

[en]Br₄·2H₂O the hydrogen atom lies more or less in the



plane, whereas in the [NH₃] salts it is displaced out of this plane by an angle of at least 30° but more likely 50–60°. ⁶ Hydrogen bonding to chloride and bromide ions is responsible for these displacements. The bonding situation of the oxygen atom and thus the superexchange pathway is affected by this. The $p_z = p_x$ oxygen orbital is fully available for π bonding to zx and yz chromium orbitals if the hydrogen position is in the plane. This is the case in [en]Br₄·2H₂O, where J_{12} and, as a consequence, J_{ab} are large. In the [NH₃] salts the $p_z = p_x$ oxygen orbital is involved in the O–H σ bond and therefore not fully available in the superexchange mechanism through π bonding, thus the reduction of J_{12} , J_{11} , and J_{13} . The further reduction of these superexchange parameters and thus of J_{ab} between [NH₃]Cl₄·4H₂O and [NH₃]Br₄·4H₂O must be fully attributed to changes of the hydrogen-bonding situation. If there are differences in the framework



between the two salts, they are likely to be the consequence of differences in the O–H...X hydrogen bond. A careful determination of atomic positions by X-ray diffraction will be a very important prerequisite for a quantitative discussion of our results.

Our interpretation of the spectroscopic properties of bis(μ -hydroxo)-bridged chromium(III) dimers differs from that by Henning and co-workers for bis(μ -oxo)-bridged chromium(III) dimers in the ZnGa₂O₄ host lattice. ⁷ The Cr–Cr separation can be estimated from the nearest-neighbor Ga–Ga distance

of 2.945 Å in the pure host. This distance is comparable to that in [NH₃]Cl₄·4H₂O. But in contrast to our conclusions for [NH₃] and [en] Henning et al. postulated a dominant direct-exchange mechanism ($J_{33} = -280 \text{ cm}^{-1}$) for the chromium dimers in ZnGa₂O₄ on the basis of optical spectroscopic data. Because ZnGa₂O₄ is cubic, these authors had no possibility to measure the polarizations of the pair absorptions. And due to this lack of polarization information they could not experimentally distinguish between two sets of orbital exchange parameters producing the same energy splitting pattern in ²E_g ⁴A_{2g}. They were forced to make a choice, and they chose the set that was compatible with the generally accepted direct-exchange mechanism in chromium oxide compounds. ⁹ Our crystals have the advantage that all the dimers are parallel. As a result we obtain polarized spectral information with respect to the molecular symmetry axes. And it is this type of information that is needed to assign the lowest energy pair transitions in [en]Br₄·2H₂O to ⁵B_{2u} and ³B_{3g} transitions and thus obtain a dominant J_{12} contribution. Our [NH₃] spectra have the additional advantage that a great deal of fine structure is resolved, resulting in an enormous increase of spectral information. We are currently reconsidering the problem of direct exchange vs. superexchange in chromium-(III) oxide compounds with bis(μ -oxo) bridging geometries between nearest neighbors.

Acknowledgments. We are indebted to L. Dubicki for very helpful correspondence and to A. Pfeuti for preparative assistance. This work was supported by the Swiss National Science Foundation (Grant No. 2.427.79).

Registry No. [(en)₂Cr(en)₂]Br₄·2H₂O, 15135-03-2; [(NH₃)₄Cr(OH)₂Cr(NH₃)₄]Cl₄·4H₂O, 82456-39-1; [(NH₃)₄Cr(OH)₂Cr(NH₃)₄]Br₄·4H₂O, 82469-00-9.

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Cation-Induced Crown Porphyrin Dimers of Oxovanadium(IV)

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Received November 23, 1981

Oxovanadium(IV) porphyrins appended with crown ether (benzo-15-crown-5) at the 5 (mono), the 5 and 10/15 (cis/trans bis), the 5, 10, and 15 (tris), and the 5, 10, 15, and 20 (tetraakis) positions have been synthesized. The cation complexation behavior of these cavity-bearing porphyrins has been studied by using optical absorption and ESR spectral methods. The cations K⁺, Cs⁺, NH₄⁺, and Ba²⁺, which require two crown ether cavities for complexation, induce dimerization of the porphyrins. The cation-induced dimerization constants for a representative tetrasubstituted porphyrin vary as K⁺ > Ba²⁺ > Cs⁺ ~ NH₄⁺, and the relative stabilities of the dimers are dependent on the type of the substitution, tetraakis > tris > cis bis. ESR spectra recorded at a sample temperature of 77 K have low-field components attributed to $\Delta M_z = \pm 2$ transitions, providing further evidence for the existence of dimers in solutions. The eclipsed sandwich dimers have V–V distances in the range 4.70 Å. The relative distributions of oxovanadium crown porphyrins in terms of monomeric and dimeric forms rest on the geometric dispositions of the crown ether appendages.

Introduction

Aggregation of macrocyclic compounds in general, and tetrapyrrole pigments in particular, is one of the properties of significance in biological systems. Central to aggregation, the dimerization process is widespread among porphyrins and their metal derivatives both in solution and in solid state. The formation of dimers in solution is shown to be dependent on concentration¹ while in some cases intentional syntheses of

covalently linked dimers have been achieved.² In the latter, it is found that variations of interplanar separations can be controlled by a proper choice of linking groups whereas, in the concentration-dependent dimers, the interplanar distances are contrived and specific to the nature of the porphyrins. In our studies in the development of supramolecular entities, having

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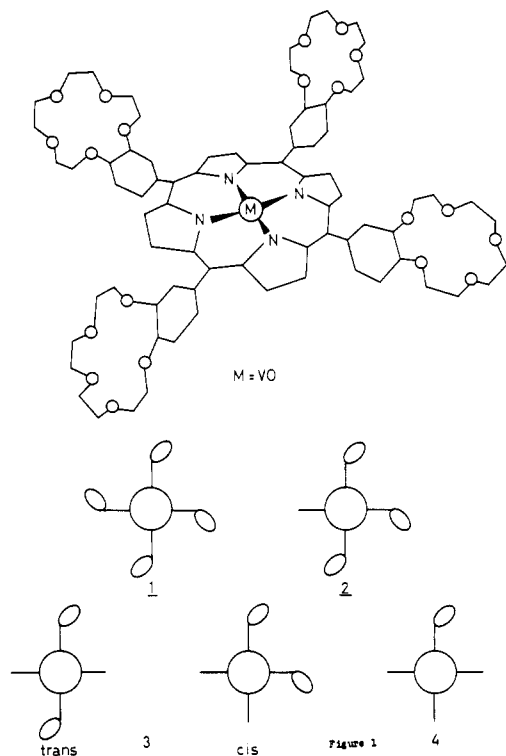


Figure 1. Chemical structure of oxovanadium(IV) tetrakis(benzo-15-crown-5)porphyrin. The partially substituted porphyrins are shown. The full circle represents the porphyrin (N_4) plane while the ellipse and line denote the substituents benzo-15-crown-5 cavity and phenyl rings in the methine positions, respectively.

crown ethers appended to the porphyrin core, we found certain cations encapsulated in the crown ether cavities promote dimerization of porphyrins.³ These cavity-bearing porphyrins are unique and offer a possibility of obtaining dimers with cations of different sizes interspersed between the porphyrin planes. In order to obtain the values of interplanar distances that are essential to the understanding of the dimerization process, we employed ESR-active oxovanadium(IV) as the central metal ion in the porphyrin cavity. The optical spectra provide additional information on the existence of dimers in solution.

