Cation or Solvent-Induced Supermolecular Phthalocyanine Formation: Crown Ether Substituted Phthalocyanines

By

N. Kobayashi and A.B.P. Lever

in

Journal of the American Chemical Society

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Phthalocyanines with four 15-crown-5 ether voids at the 3,4 positions (MtCRPc) (Mt = H, Zn, Co, Ni and Cu) have been synthesized and characterised. Dimerisation of MtCRPc is induced in solvents such as methanol and by addition of some cations (K\(^{+}\), Ca\(^{2+}\), and NH\(_{4}\)\(^{+}\)), especially K\(^{+}\). Cofacial dimer formation in the presence of these cations proceeds in a two-step three stage process, as indicated by absorption and emission spectroscopy. These species have a highly specific D\(_{4h}\) eclipsed configuration providing well defined dimeric species for spectroscopic analysis. The ESR spectrum of the cation induced dimeric CuCRPc shows axial symmetry and may be analysed in terms of an inter-planar separation of 4.1 Ångstroms. The \(^1\)H NMR spectra (#19 con'd over)
of the cation induced metal free and zinc dimers are consistent with an eclipsed configuration. Upper excited state (Soret, $S_2$) emission is observed for the first time in the phthalocyanine series.
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Cation or Solvent-Induced Supermolecular Phthalocyanine Formation: Crown
Ether Substituted Phthalocyanines.

by Nagao Kobayashi* and A.B.P.Lever*

Abstract

Phthalocyanines with four 15-crown-5 ether voids at the 3,4 positions
(MtCRPC) (Mt = H₂, Zn, Co, Ni and Cu) have been synthesized and
characterised. Dimerisation of MtCRPC is induced in solvents such as
methanol and by addition of some cations (K⁺, Ca²⁺, and NH₄⁺), especially
K⁺. Cofacial dimer formation in the presence of these cations proceeds in
a two-step three stage process, as indicated by absorption and emission
spectroscopy. These species have a highly specific D₄h eclipsed
configuration providing well defined dimeric species for spectroscopic
analysis. The ESR spectrum of the cation induced dimeric CuCRPC shows
axial symmetry and may be analysed in terms of an inter-planar
separation of 4.1 Ångstroms. The ¹H NMR spectra of the cation induced
metal free and zinc dimers are consistent with an eclipsed configuration.
Upper excited state (Soret, S₂) emission is observed for the first time in
the phthalocyanine series.
Introduction

Dimerization, often through aggregation of porphyrins\(^2\) and phthalocyanines\(^3\) has been intensively investigated. In general the mechanism of aggregation is poorly understood, the product may be contaminated with monomer and perhaps with higher aggregates, and the relative orientation of the components is obscure. We report here the preparation of phthalocyanines functionalized at the 3,4-positions with four crown ether voids (MtCRPc),\(^4\) together with their cation or solvent induced dimerization.\(^5\) Unambiguous evidence is presented which indicates the step-wise formation of two dimeric species induced by K\(^+\) ions. The first is non-cofacial, while the second is a rigidly cofacial eclipsed D\(_{4h}\) species. This provides the opportunity to study the uv/visible absorption and emission, ESR, and NMR spectra of well defined dimeric species (metal-free, Zn, Cu, Co and Ni) in terms of exciton theory. Upper excited state S\(_2\) emission is observed in phthalocyanine chemistry for the first time. The results are compared with corresponding data for the tetra-crowned porphyrins,\(^6,7\) where the orientation is twisted. We refer to the dimerisation of the monomeric MtCRPc units for ease of discussion while noting that the binuclear products contain one or more main group ions and are therefore not, strictly speaking, dimers of the mononuclear unit.

Experimental

1) Measurements: Electronic absorption spectra were recorded with a Perkin Elmer-Hitachi model 340 microprocessor spectrometer. Emission and excitation spectra were obtained with a Varian SF330 spectrofluorimeter with appropriate filters to eliminate scattered light. Fluorescence quantum yields were determined by the use of quinine bisulfate in IN H\(_2\)SO\(_4\), \(\Phi_F = 0.55\) at 298 K,\(^8a, b\) or free base tetraphenylporphyrin in benzene (\(\Phi_F\)
Data were obtained by a comparative calibration method using the same excitation wavelength and absorbance for the crown species and the calibrants, and the same emission energies.

ESR measurements were obtained using a Varian E4 spectrometer, calibrated with DPPH. FTIR spectra were recorded on a Nicolet SX20 spectrometer using KBr discs. $^1$H NMR spectra were recorded on a Varian LH360 spectrometer using deuteriochloroform alone, or containing deuterium methane or tetramethylsilane as internal standard. The FAB mass spectra were obtained by courtesy of the Nebraska Center for Mass Spectroscopy by the same method as described previously. Solvents, dimethylformamide, diethylether, methanol, ethanol, etc, were either distilled or Spectrograde.

