{1}H nmr spectrum of BFO in $CDCl_3$ consists of resonances centered at δ 9.150 and δ 8.847, corresponding to H_7 and H_5 protons respectively. On increasing addition of MTPP, the acceptor resonances are shifted to higher fields (Fig. 4). The multiplet structure of H_7 and H_5 proton resonances remains unaffected on addition of ZnTPP. On the other hand, these resonances are broadened and shifted to higher fields (relative to the ZnTPP complex) on addition of CoTPP (Table 2). The appearance of only one set of resonances in the ^{1}H nmr spectra of the complexes reveals that the rate of exchange between the free and complexed BFO is fast in the time scale. It can be shown that the observed proton resonance shifts (Δ) of the acceptor on increasing addition of donor porphyrins are related to the association constant, K, through the expression

$$[1] \quad \frac{1}{\Delta} = \frac{1}{D\Delta_c} A\left(1 - \frac{\Delta}{\Delta_c}\right) + \frac{1}{\Delta_c} + \frac{1}{KD\Delta_c}$$

where D and A represent the concentration of donor porphyrins and acceptor respectively and Δ_c is the shift in the fully formed complex. To obtain the best values of K and Δ_c we adopted a procedure similar to that described in the literature (1). This involves an initial neglect of the first term in eq. [1] to obtain

$$[2] \quad \frac{1}{\Delta} = \frac{1}{\Delta_c} + \frac{1}{KD\Delta_c}$$

Plots of $1/\Delta$ vs. $1/D$ for both H_5 and H_7 protons of BFO in the ZnTPP and CoTPP addition versus the concentration of donor porphyrin yield straight lines, with a slope of $1/K\Delta_c$ and an intercept of $1/\Delta_c$. The least-squares fit of these values thus obtained is fitted into expression [1] in a manner to get the best fit. A regression analysis programme was employed to arrive at the best values of K and Δ_c satisfying expression [1]. The values of K and Δ_c obtained for H_5 and H_7 protons are listed in Table 3.

The values of K obtained for H_5 and H_7 protons are similar

in magnitude, indicating that the π-complexation effect is felt by the protons equally. The magnitudes of K obtained using the nmr method are at variance with those obtained by the visible spectral method. We attribute the variance in K values to the different concentration ranges employed in the respective methods.

The values of Δ_c are composed of ring current and dipolar effects. Thus

$$[3] \quad \Delta_c = \Delta_{(ring)} + \Delta_{(dipolar)}$$

where $\Delta_{(ring)}$ are the shifts due to the ring current of the porphyrin and $\Delta_{(dipolar)}$ are the additional shifts due to the single unpaired electron in CoTPP. A reasonable assumption, that the shift due to the ring current in CoTPP is identical to that of ZnTPP owing to their structural similarity except for the metal ion, permits the calculation of the contribution from the dipolar term to the shifts. The pseudo contact shifts obtained for H_5 and H_7 protons are represented below. It is seen that both H_5 and H_7 protons of BFO experience shifts of similar magnititude unlike

4.41δ H_5

O_2N

NO_2

N
O
N
O

H_7

4.49δ
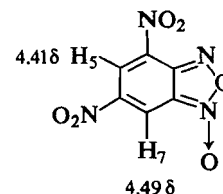
those reported for other acceptor systems (1).