In the present study we report the synthesis of oxovanadium(IV) derivatives of symmetrical as well as partially substituted (benzo-15-crown-5) porphyrins. Various cations are employed for the complexation study. The dimerization was followed by optical absorption and ESR spectral methods. The partially substituted crown ether porphyrins delineate the effect of steric influence on the energetics of the dimerization process while the cations of varying ionic sizes provide information on the interplanar separations.

Experimental Section

All solvents and chemicals used in the synthesis were of reagent grade quality. Solvents used for spectroscopic work were purified and distilled prior to use. Alkali and alkaline earth cation salts were of Analar quality. The spectrometers employed were the same as described in our earlier work.⁴

The fully and partially substituted crown porphyrins (Figure 1) were synthesized by reacting appropriate mole proportions of pyrrole and the 4'-carboxaldehyde of benzo-15-crown-5/benzaldehyde in refluxing propionic acid. A typical procedure for the synthesis of *cis*-

and *trans*-bis(benzo-15-crown-5)porphyrin is outlined here.

A mixture of 4'-carboxaldehyde of benzo-15-crown-5 (14.8 g), benzaldehyde (5.3 g), and pyrrole (6.8 g) in propionic acid (400 mL) was refluxed for 45 min and left overnight. After the removal of the solvent under reduced pressure, the residue was dissolved in $CHCl_3$ and column chromatographed (basic alumina). With a $CHCl_3/THF/CH_3OH$ (70:30:0.5) solvent mixture, a total of five fractions, each exhibiting a visible spectrum characteristic of porphyrin, were collected. The 1H NMR spectra of the fractions were used to discriminate the nature of the products (from the relative intensities of pyrrolic and crown ether protons). It was found that fractions I, II, III, IV, and V (in the order of elutions) are TPP, MCP, BCP, TrisCP and TCP, respectively.⁵ The two possible isomers of BCP, viz., the *cis* and *trans* forms, are separated from the isomeric mixture by using a basic alumina column with a $CHCl_3/THF/CH_3OH$ (70:30:0.3) solvent mixture as eluant. The *trans* isomer with a higher R_f value (0.65) was eluted first, leaving behind *cis*-BCP (R_f 0.50), which was collected as a second fraction. The R_f values provide a reasonable basis to distinguish between the *cis* and *trans* forms. The 1H NMR spectrum of *cis*-BCP (AB pattern of pyrrole protons at δ 8.867) is the same as that of *trans*-BCP.

The incorporation of the oxovanadium(IV) ion, VO^{2+} , into the different crown porphyrins was carried out by refluxing $VOSO_4$ and the porphyrins in DMF under N_2 for 30 h.⁶ The progress of the reaction was followed spectrophotometrically. The metalated derivatives were purified by using column chromatography. In all the cases a yield of 80% was obtained.

The cation interaction with vanadyl crown porphyrins has been carried out for the evaluation of K using optical absorption spectrometry at an ambient temperature of 28 °C. The concentration of vanadyl crown porphyrins was held constant at 5×10^{-5} M. The intensities of the visible bands of vanadyl crown porphyrins were monitored in the $CHCl_3/CH_3OH$ (1:1) solvent mixing with increasing addition of cations. The decreases in intensities were analyzed as described in a later section.

The ESR spectra of the vanadyl crown porphyrins and those of the dimers were recorded in a 1:1 $CHCl_3/CH_3OH$ solvent mixture at 77 K. The field strength was calibrated with an NMR probe and then with bis(2,4-pentanedionato)oxovanadium(IV) in benzene. The dimers were prepared by mixing equal volumes of a chloroform solution of vanadyl crown porphyrin and a methanolic solution of cation chlorides. These solutions of dimers were used for recording the ESR spectra at 77 K. The overall concentration of the dimer for the ESR spectra was $\sim 10^{-3}$ M.

Results and Discussion

The oxovanadium crown porphyrins, $VO(TCP)$, $VO(TrisCP)$, *cis*- $VO(BCP)$, *trans*- $VO(BCP)$, and $VO(MCP)$, exhibit two absorptions in the visible region around 550 and 589 nm. The positions of these bands remain unaffected in the different substituted porphyrins. These absorptions are highly characteristic of the metallotetraphenylporphyrins.⁷

Cation Complexation. Additions of methanolic solutions of Li^+ , Na^+ , Ca^{2+} , and Mg^{2+} to solutions containing $VO(TCP)$, $VO(TrisCP)$, and *cis*- $VO(BCP)$ in 1:1 ($CHCl_3/CH_3OH$) solution do not produce perceptible changes in the optical absorption spectra. However, dramatic effects are observed (Figure 2) when the cations employed are K^+ , Cs^+ , NH_4^+ , and Ba^{2+} . It is found that the visible bands are red shifted with increase in half-band width and lowered intensity, while the Soret band is blue shifted. These observations are diagnostic and indicate the formation of dimers in solution. It may be noted that the visible absorption spectra oxovanadium(IV) crown porphyrins in pure methanol are very similar to those of the cation-induced dimers. These spectral changes are

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- (5) For brevity the substituted porphyrins are abbreviated as TCP (1), TrisCP (2), BCP (3) (*cis* and *trans* isomers), MCP (4), designating tetrakis-, tris-, bis-, and mono(benzo-15-crown-5)porphyrins, respectively. The phenyl rings form the other substituents in the partially substituted porphyrins (see Figure 1).
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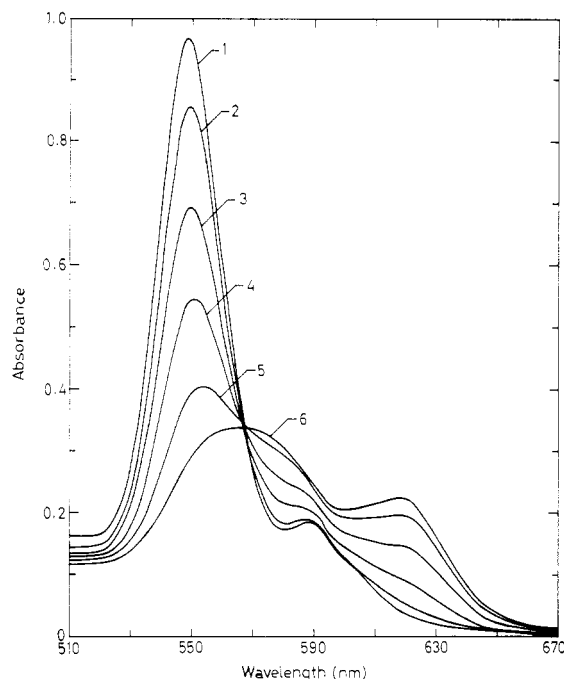