11) Synthesis

2,3-(3',4'-Dibromobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene.

Following the dibromination of 1,2-dimethoxybenzene, so-called benzo-15-crown-5 was reacted with 2 equivalents of bromine in acetic acid, using a small crystal of iodine as an initiator. Recrystallisation from ethanol gave colorless plates in 51% yield. Anal. calcd. for $C_{14}H_{18}Br_2O_5$: C, 39.5; H, 4.3. Found: C, 39.6; H, 4.3%. $^1$H NMR (CDCl$_3$, internal Me$_4$Si) 7.06 (2H, s), 4.25-3.70 (16H, m). m.p. 80-81°C.

2,3-(3',4'-Dicyanobenzo)-1,4,7,10,13-pentaoxacyclopentadeca-2-ene.

The above dibrominated benzo-15-crown-5 (8.52g, 0.02mol) and CuCN (5.4g, 0.06mol) were refluxed in dry DMF (80mL) for 5h. After rotary evaporation of about 50-60mL of DMF, concentrated ammonia (200mL, 28%) was added, and air bubbled through the solution for 12h. After washing copiously with water, the dry olive-green product was soxhlet extracted with diethyl ether for 3 days. Benzene recrystallisation provided 2.02g (31%) of colorless small needles. Anal. calcd. for $C_{16}H_{18}N_2O_5$ C, 60.4; H,
5.7; N,8.8. Found: C,60.1; H, 5.8; N, 8.5%. $^1$H NMR(CDCl$_3$) 7.14(2H,s), 4.35-3.70(16H,m). IR(KBr) ν 2223(C= N) cm$^{-1}$, m.p. 151-20°C.

Non-metallated (H$_2$CRPc) and metallated (MtCRPc) crowned phthalocyanines

H$_2$CRPc was prepared by refluxing benzo-15-crown-5 dicyanide (1.24g, 3.9 x 10$^{-3}$ mol) in 2-dimethylaminoethanol (5mL) for 17h while passing ammonia gas through the solution. The precipitate was re-precipitated from diethylether, washed with water, dried and then chromatographed on basic alumina, initially with chloroform as eluant. The initial yellow band, which was discarded, was followed by a blue band which was eluted with ethanol-chloroform, providing 0.468g (38%) of slightly bluish green powder (Anal, see Table I). $^1$H NMR(CDCl$_3$) 8.02(8H,s), 4.7-3.6(64H,m), 3.41(2H,s).

ZnCRPc was obtained by reaction of H$_2$CRPc with a large excess of zinc acetate in refluxing DCE/ethanol, for several days in the dark, until the 4-band Q spectrum of H$_2$CRPc had disappeared. After removal of the solvent, the residue was washed with water and recrystallised from chloroform-ethanol (78% yield). The FAB mass spectrum showed peaks at m/e values of 1339(M$^+$,7), 956(68), 522(22), 460(58), 424(23), 307(46) and 154(100) (relative intensities in parentheses).

Other MtCRPcs (Mt = Co(II), Fe(II), Ni(II), Cu(II)) were prepared by the "nitrile" method. The benzo-15-crown-5 dinitrile and the appropriate metal acetate were refluxed gently in ethylene glycol for several hours. The solution was filtered while hot, and the residue washed with hot ethanol, hot water, and hot ethanol, then chromatographed on basic alumina, resulting in yields between 26 and 51% of the metallated products. Elemental analyses are presented in Table I.
Results and Discussion

1) Cation complexation leading to step-wise cofacial dimer formation.

In chloroform solution, the several MtCRPc species exhibit spectra typical of well behaved mononuclear metallophthalocyanines generally with a single intense $\pi-\pi^*$ transition in the range 667-708nm with associated higher energy vibrational components, commonly referred to as the Q band, and a second intense and broader $\pi-\pi^*$ transition at 300-360nm called the Soret (Table II, Fig.1). The metal free species, $H_2$CRPc is similar but shows two closely spaced Q bands because of its lower ($D_{2h}$) symmetry. As will be demonstrated below, dimerization occurs in many other solvents or when certain cations are added to this solution. Such dimerization is readily monitored by the dramatic change in absorption, and in particular by a blue shift in both the Soret and Q band absorption.

In the case of porphyrins functionalised at the methine positions with four benzo-15-crown-5 units, increasing addition of $K^+$, $NH_4^+$, and $Ba^{2+}$ ions affected the porphyrin Q band absorption by a) a reduction in intensity, b) broadening and c) a red shift of ca 10nm. On the other hand, $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ did not cause any appreciable change in the visible region absorption. Note that the potassium ion is sandwiched between two crown ether units, and does not reside within the ether ring.