The esr spectra of the BFO complexes of Cu and VOTPP's are highly characteristic, permitting an evaluation of esr parameters (Table 4). Addition of BFO shifts the signals to higher fields, thereby decreasing the values of $g_\parallel$ and $g_\perp$ (Fig. 5). The small changes observed in metal hyperfine coupling constants and a decrease in $A_\parallel^M$ relative to the MTPP's signify molecular complexation. In the case of the CuTPP complex, a simultaneous increase in $A_\parallel^N$ and $A_\perp^N$ values is observed. The esr spectrum of the CoTPP—BFO complex is often plagued with the
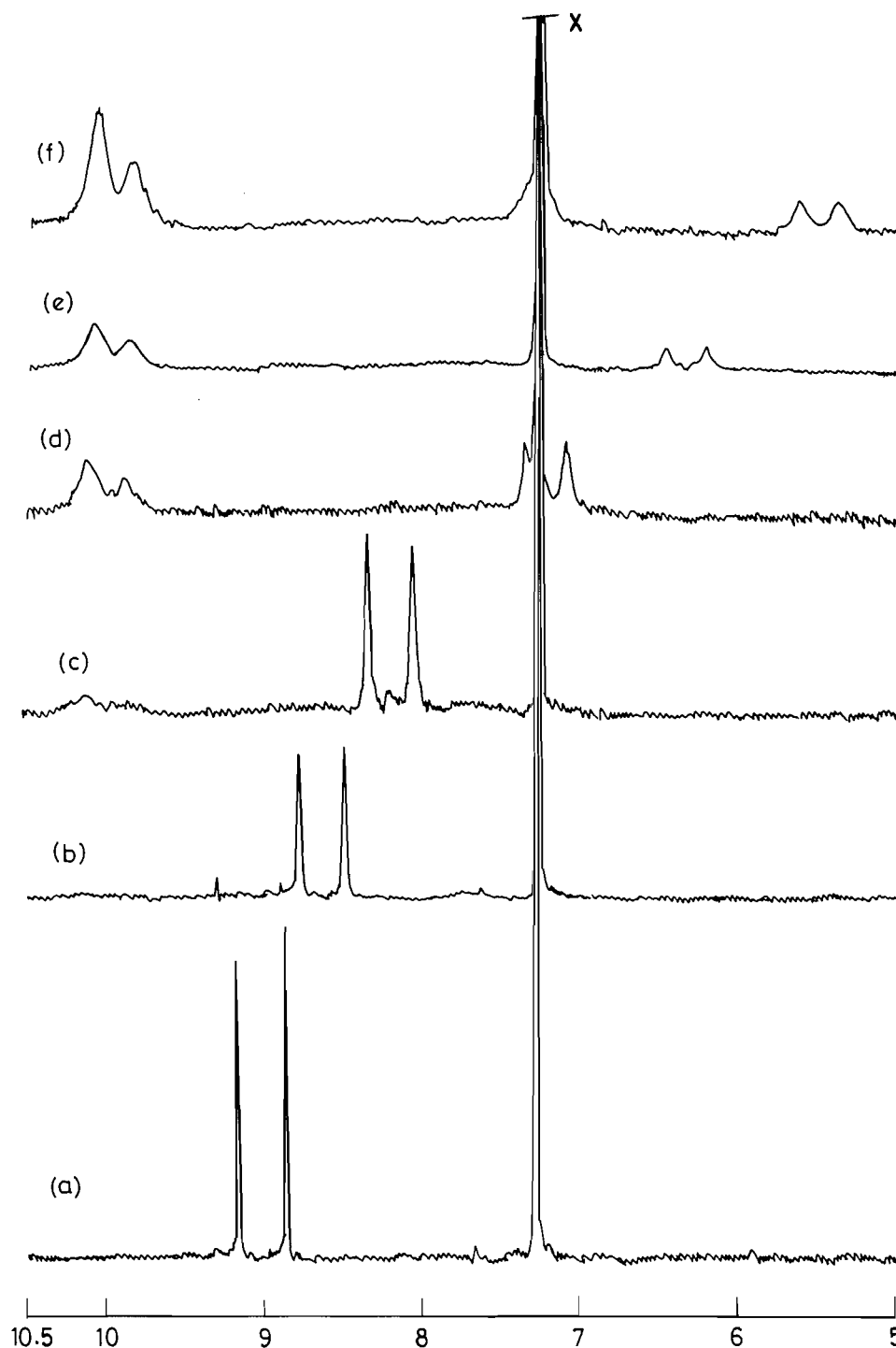
FIG. 4. Chemical shifts of BFO $(1.09 \times 10^{-2} M)$ proton resonances with increasing addition of CoTPP; (a) nil; (b) $7.5 \times 10^{-4} M$; (c) $2.55 \times 10^{-4} M$; (d) $4.51 \times 10^{-3} M$; (e) $6.01 \times 10^{-3} M$; and (f) $7.51 \times 10^{-3} M$. Mark (X) denotes solvent peak.

signals arising from its molecular oxygen adduct. The spectrum obtained exhibits a strong signal at $g = 2.08$, typical of an oxygen adduct (9), and weak signals in the low-field region, resembling closely that of the CoTPP–TNB complex (2) and indicating the existence of a mixture of pure CoTPP–BFO complex and its oxygen adduct. In view of this, the esr parameters of the oxygen-free CoTPP–BFO complex could not be calculated unambiguously. The π-complexation by metal TPP's causes a change in the electron distribution over the porphyrin core, affecting the electronic energy levels of the central metal ions. Though a manifestation of this effect is seen only in the changes of $A_\parallel^M$ values to VOTPP, it has been possible to quantitatively assess this in the CuTPP complexes. The perturbance of electronic levels of Cu is seen in the slight decrease in the value of the covalency factor α^2. It is calculated using the procedure described by Kievelson and Neiman (10); the change in the α^2 value relative to CuTPP is found to be -0.01391, signifying that the σ bonding is slightly more covalent in the molecular complex. Such changes are interpreted in terms of a small increase in the π-electron density of N or in