Figure 2. Visible absorption spectra of 5×10^{-5} M VO(TCP) (1) and different solutions containing various concentrations of $\text{Ba}(\text{ClO}_4)_2$ in $\text{CH}_3\text{OH}/\text{CHCl}_3$ (1:1) solvent mixture. Concentrations of $\text{Ba}(\text{ClO}_4)_2$ added to solution 1: (2) 7.5×10^{-5} M; (3) 1.2×10^{-4} M; (4) 1.5×10^{-4} M; (5) 2.0×10^{-4} M; (6) 3×10^{-4} M.

interpreted in terms of solvent coordination to the monomeric vanadyl crown porphyrins (vide infra). It is noteworthy that the visible absorption spectra of vanadyl crown porphyrins in the solvent mixture, $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:1), are very similar to those in pure CHCl_3 , thereby indicating the absence of solvent coordination to oxovanadium(IV) in this solvent mixture.

The progressive decrease in intensity of the red bands on increasing addition of cations affords a viable method to estimate the energetics of the dimerization process. The cation-induced dimerization can be represented as



where P and C^+ represent vanadyl crown porphyrins and the cations, respectively. The overall formation constant of (1) is given as

$$K = [(\text{P}_2\text{C}_n)^{n+}] / ([\text{P}]^2[\text{C}^+]^n) \quad (2)$$

If it is assumed that x mol of the dimer is formed at any instant, then it can be shown that

$$K = x / ((P_t - 2x)^2(C_t - nx)^n) \quad (3)$$

where P_t and C_t denote the total concentrations of vanadyl crown porphyrin and cation, respectively. The values of K can be calculated by using a variety of approximations. In the present study these values are derived from the first principles. The values of P_t , C_t , and n are known from the experimental data while the unknown parameters are K and x . The method adopted here assumes different values for K and computes the values of x for each presumed value of K and for the experimentally known parameters P_t , C_t , and n . The absorbance value of the monomeric oxovanadium crown porphyrin is designated as A_p while the absorbance of pure dimer is represented as A_d . The cation additions result in dimer formation, leading to a decrease in the absorbance values of the monomeric vanadyl crown porphyrin. This decrease in absorbance is designated as A_n and is composed of the absorbance of the dimer formed and the absorbance of free monomeric porphyrin

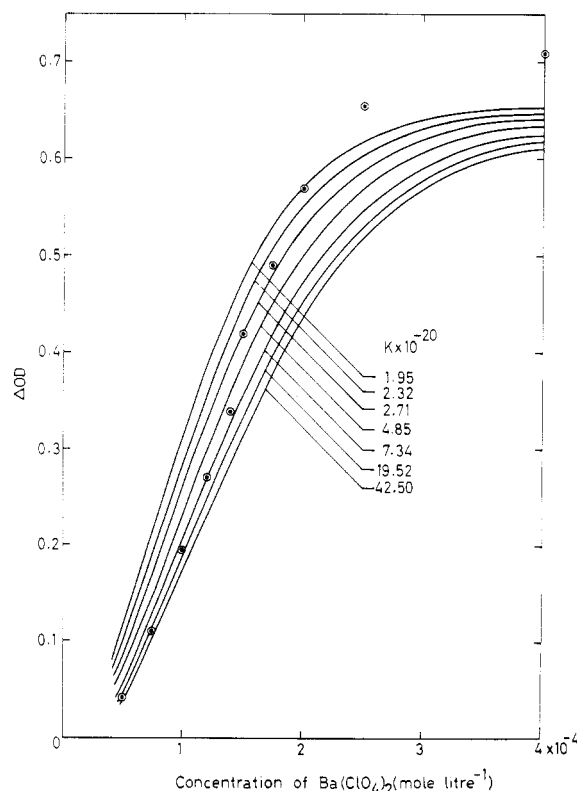


Figure 3. Difference in absorbance values (ΔOD) vs. the concentrations of the added $\text{Ba}(\text{ClO}_4)_2$ for various values of K for Ba^{2+} -induced dimerization of VO(TCP): solid lines, theoretical plots; points, experimental data.

that is present in the mixture at equilibrium 1. This can be represented as

$$A_n = A_p + A_d \quad (4)$$

Since the absorbance is equivalent to ϵCl where ϵ is the molar absorption equivalent, C is the concentration, and l the path length, eq 4 can be rewritten as

$$A_n = \epsilon_p(P_t - 2x)l + \epsilon_d xl \quad (5)$$

where ϵ_p and ϵ_d are the molar absorption coefficients of the monomeric oxovanadium crown porphyrin and the cation-induced crown porphyrin dimer, respectively. These values are determined independently from the absorption spectrum of the vanadyl crown porphyrin and that of the pure dimer. The path length, l , was unity and remained invariant throughout the absorbance measurements. In such situations, the difference between the absorbance values of the monomeric vanadyl crown porphyrin and those of the dimer produced by the addition of cations can easily be shown to be

$$A_p - A_n = \Delta\text{OD} = x(2\epsilon_p - \epsilon_d) \quad (6)$$

A computer program was devised which computed the values of x at each concentration of the added cations for every assumed value of K .⁸ The values of x thus computed can be fitted into the relation (6) to calculate ΔOD values. This provides various values of ΔOD as a function of the concentration of the added cation salts for each presumed value of K . Theoretical plots of ΔOD (calculated from x) vs. the concentration of cation salts (C_t) for various values of K were constructed. The experimental points were then mapped into

(8) A computer program was devised to carry out the calculation by using the Newton-Raphson method. The appropriate values of x are generated for different K values. The program also computes the optical absorbance values of different dimer concentrations, resulting in the addition of cations to the vanadyl crown porphyrins.

Table I. Formation Constants of Oxovanadium Crown Porphyrin Dimers Induced by Different Cations in Chloroform/Methanol (1:1) Media

cations	log <i>K</i>		
	VO(TCP)	VO(TrisCP)	<i>cis</i> -VO(BCP)
K ⁺	27.6 ± 2.5	15.8 ± 1.8	12.7 ± 1.2
Cs ⁺	16.9 ± 1.4	<i>a</i>	<i>a</i>
NH ₄ ⁺	16.4 ± 1.6	11.2 ± 1.5	<i>a</i>
Ba ²⁺	20.7 ± 2.0	14.0 ± 1.7	<i>a</i>

^a The formation of crown porphyrin dimers is inferred by the decrease in absorbance of Q bands. However, quantitative evaluation of formation constants is rendered difficult because of the ensuing precipitation of the added cation salts even at low concentrations.

this plot, and the best fit was chosen for the value of the overall formation constant of the dimer. A representative plot for the Ba²⁺-induced dimerisation of VO(TCP) is given in Figure 3. It was found that, in the cation complexation studies, the overall reaction as represented in (1) seems to go to completion at lower concentrations of the added cations. The values of *K* thus computed are given in Table I.