The MtCRPc species behave quite differently. Thus $K^+$, $NH_4^+$, $Ca^{2+}$ and $Na^+$ all alter the spectra appreciably, though not all in the same fashion, while $Ba^{2+}$, $Cs^+$ and $Mg^{2+}$ have little effect. The ionic radii of cations which produce significant changes in the electronic spectra of the MtCRPc species, are equal or smaller than those required in the porphyrin series. In the crown phthalocyanine case, addition of $K^+$, $NH_4^+$ and $Ca^{2+}$
causes a) a reduction in Q band intensity around 660-700nm (the so-called monomer peak) and an increase in peak intensity around 620-640nm, (the so-called dimer peak) i.e. a blue shift of the Q band of ca 30-60nm, b) a blue shift in the Soret (10-20nm) and c) some broadening in the Q band region (Fig.1A, Table II). Such changes are most obvious for K+ with respect to the amount needed to affect them.

Absorbance intensities in the 660-700 and 620-640nm ranges change markedly with K+ concentration up to \([K^+] /[MtCRPc] = ca 2\). Previous experience with aggregated and binuclear phthalocyanines\(^{13}\) shows that the loss of low energy Q band absorption, near 660-700nm, of the monomeric species, and the shift to a broad absorption near 620-640nm is consistent with electronic coupling between a pair (or more) of phthalocyanine units. In this case, as will be documented more fully below, dimerisation is the exclusive process.

From the plot (Fig.2) of the intensity changes with \([K^+]\), there is evidence for a two-step three stage process. The first, second and third stages occur approximately at \([K^+] /[MtCRPc]\) values of 0-0.5, 0.5 - 1.5 and over 1.5, respectively. The K+ induced two-step three stage process is also obvious from the shift in position of the isosbestic points (Fig.1).\(^{15}\)

Assuming the monomer-dimer equilibrium (eq.1) for the K+ triggered spectroscopic change:

\[
K
nK^+ + 2 \text{ monomer} \leftrightarrow \text{dimer.} K^+_n \quad (1)
\]

the specific monomer and dimer concentrations were derived using the method of West and Pearce\(^{16}\), using as data the changes of intensity at two wavelengths, as a function of \([K^+]\). The pure monomer spectrum\(^{17}\) was assumed to be present in the absence of K+. Using this procedure, proof
of formation of the dimer may be obtained by plotting the calculated log[monomer] against calculated log[dimer]. A slope of 2 will be obtained if eqn.(i) is applicable. Formation of higher oligomers would cause the slope to be more steep than 2. Indeed as revealed in Fig.3 there is a region where the slope is 2.0. When $K^+$ ions are added to a MtCRPc solution, the monomer concentration decreases sharply, and a region with slope = ca 2.0 continues until $[K^+]/[MtCRPc] = 0.5$. After this point, the slope of the plot approaches zero, especially beyond the region $[K^+]/[MtCRPc] > 1.0$.

Thus the monomer-dimer conversion proceeds with a very high formation constant ($K$ for eqn.1 with $n = 1$, $6.12 \times 10^9$ L$^2$/mol$^{-2}$) until two MtCRPc units bind ONE cation. Subsequently the spectroscopic changes in the $[K^+]/[MtCRPc] > 1.0$ region are no longer a monomer to dimer transformation process, but, rather rearrangement of one form of dimer to another. The region $0.5 \leq [K^+]/[MtCRPc] \leq 1.5$ can be considered to be the transition stage where the MtCRPc-cation-MtCRPc complex combines with a 2nd and 3rd cation. Considering that the blue shift in the Q and Soret absorption in the dimers can be explained by an exciton interaction, and that the ESR data for CuCRPc in the presence of $K^+$ or $Ca^{2+}$ (vide infra) will indicate the presence of two copper atoms in very close proximity, the last stage ($[K^+]/[MtCRPc] > 1.5$ in Fig.2) can be ascribed to cofacial complex formation. Thus after formation of a non-cofacial MtCRPc-cation-MtCRPc dimeric complex, increasing cation concentration causes a conformational change in the dimer wherein the two phthalocyanine halves encapsulate two or more cations leading to the formation of the cofacial dimer, i.e. a supermolecular phthalocyanine is attained. Probably encapsulation continues until the available sites are saturated, i.e. until two MtCRPc units bind four cations in rigid eclipsed dimer. The inset of Fig.3 shows
the calculated monomer and dimer concentrations of NiCRPc as a function of 

\([K^+]/[NiCRPc]\). Although not shown, similar behaviour is observed with the 

other MtCRPc species; thus dimerisation is essentially complete (but not 

cofacial dimerisation) when \([K^+]/[MtCRPc] > 1.0\).

The addition of sodium ions did lead to a change in spectrum (Fig.1B) 
in contradistinction to the porphyrin series. The band due to the 

monomer species decreases in intensity, while there is growth in the band 
due to the dimeric species. Sodium ions are, however, unable to effect the 

complete conversion to a spectrum, obtained with potassium ions, typical 
of the cofacial species.

ii) Solvent induced dimerisation.