TABLE 2. Concentrations of MTPP and the observed shifts (δ) of BFO protons[a,b]

Concentration of MTPP $\times 10^{-3}$ mol/dm^3	H$_7$	Shift	H$_5$	Shift
ZNTPP				
BFO	9.151	—	8.848	—
1.12	9.065	0.086	8.755	0.093
2.24	8.986	0.165	8.669	0.179
4.48	8.383	0.313	8.510	0.338
6.72	8.708	0.443	8.369	0.479
8.40	8.635	0.516	8.289	0.559
CoTPP				
BFO	9.150 (4)	—	8.847 (4)	—
0.75	8.791 (8)	0.359	8.500 (6)	0.347
2.25	8.339 (12)	0.811	8.059 (14)	0.788
4.51	7.318 (18)	1.832	7.064 (19)	1.783
6.01	6.473 (23)	2.677	6.198 (24)	2.649
7.51	5.635 (30)	3.515	5.392 (31)	3.455

[a]Concentration of BFO employed is 1.09×10^{-2} M.
[b]The values in parenthesis represent the linewidths in Hertz.

TABLE 3. The ^{1}H nuclear magnetic resonance data evaluated for Zn and CoTPP−BFO complexes

Proton	Δ_c (δ)	K dm^3 mol^{-1}
ZnTPP−BFO		
H$_5$	2.514±0.210	58.3±10
H$_7$	2.733±0.210	56.0±10
CoTPP−BFO		
H$_5$	7.010±0.315	70.7±12
H$_7$	7.140±0.315	69.9±12

TABLE 4. Electron spin resonance parameters of MTPP complexes with BFO in toluene at 100 K

Complex	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\perp}^M$ cm^{-1}	$10^4 A_{\parallel}^M$ cm^{-1}	$10^4 A_{\perp}^N$ cm^{-1}	$10^4 A_{\parallel}^N$ cm^{-1}
CuTPP	2.185	2.047	31.50	208.10	15.70	14.70
CuTPP−BFO	2.179	2.038	32.82	206.66	16.81	15.72
VOTPP	1.968	1.997	57.60	164.30	—	—
VOTPP−BFO	1.961	1.989	59.10	160.71	—	—
CoTPP	1.971	2.80	210.00	141.00	—	—
CoTPPP−BFO[a]	2.007	2.120	—	—	—	—

[a]Corresponds to CoTPP−BFO:O$_2$.

the increase in electronic charge on copper in the molecular complex relative to CuTPP (2).

Discussion

An examination of Table 1 reveals that the association constants for the BFO interaction with MTPP's follow the order Pd^{2+} > Co^{2+} > Cu^{2+} > Ni^{2+} ~ VO^{2+} ~ 2H > Zn^{2+}, similar to that observed for the corresponding complexes of TNB. However, the magnitudes of K are higher than those observed for the TNB complexes. This can be interpreted in terms of the planar disposition of the NO$_2$ groups in BFO. Shinomiya (11) has pointed out that a maximum stability in the complexes can
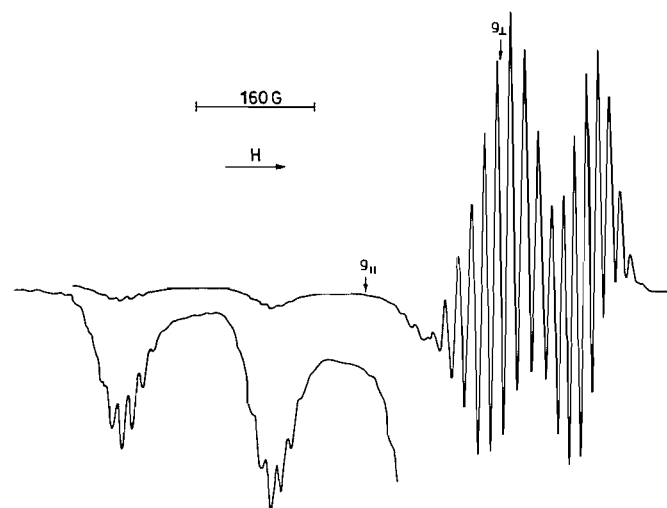