A perusal of the magnitudes of the obtained *K* values implies the order K⁺ > Ba²⁺ > NH₄⁺ ~ Cs⁺, and this is independent of the number of ether moieties appended to the vanadyl porphyrin. The relative order is consistent with the benzo-15-crown-5 complexation with cations.⁹ For any individual cation the *K* values for the substituted porphyrins are found to be in the order VO(TCP) > VO(TrisCP) > *cis*-VO(BCP). A quantitative evaluation of *K* is rendered difficult in the case of *trans*-VO(BCP) due to its poor solubility in the solvent system. At this point, it is worthwhile to examine the different modes of the dimerization process and inquire whether the porphyrin moiety enhances the formation constants of cation complexation of appended benzo-15-crown-5 or whether it is the intrinsic dimerization of the porphyrin that is responsible for the higher *K* values. The process of dimerization can proceed via either (a) cation complexation by two crown ether moieties each originating from independent crown porphyrins or (b) a preexistent crown porphyrin dimer in the solution acting as a precursor and the added cations promoting further accretion of the dimers of the macrocycle. We examined the possibility of dimer formation in the solutions of crown porphyrins at various dilutions in the absence of cations. It was found that the absorbance values of the red bands obey the Beer-Lambert relationship in the concentration range 10⁻⁴–10⁻⁶ M, thereby discounting the existence of dimers prior to the addition of cations. This result is worth noting and illustrates the importance of cations in promoting the dimer formation. The dimers thus formed are distinct and different from those reported earlier where the aggregation is promoted by the concentration effects.¹ It is reasonable to presume that the cation prefers two crown ether cavities from two independent crown porphyrins, and the energetics of such a process is more favorable than that of the steric strain of the two ether moieties appended to the same crown porphyrin to complex a cation. Once a cation is bound between the two ether moieties, thereby bringing the porphyrin planes together, further cation complexation by other ether moieties can proceed with ease.

The magnitudes of the overall formation constants are very large. The literature values¹ for the dimer formation of the substituted porphyrins and phthalocyanines induced by concentration effects are on the order of 10⁵–10⁶ L mol⁻¹. The problem of ascertaining the contribution of the dimerization constant to the overall stability of the cation-induced dimers

Table II. Electronic Spectral Data for VO(TCP) in Different Solvents^a

solvents	vis bands λ _{max} , nm (ε _{mM})	
chloroform	549 (21)	588 (3.8)
methylene chloride	549 (21)	588 (4.4)
methanol ^b	556 (13)	604 (5.6)
benzene	549 (21)	589 (4.4)
pyridine ^b	557 (13)	610 (7.6)
acetic acid	547 (20)	587 (4.0)
1,4-dioxane	549 (19)	591 (5.0)
dimethylformamide	550 (17)	590 (4.8)
acetone	547 (20)	586 (4.4)
acetonitrile	547 (18)	586 (4.6)
tetrahydrofuran	549 (19)	590 (4.2)

^a The Soret absorption of VO(TCP) in different solvents

remains unshifted at 428 nm except in methanol and pyridine.

^b In pyridine a red shift of 14 nm of Soret absorption is observed while only a marginal red shift of 2 nm is seen in methanol solvent.

of crown porphyrins is rendered difficult. This is because of the fact that the formation constant of metal-polydentate ligand systems is not the average sum or product of the stabilities of individual groups that coordinate the metal ion. Under these circumstances, we tend to believe that the higher magnitudes of the formation constants observed in the present study are a composite of the dimer formation constant and the cation complex stability. This only indicates that these cavity-bearing porphyrins exhibit high selectivity for cations that promote dimerization. The property of the cations that induce dimerization is next examined. It is known that the relative size of the cation and the hole diameter of the ether determines the stoichiometry of the resulting complex.¹⁰ Thus, K⁺, Cs⁺, NH₄⁺, and Ba²⁺ form 1:2 (cation:ether) complexes with benzo-15-crown-5 while Na⁺, Ca²⁺, and Mg²⁺ form only 1:1 complexes. Therefore, it is reasonable to expect that the cations that induce dimerization should essentially form 1:2 complexes with the ether, and this also is borne out in the present study.

Solvent Effects. It is observed that the optical absorption spectrum of VO(TCP) remains virtually unchanged in position and intensity in a variety of solvents. Interestingly, a red shift (~8–10 nm) of the visible bands was observed when pyridine and methanol were employed as solvents (Table II). This was also accompanied by a reduction in intensity. The absorption profile is similar to the one observed on cation addition. We attribute this to solvent coordination to the oxovanadium cation of the porphyrin rather than dimer formation.¹¹ The spectral features of VO(TCP) in aqueous SDS remain the same as observed in the nonpolar solvents. It is pertinent to note that only a small percent (1%) of SDS is enough to bring 5 × 10⁻⁵ M VO(TCP) to the aqueous medium when compared to the amount of SDS required (5%) for VO(TPP). However, attempts to solubilize the cation-induced dimers in aqueous phase by the addition of SDS result in the formation of monomers.

Effect of Crown Ethers. It is of interest to probe into the stability of the dimers in solution in the presence of free crown ethers, viz., benzo-15-crown-5 and 18-crown-6. The optical absorption spectrum of VO(TCP) remains unaltered on ad-

(10) The cavity size of benzo-15-crown-5 is estimated from CPK models to be 1.7–2.2 Å. The ionic diameters of the cations that require two crown ether cavities are K⁺ 2.66, Cs⁺ 3.34, Ba²⁺ 2.70, and NH₄⁺ 2.84 Å (see: Pedersen, C. J. In "Synthetic Multidentate Macrocyclic Compounds"; Izatt, R. M., Christensen, J. J., Eds.; Academic Press: New York, 1978; Chapter 4.

(11) The formation of dimers is normally inferred from the red shift of the Q bands and the blue shift of the Soret band of the porphyrins. It is seen in the case of methanol and pyridine that, although a red shift of the Q bands is observed, the Soret absorption is red shifted, characteristic of solvent coordination (Walker, F. A.; Hui, E.; Walker, J. M. *J. Am. Chem. Soc.* 1975, 97, 2390).