The intensity of the MtCRPc \(Q\) band peak (around 660-700nm) decreases 

if the solvent is changed from chloroform to methylene chloride, benzene, 

DMF, dimethyl sulfoxide, toluene, THF, ethyl acetate, methanol etc. In 
such circumstances the change in spectrum exactly parallels that observed 

upon \(K^+\) addition. Such spectroscopic changes are also observed in mixed 

solvents, e.g. Fig.4a shows the effect of mixing methanol into chloroform, 

upon the CoCRPc spectrum. With increasing ratio of methanol to chloroform, 

the peak height at 668nm (mainly monomer) decreases but that at 625nm 

(mainly dimer) increases. For comparison, Fig.4b shows the corresponding 
data for addition of \(K^+\). The dimeric spectrum induced by the methanol 
solvent (\(\text{CHCl}_3:\text{MeOH} = 2:1 \text{ v/v}\)) is essentially identical to that obtained 
at a \([K^+]/[CoCRPc] = 1.6\) ratio which demonstrates that the mixed solvent 
is giving rise to cofacial dimer formation. Unfortunately the very low 
solubility of the metallated crown phthalocyanines in dimer-forming 
solvents (ca. \(1 \times 10^{-5}\)M) precludes other methods of characterisation. Note 
that the solubility of the monomers in chloroform is several orders 
greater.
Electron Spin Resonance.

Of the several MtCRPc species investigated, CuCRPc is expected to provide the most definitive ESR spectra. Preliminary studies showed that data collection in a chloroform-methanol mixture provided better data than pure chloroform. The spectrum of CuCRPc obtained in the absence of any cations (Fig.5A) is structureless and seems to be that of a somewhat aggregated species.

Addition of an excess of sodium ions led to the development of a well defined structured signal (Fig.5B-a) in frozen solution, basically very similar to previously observed monomeric copper porphyrin and phthalocyanine species, e.g. copper(II) tetraphenylporphyrin. The spectrum is clearly axial and contains both copper hyperfine and nitrogen (from the four coordinating phthalocyanine nitrogen atoms) super-hyperfine structure. The parameters \( g_{||} = 2.166, g_{\perp} = 2.049, \) and \( A_{||}^{\text{Cu}} = 228 \times 10^{-4}, A_{\perp}^{\text{N}} = 16.7 \times 10^{-4}, A_{||}^{\text{N}} = 14.3 \times 10^{-4} \text{ cm}^{-1} \) are typical values for a species of this type. As developed further below, the solution giving rise to this spectrum contains about 50% mononuclear species, and 50% of the non-cofacial dimer almost certainly with sodium ions occupying the ether voids in both cases. In the absence of sodium ions, the solution is partially aggregated resulting in broadening of the resonance signals. In the presence of sodium ions, the resulting positive charge keep the copper atoms separated and a clean highly resolved ESR spectrum is observed.

Dramatic changes in the ESR spectrum of CuCRPc occur when \( K^+ \) or \( Ca^{2+} \) ions are added (Fig.5C,D). This observation differs from the corresponding Cu(II) crown porphyrin where \( K^+ \), but not \( Ca^{2+} \), was effective. Thus with CuCRPc both cations yield two strong perpendicular transitions in the \( g = 2 \) region. These transitions do not exhibit nitrogen super-hyperfine coupling but do show the characteristic seven line pattern expected for
two equivalent Cu(II) ions coupled together.\(^{22}\) In the half-field region
\((\Delta H = \pm 12)\), seven equally spaced lines \((87-88 \text{ gauss separation})\) are
observed. These data provide unmistakable evidence for the formation of a
symmetric dimeric molecule. The absence of any ESR signal originating from
a monomeric CuCRPc molecule, under these conditions, attests to a high
formation constant. Moreover, the overall band envelope is essentially
identical to those of various well defined symmetric binuclear and coupled
copper complexes in the literature.\(^{23}\) The data in Figs. 5C and 5D also
exclude any significant proportion of higher aggregate.

The ESR parameters for these spectra are collected in Table III,
having been evaluated by standard procedures.\(^{24}\) Most importantly it is
possible to evaluate the Cu-Cu distance from the zero field splitting
parameters.\(^{25}\) In this fashion the calculated Cu-Cu distance is found to be
c.a. 4.1 Angstroms, in the presence of both \(K^+\) or \(Ca^{2+}\). This is nearly
identical to the distance estimated from CPK molecular models.\(^{26}\) Note that
in the presence of ammonium ions, dimerisation does occur and two strong
perpendicular transitions are observed, but the seven line pattern is not
resolved.

iv) \(^1H\) NMR Spectra.

The \(^1H\) NMR spectrum of ZnCRPc is shown in Fig. 6, both in the presence
and absence of cations. The spectrum of mononuclear ZnCRPc is complex, in
the high field region, due to a large number of chemically inequivalent
ether fragments, but the signals are well separated by the ring current
anisotropy of the phthalocyanine core. Assignments are shown in Fig. 6.