FIG. 5. The esr spectrum of the CuTPP−BFO complex in toluene at 110 K.
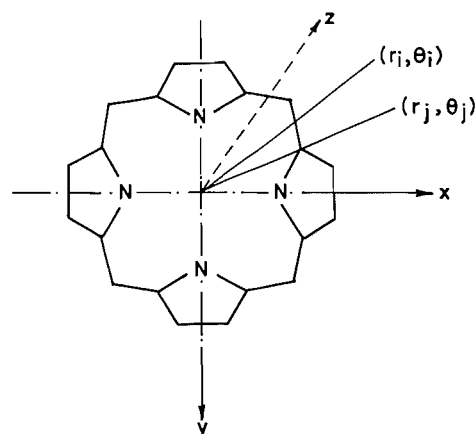

FIG. 6. Coordinate system for metal and acceptor protons.

be accomplished if the nitro groups are allowed to be coplanar with the benzene ring to which they are attached. It is worthwhile to point out that the magnitudes of K are lower than those observed for polynitro fluorenone complexes (12). We attribute this to the relatively smaller size of BFO. The thermodynamic parameters of the MTPP−BFO interaction are not significantly different on variation of the metal. It is worthy to mention here that the decreases in ΔH values observed in the present study are higher than those observed for TNB complexes. In molecular complexing systems, the values of ΔH signify the efficiency of packing of donor and acceptor in the complex. This can be enhanced if the molecules involved in the complex formation are planar, such that plane-to-plane overlap leads to a better packing of the donor and acceptor. We believe such effects are operative in the present study. Attempts to obtain single crystals of these complexes have so far been unsuccessful.

In order to demonstrate that the interaction of BFO with MTPP is not of the coordinative type, we studied the ir spectra of the complexes. The strong band, ~1550 cm^{-1}, in BFO has been assigned to the N→O stretching frequency (13). The —C=N— stretching vibration in BFO occurs as a weak band at 1625 cm^{-1}, while the asymmetric and symmetric stretching vibrations of the NO$_2$ groups appear at 1530 and 1320 cm^{-1}, respectively. In the complexes, these vibrations remain virtu-

ally unaffected. Further, the donor porphyrin vibrations are only marginally affected. These observations indicate the absence of any specific site interaction of BFO with MTPP's. Moreover, the esr spectral changes, i.e. decrease in g values and increase in A values, are in contrast to those observed in the interaction of MTPP's with axially coordinating ligands (14).

An attempt has been made here to probe into possible solution structures of the molecular complexes using ^{1}H nmr and esr data of the complexes. The dipolar shifts and broadening of the acceptor proton signals in the CoTPP–BFO complex are used to locate the protons of BFO with respect to the Co(II) centre in the complex. The linewidths of the BFO proton resonances on addition of CoTPP are given in Table 2. The broadening ratios are obtained using the expression of Sternlicht (15). The estimates of broadening ratios were obtained at 270 MHz by subtracting the diamagnetic line widths of BFO multiplets from those in the presence of CoTPP. This indicated that both H_5 and H_7 proton resonances were about seven times as broad as in free BFO. The absence of any preferential broadening of acceptor protons underscores the plane–plane overlap of the acceptor with donor in these complexes. The dipolar shifts experienced by the acceptor protons in the CoTPP–BFO complex are all to higher fields, justifying that there exists no direct spin-transfer. Calculation of such shifts is based on the evaluation of the geometric factors, $(3\cos^2 \theta - 1) r^{-3}$, where θ is the angle the acceptor proton subtends with Co(II) and the said proton (Fig. 6). The X-ray structure of CoTPP (14) was taken to define the stereochemistry, and the bond angles and bond lengths of BFO are approximated to that of TNB. The molecular framework of the complex is then defined by placing BFO parallel to CoTPP at a distance R, such that the centre of the aryl ring passes through the Co(II) ion. Moreoever, for a fixed distance R, tilt angles are varied from 0 to 30°. The distances r_0 and r_j from Co(II) to H_5 and H_7 protons of the acceptor and the angles subtended are computed for various values of R (3.5–4.0 Å) and tilt angles. The dipolar shifts are calculated using the geometric factors according to ref. 16.

$$[4] \quad \left(\frac{\Delta H}{H}\right)_i \Big/ \left(\frac{\Delta H}{H}\right)_j = (3\cos^2 \theta_i - 1) r_i^{-3} / (3\cos^2 \theta_j - 1) r_j^{-3}$$

Most of the structures scanned in this fashion do not fit well

into the experimentally observed ratio of dipolar shifts, probably because of the random orientations of the molecules in the solvent. The determination of structure must, however, await a detailed X-ray examination. The present study points out that the interaction of BFO with porphyrins occurs only in the periphery.

Acknowledgements

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