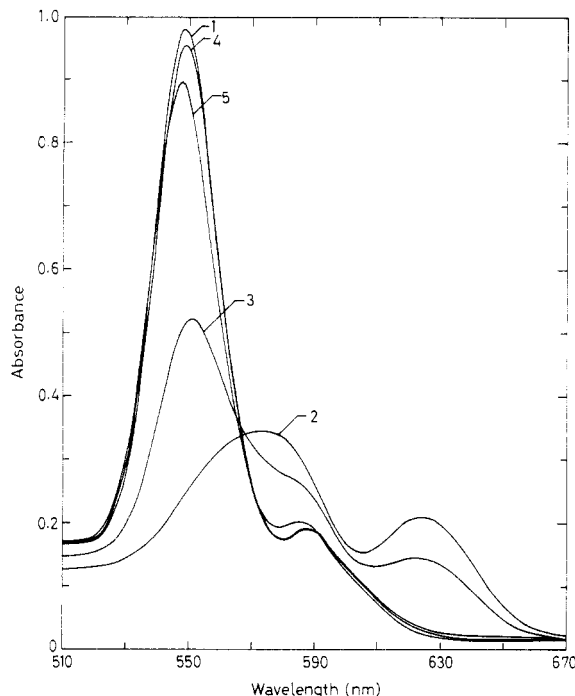


Figure 4. Visible absorption spectra of (1) an equimolar mixture of VO(TCP) and benzo-15-crown-5 (5.0×10^{-5} M) and (2) solution 1 after the addition of 1.00×10^{-4} M KCl. The effect of the addition of free crown ethers to the solution containing VO(TCP) and K^+ (dimer) is shown in curves 3–5, where curves 3 and 4 correspond to the concentration of benzo-15-crown-5, 1.60×10^{-3} and 3.50×10^{-3} M, respectively, while curve 5 denotes the addition of 3.65×10^{-4} M 18-crown-6.

dition of crown ethers, thereby indicating absence of molecular complexation between the porphyrin and crown ethers. It is observed that initial addition of free benzo-15-crown-5 to a solution ($CHCl_3/CH_3OH$, 1:1) containing the dimer $[VO(TCP)]_2(K^+)_4$ does not change the absorption profile until a critical concentration (equimolar) is reached. Further addition of the ether dissociates the dimer, and it is found that at least a 3×10^{-3} M concentration of free ether (120 times the concentration of the dimer) is necessary to bring all the dimer to the monomer fold, as seen from the optical spectra (Figure 4). Under similar conditions it is noticed that the amount of 18-crown-6 required to disaggregate the dimer is only 3.5×10^{-4} M. This suggests that the bound cations in the dimer are freed more effectively by 18-crown-6 rather than benzo-15-crown-5 owing to the higher formation constant of the K-(18-crown-6) complex than that of the corresponding benzo-15-crown-5 complex.⁹ On the other hand, addition of K-(benzo-15-crown-5)₂CNS or K(18-crown-6)CNS in $CHCl_3/CH_3OH$ (1:1) to a solution of VO(TCP) induces dimerization, indicating the facility of K^+ exchange between K^+ bound to the crown porphyrins in the complex.

ESR Spectroscopy. The ESR spectra of VO^{2+} derivatives of the fully and partially substituted crown porphyrins in a $CHCl_3/CH_3OH$ mixture (1:1) at 77 K are typical of VO(TPP) (Figure 5). The ESR parameters of these crown porphyrins do not show much variation, indicating absence of any effect arising from crown ether substitution in the meso positions. Addition of cations Na^+ , Ca^{2+} , and Mg^{2+} to these crown porphyrins results in the encapsulation of four positive ions in the peripheral ether cavities. The ESR spectra of these complexes in solution do not show any marked changes, indicating that the unpaired electron in oxovanadium is essentially localized in the porphyrinato core.

Interesting changes in the ESR spectra of vanadyl crown porphyrins are observed on addition of cations K^+ , Cs^+ , NH_4^+ ,

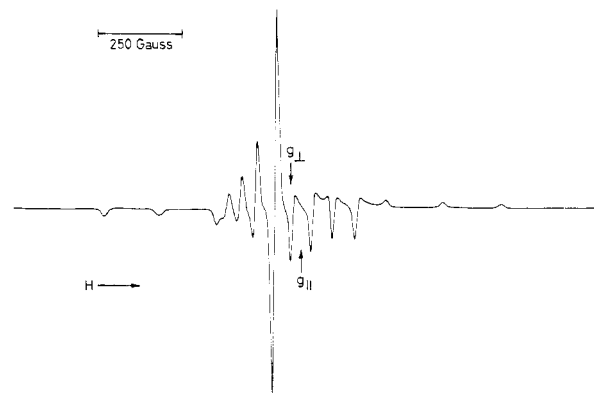


Figure 5. ESR spectrum of VO(TCP) in $CHCl_3/MeOH$ (1:1) glass.

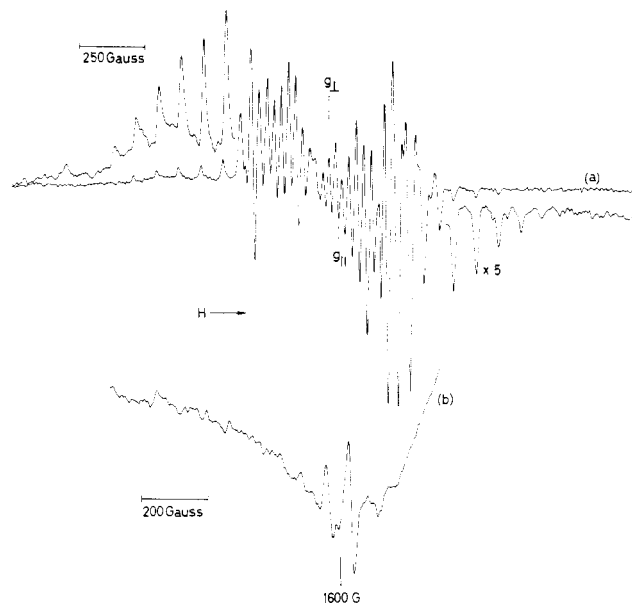


Figure 6. ESR spectrum of the VO(TCP)- K^+ complex in $CHCl_3/MeOH$ (1:1) glass. The vertically expanded parallel components on either side of the perpendicular region are shown. The $\Delta M_s \pm 2$ transition is shown in (b).

and Ba^{2+} . The spectra obtained are typical triplet state with axial symmetry, the hyperfine splitting indicating the presence of two equivalent interacting VO^{2+} nuclei (Figure 6). Interaction of two VO^{2+} ions with spin $1/2$ will give rise to singlet ($S = 0$) and triplet ($S = 1$) states, the separation of which depends on the magnitude of isotropic exchange interaction $-JS_1S_2$ while the separation of the levels within the triplet state is governed by the magnetic dipole-dipole interaction and anisotropic exchange terms. In the case of VO(IV) and Cu(II) ions, the isotropic exchange is considered small, and the dominant contribution arises mainly from magnetic dipole-dipole interactions with negligible contribution from exchange terms. With the assumption that the dimer is axially symmetric and the z axis of the system and the direction of the applied magnetic field are parallel and coincide with V-V vector, the spin Hamiltonian can be represented as in (7) and (8),¹² where H_D is Hamiltonian for dipolar interaction. The

$$H = g_{\parallel}\beta H_z(S_{1z} + S_{2z}) + g_{\perp}\beta[H_x(S_{1x} + S_{2x}) + H_y(S_{1y} + S_{2y})] + A(S_{1z}I_{1z} + S_{2z}I_{2z}) + B(S_{1x}I_{1x} + S_{2x}I_{2x} + S_{1y}I_{1y} + S_{2y}I_{2y}) + H_D \quad (7)$$

$$H_D = (\beta^2/r^3)[g_x^2S_{1x}S_{2x} + g_y^2S_{1y}S_{2y} - 2g_{\parallel}^2S_{1z}S_{2z}] \quad (8)$$

(12) Subramanian, J. In "Porphyrins and Metalloporphyrins"; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 13.