The addition of \(CaCl_2\) to a solution of ZnCRPc \(([Ca^{2+}] / [ZnCRPc] \text{ ca.}
10)\) increases the complexity of the high field region (Fig. 6b) and the
signals spread out, especially downfield. These data are consistent with
cofacial dimer formation (Fig. 7). The singlet of aromatic protons does not
significantly shift but becomes sharper, due, probably to the restricted rotation of the O-CH₂-CH₂-O groups or to the greater rigidity imposed by encapsulation of the cations. The negligible shift of the singlet is expected since the 3,4-protons of one phthalocyanine fall in the "black region" of the anisotropic shielding effect of the second ring, assuming the interplanar distance is close to 4.1 Å.

The pyrrole protons of H₂CRPc shift from -3.41 ppm to -8.09 ppm with cofacial dimer formation consistent with the structure in Fig.7. This large upfield shift indicates an intense diamagnetic ring current interaction in this dimer.

v) Emission spectroscopy.

Fluorescent emission from the lowest π-π* (Q band) state is common in metal free, zinc and other main group phthalocyanines. Both mononuclear H₂CRPc and ZnCRPc exhibit such emission near 700 nm. The excitation spectrum of this emission (Fig.8a) parallels that of other mononuclear phthalocyanines except for a rather prominent excitation near 430 nm which is also observed in absorption (Table II). This is rather unusual for a phthalocyanine unit and may involve the ether oxygen lone pairs.

Emission from the upper excited π-π* state (Soret), so-called S₂ emission is not uncommon in porphyrin chemistry. We have recently noted that several binuclear and tetranuclear phthalocyanines also exhibit upper excited state emission and also find that both metal free and zinc crown phthalocyanine monomer species exhibit emission in chloroform near 430 nm (Fig.8). These are the first examples of phthalocyanine upper excited state emission.

The crown S₂ emission is broader than the S₁ emission and the band shape is similar to that observed for tetrabenzoporphyrin free base and its
zinc derivative. The excitation spectra of the $S_2$ emission is similar, but not identical, to the $S_1$ excitation spectra (Fig.8A, Table II). Assuming that the $S_2$ emission originates in the same transition which gives rise to the well developed 420nm absorption, then the Stokes shift for $S_2$ emission is, as in the porphyrin species, very small.

Using the known quantum yields of quinine sulfate\textsuperscript{8a,b} (for $S_2$) and free base tetraphenylporphyrin\textsuperscript{6c} for calibration, the quantum yields for $S_1$ and $S_2$ emission were determined to be, in chloroform, 0.7 and $1 \times 10^{-2}$ for H$_2$CRPc. Some solution instability precluded an accurate determination for ZnCrPc. The $S_1$ quantum yield is very similar to those observed earlier for unsubstituted metal free and zinc phthalocyanine species\textsuperscript{30,31}

Addition of K$^+$ to metal free and zinc crown Pc monomers in chloroform (concentration $< 5 \times 10^{-6}$M) leads to quenching of both the $S_1$ and $S_2$ emission, in a parallel fashion (Fig.8b). The concentration of K$^+$ ion required to quench the fluorescence intensity of a crowned porphyrin is apparently very much less than the concentration of the cation required to reduce the optical density of the porphyrin in the ground state.\textsuperscript{7a} In the crowned phthalocyanine system (Fig.9), on the other hand, the quenching behaviour corresponds almost exactly to that in the absorption study (Fig.2). The Stern-Volmer plot for $S_1$ emission (Fig.9A) is clearly consistent with step-wise encapsulation of the K$^+$ ions. In the $0 < [K^+]/[H_2CRPc] < 0.5$ region where the non-cofacial H$_2$CRPc-K$^+$-H$_2$CRPc species forms (Figs.2,3), quenching is not marked, though it does occur to a small degree. However with further increase in [K$^+$], quenching is greatly enhanced while above [K$^+$]/[H$_2$CRPc] = ca. 1.5 the emission intensity become almost constant. The residual emission intensity has an excitation spectrum identical to that of the monomer species and an intensity about 1/700 of the initial intensity. It is due to the small amount of monomer.
species in equilibrium with the cofacial species, implying that the 
cofacial dimer does not emit.\(^3\)

The quenching of the \(S_2\) emission parallels that of the \(S_1\) quenching 
except that the degree of quenching is much less marked (Fig.9b). There is 
also some remaining \(S_2\) emission which appears to arise from the cofacial 
dimer since it is relatively very much more intense than can be reconciled 
with the equilibrium monomer content (intensity \(2/5\) of initial value, upon 
cofacial dimer formation) (Fig.9b). However the excitation spectrum of 
this residual \(S_2\) emission is the same as in the monomeric species. There 
remains the suspicion that the \(S_2\) emission does not indeed originate from 
the phthalocyanine but from an impurity. This possibility appears excluded 
by the similarity of its excitation spectrum to the Soret absorption, and 
the similarity of its quenching behaviour to that of \(S_1\), but, as noted 
above, there are some inconsistencies.