Table III. ESR Data for Oxovanadium(IV) Crown Porphyrins and Their Selected Cation-Induced Dimers

porphyrins	$g_{\parallel}$	$g_{\perp}$	$10^4 A_{\parallel}, \text{cm}^{-1}$	$10^4 A_{\perp}, \text{cm}^{-1}$	$D, ^a \text{G}$	$R, ^a \text{\AA}$
VO(TCP)	1.964	1.985	154.7	52.96		
VO(TrisCP)	1.966	1.986	154.7	51.93		
cis-VO(BCP)	1.965	1.986	154.8	51.74		
trans-VO(BCP)	1.965	1.984	154.8	51.70		
[VO(TCP)] ₂ (K ⁺) ₄	1.967	1.987	77.15	25.98	268.5	4.70
					261.0	4.73
[VO(TCP)] ₂ (NH ₄ ⁺) ₄	1.962	1.983	76.05	25.92	268.5	4.65
					262.0	4.72
[VO(TCP)] ₂ (Cs ⁺) ₄	1.963	1.983	77.91	25.46	266.0	4.70
					255.0	4.75
[VO(TrisCP)] ₂ (K ⁺) ₃	1.966	1.985	77.55	25.48	263.0	4.70
					252.0	4.80
[VO(TrisCP)] ₂ (NH ₄ ⁺) ₃	1.964	1.985	77.03	25.95	256.5	4.75
					251.0	4.80
[cis-VO(BCP)] ₂ (K ⁺) ₃	1.966	1.982	76.65	25.63	263.5	4.70
					251.0	4.80
[trans-VO(BCP)] ₂ (K ⁺) ₂ ^b	1.965	1.983	76.59	25.46	262.5	4.70
					251.0	4.80

^a Two values of D and R are reported. The first entry corresponds to the parallel region and the second to the perpendicular region. ^b The precipitation of the porphyrins was noticed on addition of K⁺ salt. The ESR spectra of the decanted solutions were recorded.

zero-field splitting within the triplet state arises from the dipolar terms. With this brief background the ESR spectra can be analyzed. The eight-line pattern arising from both the parallel and perpendicular regions is now decomposed due to the zero-field splitting into two sets each containing fifteen lines corresponding to a total spin of 7 ($I = 7/2$ for VO²⁺ ion). The sets of lines in the perpendicular region are separated by the zero-field parameter, D , while the parallel sets are separated by $2D$. Because of the similarity of $g_{\parallel}$ and $g_{\perp}$ values, the lines from both the parts are superimposed. It is found that the parallel lines are equally spaced while those from the perpendicular part are distributed with more spacing in the high-field region rather than in the low-field region.

The appearance of a weak transition ($\Delta M_s = \pm 2$) arising from the triplet state ($S = 1$) in the half-field region, $g = 4$, provides a strong support for the existence of dimers in solution. It is gratifying to note the well-resolved spectrum in the high-field region, indicating the formation of dimers,¹³ permits the evaluation of ESR parameters (Table III).

The hyperfine splitting $A_{\parallel}$ and $A_{\perp}$ values of these dimers are half of the hyperfine coupling values observed for the VO(TCP) alone. Further, the g and A values found in the dimers are similar in magnitude to those of the vanadyl crown porphyrins, indicating that the coordination environment of the VO²⁺ ions in the dimer is identical with that of the vanadyl porphyrin alone. The values of D observed in both parallel and perpendicular regions are used to calculate the interatomic distance (V-V) in the dimers with use of the expression¹⁴

$$R = \left[\frac{3/4 g^2 \beta^2 (1 - 3 \cos^2 \theta)}{D} \right]^{1/3} \quad (9)$$

For an axial dimer

$$R = (0.65 g^2 / D)^{1/3} \quad (10)$$

The values thus calculated are given in Table III.

The characteristic ESR spectra of the dimers and the evaluated ESR parameters permit a proposition for the structure of the dimers (Figure 7). It was pointed out earlier that the formation of a dimer is caused by the cations that require two crown ether cavities for complexation. The axially symmetric nature of the dimers with a V-V separation of ~ 4.7 Å necessitates that the two porphyrin planes each containing

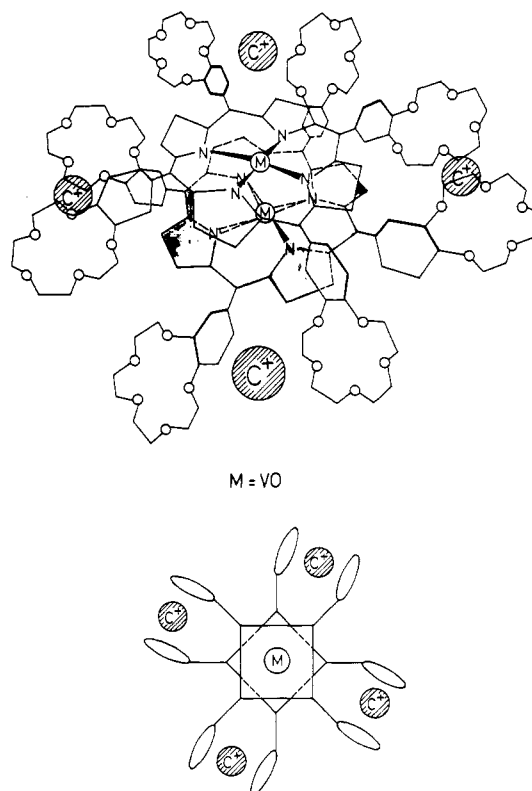


Figure 7. Possible structure for the cation-induced dimer of VO(TCP). Rotation of porphyrin planes in the dimer is depicted in the lower part of the figure.

an oxovanadium ion be parallel. Stacking the planes one over the other with the meso positions of one exactly over the other will be unfavorable for cation encapsulation by the crown ethers since the aryl part of the ether is perpendicular to the plane of the porphyrin. This, then stipulates a rotation by ca. 40–45° of one of the porphyrin planes with respect to another such that the crown ethers from each of the porphyrins are displaced to accommodate the cations in a lateral fashion. A substantive support for the proposed structure is also seen from the theoretical calculations of Lucia et al.¹⁵ for copper phthalocyanine where the eclipsed dimer (rotation by 45°) is the most favored conformation from energy considerations.

(13) Normally in the ESR spectra of concentration-dependent dimers the low-field region ($\Delta M_s = \pm 2$) is well resolved while the $\Delta M_s = \pm 1$ transition is often masked by the strong signals of the monomer.
(14) Chasteen, N. D.; Belford, R. L. *Inorg. Chem.* 1970, 9, 169.

(15) Lucia, E. A.; Verdrame, F. D.; Taddei, G. J. *Chem. Phys.* 1970, 52, 2307.

Table IV. Vanadium-Vanadium Distances, $R(V-V)$, in the Dimers of Different Oxovanadium(IV) Complexes^a

systems	$R(V-V)$, Å	ξ , ^b deg	ref
vanadyl (+)-tartrate (50% water-glycol, 77 K)	4.08	28	c
	(4.08)	(28)	d
vanadyl (±)-tartrate (50% water-glycol, 77 K)	4.18	0-10	c
	(4.35)	(3)	e
vanadyl-tetrakis(aminomethyl)methane complex	4.8 ± 0.5	50 ± 5	f
vanadyl deuteroporphyrin IX dimethyl ester	3.4		g
vanadyl deuteroporphyrin IX dibutyl ester	3.5		g
vanadyl protoporphyrin IX dimethyl ester	3.5		g
vanadyl tetrasulfonatophthalocyanine	4.5 ± 0.1		h
vanadyl octaethylporphyrin cation radical dimer	4.7		i
vanadyl crown porphyrins	4.7		j

^a The values in the parenthesis correspond to crystallographic data. ^b Angle of deviation from axial symmetry. ^c Toy, A. D.; Smith, T. D.; Pilbrow, J. R. *Aust. J. Chem.* 1974, 27, 1.

^d Setten, E. *Acta Crystallogr., Sect. B* 1969, B25, 1480.

^e Forrest, J. C.; Prout, C. K. *J. Chem. Soc. A* 1967, 1312.

^f Carr, S. G.; Smith, T. D.; Pilbrow, J. R. *J. Chem. Soc., Faraday Trans. 2* 1974, 497. ^g Boyd, P. D. W.; Smith, T. D.; Price, J. H.; Pilbrow, J. R. *J. Chem. Phys.* 1972, 56, 1253. ^h Boyd, P. D. W.; Smith, T. D. *J. Chem. Soc., Dalton Trans.* 1972, 839.

ⁱ Subramanian, J., private communication. ^j Present work.

The $R(V-V)$ values obtained in the present study are compared with those of reported systems of axially symmetric dimers (Table IV). The distances R of the different VO^{2+} dimers only indicate the V-V separations. It is worthwhile to examine the interplanar separations (distance between the porphyrin planes) in the dimers. In our earlier studies on copper crown porphyrin dimers^{3a} $R(Cu-Cu)$ is estimated to be 4.2 Å from the ESR data. The $Cu(II)$ ions are situated in the plane of the porphyrin, and thus $R(Cu-Cu)$ truly represents the interplanar separation. It is reasonable to presume that the vanadium atom is displaced by ~ 0.5 Å from the plane of the porphyrin, as found in the X-ray structures of vanadyl deoxyphylloerythroetioporphyrin¹⁶ and $VO(OEP)$.¹⁷ Such a situation would essentially lead to an interplanar separation of 3.7 Å in the oxovanadium crown porphyrin dimers similar to that observed in deuterio- and protoporphyrin IX dimethyl ester dimers.

It is fruitful to probe into the effect produced by geometrical disposition of the crown ether moieties in the partially substituted porphyrins and the different cations on the $R(V-V)$ values. It is found that the magnitudes of $R(V-V)$ remain invariant (within the limits of experimental uncertainty) in the dimers formed by various crown porphyrins. The well-resolved ESR spectra of the dimers in the high-field region display lines characteristic of monomer crown porphyrin (3250 G) as well as the dimer. The ratio of the first-derivative-signal (monomer and dimer) heights when plotted against the number of appended crown ethers in the porphyrin core shows the following decreasing order of the extent of dimerization for the same amount of the added K^+ ion: $VO(TCP) > trans-VO(BCP) > VO(TrisCP) > cis-VO(BCP)$ (Figure 8). The least extent of dimer formation for $cis-VO(BCP)$ is understandable in view of the possible existence of two structurally different conformers. The dimer that results in cis -oriented porphyrins can have either an axially symmetric one or a linear one where the porphyrin planes are adjacent to one another and resemble the covalently linked dimers of Collman et al.^{2b} From ESR studies one is able to detect only the axial dimers and hence the decrease in the extent of dimer formation in

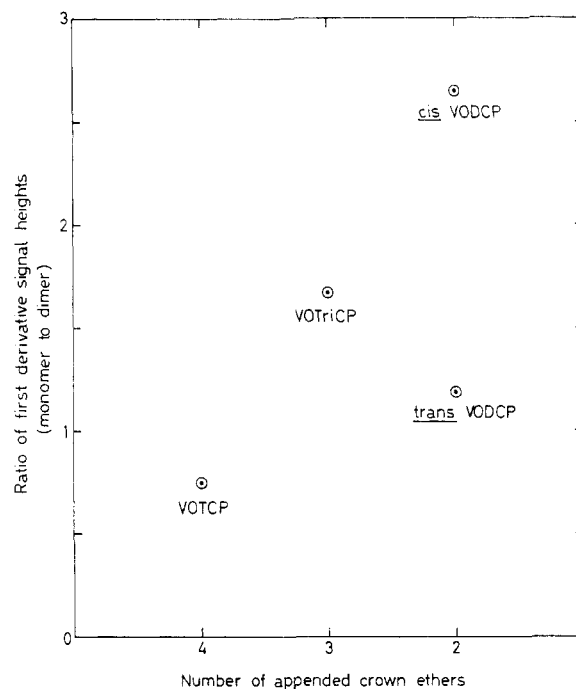


Figure 8. Plot of the ratio of the first-derivative-signal heights (monomer to dimer) vs. the number of appended crown ether moieties in oxovanadium porphyrins (the K^+ -ion-induced dimerization is represented here). (In this figure VODCP is $VO(BCP)$ and VOTriCP is $VO(TrisCP)$ as used in the text.)

$cis-VO(BCP)$. The observation that the extent of dimer formation in $VO(TrisCP)$ is relatively lower than that in $trans-VO(BCP)$ can be explained in terms of steric requirements that result in two possible dimers similar to the one described in $cis-VO(BCP)$.

It is found that different cations, K^+ , Cs^+ , NH_4^+ and Ba^{2+} , induce the formation of dimers and these are the ones that form complexes with benzo-15-crown-5 in 1:2 (cation:crown ether) stoichiometry. The $R(V-V)$ values in all these cases remain insensitive to cation sizes. The encapsulation of cations of different sizes by the crown porphyrins can be visualized by model-building studies. A CPK model for the dimer was constructed with use of the X-ray structural data on vanadyl porphyrin^{16,17} and the K^+ complex of benzo-15-crown-5.¹⁸ The latter reveals that the ether oxygens and aryl ring are essentially coplanar and K^+ is sandwiched between two crown ether moieties with a separation of 3.4 Å. The vector distance between the central metal ion of the porphyrin and the center of plane defined by the appended ether moiety is computed to be ~ 10 Å. These two distances and the observation that the ether oxygen planes can deviate by 30° from the coplanarity of the aryl ring¹⁹ permit an evaluation of the angle to which the porphyrin planes in the dimer have to be rotated to accommodate the cations. The distance traversed by the ether oxygen plane is estimated to be ~ 1.5 Å for 30° deviation from coplanarity with the aryl part (Figure 9). In order to accommodate the cations by the crown ether moieties in a compact fashion (~ 3.5 Å separation), it is essential to rotate the porphyrin planes by $\sim 40^\circ$ and to have the ether oxygen planes deviate from coplanarity with the aryl part within the limits of $0-30^\circ$. Any increase or decrease in the interplanar (porphyrins) distance does not have any perceptible effect. The

(17) Molinaro, F. S.; Ibers, J. A. *Inorg. Chem.* 1976, 15, 2279.