The addition of Na\(^+\) ion to a chloroform \(\text{H}_2\text{CRPc}\) solution also 
quenches, to some degree, both the \(S_1\) and \(S_2\) emission (Fig.9C). However 
much higher concentrations of Na\(^+\) are needed and it is clearly much \textit{less} 
efficient. In the crown porphyrin case,\(^7\)a Na\(^+\) did not perturb emission. 
As indicated above, Na\(^+\) ion only takes the species to the second 
non-cofacial dimer stage.

(vi) Absorption spectra (Table II).

a) Mononuclear species and cofacial dimer.

The mononuclear species have absorption spectra in chloroform (Fig.2, 
Table II) typical of mononuclear \(\text{MtPc}\) species\(^3\) though with a prominent 
shoulder or peak near 420nm which is not so common. Its appearance is 
reminiscent of the hyper-porphyrin spectra, showing similar additional 
absorption but the latter arises as a consequence of the central ion
having an (np_z)^2 pair of electrons, e.g. Pb(II). This 420nm band shifts but does not disappear upon cofacial dimer formation.

The formation of the cofacial dimeric species provides a convenient method of studying exciton coupling in an eclipsed phthalocyanine species. Some spectra of fully eclipsed cofacial species are shown in Fig. 0, and the data collected in Table II. Note that under the conditions [K]/[MCRPc] > 1.5, the quantity of mononuclear species in equilibrium with the cofacial dimer is less than 0.2% and therefore its spectrum makes no significant contribution to the spectra reported here for the cofacial species. The most interesting feature of the cofacial dimeric spectra is the single rather broad (compared to the monomer) and symmetrical Q band absorption. Although the molar extinction coefficients of the cofacial dimer Q bands are approximately one-half of the corresponding monomer Q bands, the oscillator strengths are essentially identical, i.e. there is no loss in transition probability in forming the dimer (see Table II).

Thus exciton coupling of the two Q S_1 states leads to two new levels corresponding to an in-phase and out-of-phase coupling. Transitions to the lower, out-of-phase, component are forbidden rigorously in an eclipsed D_4h species. For compounds which show typical monomeric and dimeric spectra (MCRPc, M = Zn, Cu, Ni and Cu), the Q band blue shift upon dimerization is about 880 - 980 cm^{-1}. For parallel eclipsed dimers with negligible distortion from D_4h symmetry, the dipole-dipole excitation splitting, V, is given by eqn.(2):^37

\[ V = \frac{e^2 M^2}{4 \pi \varepsilon_0 c R^3} \]  \hspace{1cm} (2a)

\[ V = 1.16 \times 10^5 M^2/R^3 \]  \hspace{1cm} (2b)

where M, and R are the dipole length, and the inter-molecular separation respectively, \( \varepsilon_0 \) is the permittivity in a vacuum and the other parameters have their usual meaning. V is given in wavenumbers in (2b) if
M and R are expressed in Angstroms. The dipole length in Angstroms can be estimated from eqn.(3):30

\[ M^2 = \left( \frac{\epsilon_{\text{max}}}{2513 G} \right) (\Delta \lambda / \lambda) \]  

(3)

where \( G \) is the degeneracy, 2 in this case, \( \Delta \lambda \) is the halfbandwidth, \( \lambda \) is the wavelength and \( \epsilon_{\text{max}} \) is the molar extinction coefficient of the dimer Q band, respectively. In this fashion the M values are estimated to be about 0.68 - 0.98\( \AA \) (Table IV). Alternatively M may be estimated from the oscillator strength38 yielding the same result. Assuming a distance of \( R = 4.4\ \AA \), from ESR, the exciton splitting is calculated to be about 770 - 1600 cm\(^{-1}\). The exciton splitting may also be estimated as twice the energy difference between the mononuclear Q band and dimeric Q band peak energies, yielding about 1760, 1960, 1910 and 1960 cm\(^{-1}\) for Ni, Co, Cu and ZnCRPcs respectively. This compares with an exciton splitting of about 2500 cm\(^{-1}\) for the binuclear bridged cofacial phthalocyanine species.13 Using these data and eqn.(3), provides an alternate route to estimating inter-metallic distances, leading to the data shown in Table IV; the electronic spectra and electron spin resonance experiments yield comparable results.

The Soret band is much less obviously affected by formation of the cofacial dimer. There is generally a small blue shift but little change in intensity. Nevertheless the shift is comparable to that seen in the Q band.5a Thus coupling of the Soret states does appear to have taken place even though little quenching of the \( S_2 \) emission apparently occurs.

b) Non-cofacial dimer.