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

(19) The crystal structure of benzo-15-crown-5 reveals that the plane containing ether oxygens makes an angle of 31° with the phenyl ring; Hanson, I. R. *Acta Crystallogr., Sect. B* 1978, B34, 1026.

(16) Petterson, R. C. *Acta Crystallogr., Sect. B* 1969, B25, 2527.

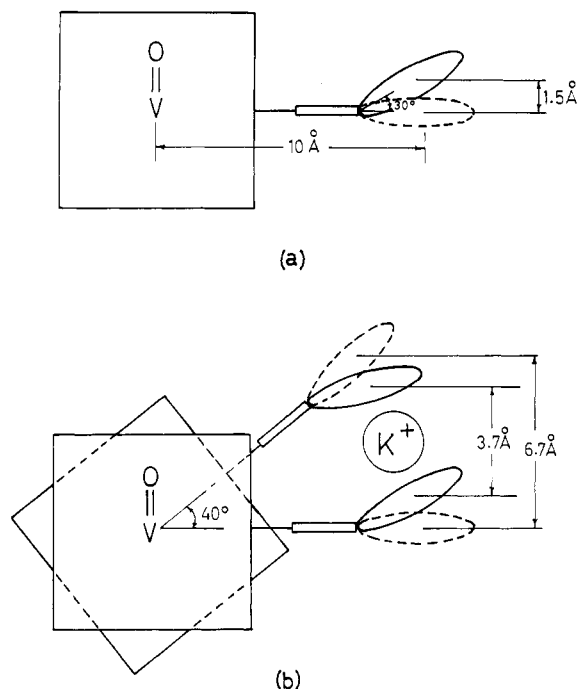


Figure 9. Vertical view of oxovanadium crown porphyrin dimers. The angle of deviation of the ether oxygen plane from the coplanarity with the aryl ring of the ether and the distance through which the center of the ether oxygen plane is displaced are given in (a). Rotation of the porphyrin planes by 40° with the crown ether voids coparallel to the aryl ring resulting in 6.7-Å separation and deviation of 30° from coplanarity with the aryl ring leading to 3.7-Å separation are shown in (b) (see text).

flexibility of the crown ether oxygen planes to deviate from coplanarity to accommodate the cations of different sizes is an important feature of these crown porphyrins.

The optical spectral shifts consequent upon addition of cations to the monomeric forms of vanadyl crown porphyrins provide identification of dimer formation. The relative magnitudes of the red shifts of the Q bands follow the number of crown ether moieties attached to the vanadyl porphyrin, $\text{VO}(\text{TCP}) > \text{VO}(\text{TrisCP}) > \text{cis-VO}(\text{BCP})$. For a representative $\text{VO}(\text{TCP})$, the magnitude of the shifts induced by

different cations follows the order $\text{K}^+ > \text{NH}_4^+ \sim \text{Ba}^{2+} \sim \text{Cs}^+$. The exciton formalism has been useful to explain the spectral shifts in porphyrin and chlorin aggregates.²⁰ However, the diverse spectral shift data, obtained in the face to face porphyrins, could not be rationalized in terms of a complete theoretical framework.²¹ The dimers reported in the present study are different from those reported in aqueous solutions wherein the instability of the dimer depends on the nature of the central metal ion in the porphyrin cavity. A comparison of the relative shifts in the Q bands for a representative TCP with different divalent central metal ions follows the order $\text{VO} > \text{Zn} \sim \text{Cu} \sim \text{Co}$. The cations essentially bring the two porphyrin planes together such that the incipient π - π interactions are augmented. This study has provided an interesting means to synthesize dimers having two dissimilar metals without a covalent attachment and essentially furnishing models for dimetal enzymes. Work in this direction is in progress and will be reported in the future.

Acknowledgment. This work is supported by the Science Engineering Research Council, Department of Science and Technology, Government of India, New Delhi. V.T. is grateful to the Department of Atomic Energy, Trombay, Bombay, for a fellowship.

Registry No. $\text{VO}(\text{TCP})$, 81642-65-1; $\text{VO}(\text{TrisCP})$, 82469-04-3; $\text{cis-VO}(\text{BCP})$, 82469-05-4; $\text{trans-VO}(\text{BCP})$, 82469-06-5; $[\text{VO}(\text{TCP})]_2\text{K}_4$, 82521-41-3; $[\text{VO}(\text{TCP})]_2(\text{NH}_4)_4$, 82469-07-6; $[\text{VO}(\text{TCP})]_2\text{Cs}_4$, 82521-40-2; $[\text{VO}(\text{TrisCP})]_2\text{K}_3$, 82469-08-7; $[\text{VO}(\text{TrisCP})]_2(\text{NH}_4)_3$, 82469-09-8; $[\text{cis-VO}(\text{BCP})]_2\text{K}_2$, 82469-10-1; $[\text{trans-VO}(\text{BCP})]_2\text{K}_2$, 82469-11-2; $[\text{VO}(\text{TCP})]_2\text{Ba}_4$, 82521-39-9; $[\text{VO}(\text{TrisCP})]_2\text{Cs}_3$, 82469-12-3; $[\text{VO}(\text{TrisCP})]_2\text{Ba}_3$, 82469-13-4; $[\text{cis-VO}(\text{BCP})]_2\text{Cs}_2$, 82469-14-5; $[\text{cis-VO}(\text{BCP})]_2(\text{NH}_4)_2$, 82469-15-6; $[\text{cis-VO}(\text{BCP})]_2\text{Ba}_2$, 82469-16-7; $\text{VO}(\text{MCP})$, 82469-17-8.

- (20) (a) Gouterman, M.; Holten, D.; Liberman, E. *Chem. Phys.* **1977**, *25*, 139. (b) Shipman, L. L.; Cotton, T. M.; Norris, J. R.; Katz, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 8222.
- (21) The spectral shifts reported for the various synthetic face to face porphyrin dimers are not in accordance with the predictions based on exciton formalism. Thus, reported alkyl-linked porphyrin dimers (Paine, J. B., III; Dolphin, D.; Gouterman, D. *Can. J. Chem.* **1978**, *56*, 1712) and a doubly linked chlorin system (Wasielowski, M. R.; Svec, W. A.; Cope, B. T. *J. Am. Chem. Soc.* **1978**, *100*, 1961) display no spectral shifts while the covalently linked tetraphenylporphyrin dimer reported in ref 2c shows a broadened Soret band and red-shifted Q bands. These observations indicate the different orientations that are possible in solution which are responsible for the anomalous shifts.