The spectra of the non-cofacial dimer, obtained with \([K^+]/[MtCRPc] = 0.5\), are collected in Fig.10, while the spectrum of the sodium ion induced non-cofacial dimer of CuCRPc is shown in Fig.1, in both cases in admixture with the mononuclear species. With \([K^+]/[MtCRPc] = 0.5\), there is
approximately 50% of monomeric species in equilibrium with the non-cofacial dimer. In Fig.11 the spectra of several non-cofacial dimeric species are shown, obtained by subtracting the spectrum of the mononuclear species from the admixed spectra. One observes that the resulting spectrum is very similar to that of the cofacial species and with an intensity, per dimeric unit, slightly less than that of the cofacial dimer. There is also evidence for the existence of a new shoulder or peak to the blue of the main Q band absorption, and little evidence for any additional absorption to the red of the Q dimer peak. There is no shifting in the Soret band (Fig.1).

The initial non-cofacial dimer, second stage product, reasonably consists of a dimeric molecule whose two halves are joined together at one ether unit by a bridging potassium ion. In fluid solution there may be many conformational forms of this dimeric unit. The electronic spectrum will consist of a 'snap-shot' of all possible conformations. If there is free rotation about the potassium ion, then many conformational forms will have symmetry much lower than D4h. Such a situation will give rise to substantial absorption to the red of the cofacial dimeric peak, yet this does not appear to be observed, rather, additional absorption is seen to the blue. Suppose instead that the ether voids, which are rather bulky, inhibit such rotation, and restrict the molecule to an end-to-end stretched out 180° conformation of C2h symmetry, viewed edgeways-on as a step conformation. Such a conformation would show two higher energy peaks due to the splitting of the otherwise degenerate exciton coupled state, but transitions to the two lower energy states remain strictly forbidden. Thus the data appear to support such a linear step conformation. Recall, further, that the ESR spectrum of the CuCRPc-Na⁺-CuCRPc solution shows no evidence for Cu-Cu coupling,
consistent with the stretched out formulation.

Note further that the two parts of the step must be parallel - if their angle were greater than 180°, i.e. they were tilted away from each other, absorption to the red of the dimer peak would be expected. Such tilting must be absent or small.

It is noteworthy that the mononuclear emission from $S_1$ is not quenched to any significant extent upon formation of the stage 2 non-cofacial dimer irrespective of whether it is potassium or sodium ion induced. Since the electronic spectra of these species show significant electronic coupling effects, such an observation is rather surprising.

Concluding Remarks

The structure of the final stage 3 dimeric species, assigned to a fully eclipsed cofacial D$_{4h}$ dimer is required when we assume that the two halves are held together by potassium ions bridging crown ether units. With four K$^+$ ions shared by two MtCRPc units, a parallel arrangement of the Pc planes can surely be anticipated. This structure is supported by the Cu ESR spectrum, by the presence of a single very symmetric, rather weak and rather narrow Q absorption band (compared with the half-bandwidths for more flexible binuclear phthalocyanine species) by the emission and also by the NMR spectra. Note, too, that the cofacial free base [H$_2$CRPc]$_2$K$_4$ species also possesses a single relatively narrow Q band absorption suggesting it too possesses D$_{4h}$ symmetry and that the four hydrogen atoms are, therefore, equally shared between the four pyrrole nitrogen atoms.

This result is contrasted with the cation induced porphyrin dimer$^{7a}$. Due to the position of the 15-crown-5 units (meso position) they were constrained to adopt a lateral complexation of the cation. Consequently,
the macrocyclic rings are rotated by ca. 45° (usually) with respect to each other in a staggered dimer.

This difference in coordination style may explain the difference in cation behaviour in the two series. Thus the larger Ba\(^{2+}\) ion, ineffective in the MtCRPc series, can dimerize the porphyrin whose inter-crown distance can be expanded by further rotation of the porphyrin rings, without weakening the porphyrin-porphyrin π-π stabilization. In the MtCRPc case, expanding the crown-crown distance, will weaken the Pc-Pc interaction.

It is also interesting that Ca\(^{2+}\) which does not dimerize the crown porphyrin and which forms a 1:1 (internal) adduct with 15-crown-5, is, nevertheless, able to generate a cofacial bridged MtCRPc dimer. It is evident that the free energy gained by forming a 1:1 crown ether complex is exceeded, in this case, by forming a 1:2 Ca\(^{2+}\):crown species and the cofacial dimeric \([\text{MtCRPc}]_2[\text{Ca}^{2+}]_4\).

Lastly we would like to stress the importance of the eclipsed cofacial dimers realized in the present study. Although several covalently bound cofacial porphyrin\(^{39}\) and phthalocyanine\(^{27}\) dimers have been reported, they are all skewed\(^{37}\) and/or staggered\(^{7,27}\) while not yet proven by x-ray studies, it is likely from the data presented here, that these cofacial crown MtCRPc phthalocyanines are perfectly eclipsed and will therefore be archetypes for future studies in this area.

Acknowledgments

We thank the Office of Naval Research (Washington) for financial support. We are also indebted to S.Hirao for help in the synthesis of benzo-15-crown-5 dibromide, and to H.Lam for NMR assistance.
Figure 1. Change of absorption spectra of (A) H₂CRPCc and (B) CuCRPC (below) by the addition of CH₃COOK or CH₃COONa respectively, to 3ml of a CHCl₃ solution of H₂CRPC or CuCRPC in a 10mm cell. The CH₃COOK and CH₃COONa were each dissolved in CHCl₃-MeOH(95:5 v/v) and were added using a microsyringe. 60µL were added in all. Arrows indicate the direction of the spectroscopic change. In (B) the final spectrum is that of a CH₃COONa saturated solution.

Figure 2. The dependence of absorbance of several MtCRPcs on [K⁺]/[MtCRPC] for several wavelengths. Experiments were conducted as described in Fig. 1.

Figure 3. Plots of log [Monomer] versus log [Dimer] for several MtCRPC in CHCl₃ solution. Experimental data as appeared in Fig. 1 were analyzed using a computer program based on the approximation method of West and Pearce. The solid lines are drawn with the theoretical slope of 2. The inset shows the dependence of monomer and/or dimer concentration of NiCRPC on [K⁺]/NiCRPC calculated for our experimental system.

Figure 4. (A) Absorption spectra of CoCRPC in CHCl₃-MeOH mixtures, a; CHCl₃ alone, b; CHCl₃:MeOH = 2.9:0.1 v/v, c; CHCl₃:MeOH = 2.8:0.2 v/v, d; CHCl₃:MeOH = 2.4:0.6 v/v, e; CHCl₃:MeOH = 2.0:1.0 v/v.

(B) Change in absorption spectrum of CoCRPC by the addition of CH₃COOK. Experiments were carried out as described for Fig.1. The spectrum shown by an open arrow was recorded at [K⁺]/[CoCRPC] = 1.63.
Figure 5. ESR spectra of CuCRPc in CHCl₃ - MeOH (ca. 4:1 v/v), A; in the absence of any cation, and in the presence of B; saturated CH₃COONa at (a) 77 K, and b) room temperature, C; CH₃COOK, ([K⁺]/[CuCRPc] = 4) and D; CaCl₂ ([Ca²⁺]/[CuCRPc] = 10) [CuCRPc]mH = 1.

Figure 6. 300 MHz proton NMR spectra of ZnCRPc in A; CDCl₃ and B; CDCl₃ containing trace amount of CD₃OD in the presence of CaCl₂. Signals marked X and * are due to solvents.

Figure 7. A proposed structure for the cation-induced dimer of MtCRPc. Solid circles indicate cations such as K⁺ and Ca²⁺.

Figure 8. Emission and excitation spectra of H₂CRPc in A; CHCl₃ (emission excited at 350nm) B; in the presence of CH₃COOK in CHCl₃ containing 0.1 v/v percent of MeOH and C; in the presence of CH₃COONa in CHCl₃ containing 0.1% v/v MeOH. [H₂CRPc]/M = 4.91 x 10⁻⁶, [CH₃COOK]/[H₂CRPc] = 2.62. [CH₃COONa]/[H₂CRPc] = 98. Excitation spectra were recorded for emission peaks at A; 704 nm and B; 429nm and C; 429nm.

Figure 9. Stern-Volmer plots of the emission of H₂CRPc. (a) S₁ emission quenched by K⁺ ion; (b) S₂ emission quenched with K⁺ ion; (c) S₂ emission quenched with Na⁺ ion.

Figure 10. Absorption spectra of several MtCRPc species as indicated. Monomeric species (_______)(in chloroform), cofacial [MtCRPc]₂K⁺₄ species (-----)(in chloroform with 0.1% methanol), and solutions with [K⁺]/[MtCRPc] = 0.5 containing a roughly 50:50 mixture of monomeric and non-cofacial [MtCRPc]-K⁺-[MtCRPc] species (_______) (in chloroform with 0.02% methanol).
Figure 11. Estimated spectra of several non-cofacial \([\text{MtCRPc}]^{-}\cdot[\text{MtCRPc}]^+\) species obtained from data in Fig.10 by subtraction of the monomeric component. The spectra in the region of the dotted lines are approximate due to uncertainty in the amount of monomeric species to subtract (ca. 40-50%).
References

1) Visiting Professor from the Pharmaceutical Institute, Tohoku University, Sendai, Japan.


4) Abbreviations used in this study: Pc, phthalocyaninato dianion; CRPc, tetra(15-crown-5)ed phthalocyaninato dianion; ESR, electron spin resonance; FAB, fast atom bombardment; NMR, nuclear magnetic resonance; DPPH, diphenylpicrylhydrazyl; DCB, 1,2-dichloroethane; DMF, dimethylformamide; THF, tetrahydrofuran; FTIR, fourier transform infrared.


    (b) idem. Inorg. Chem 1982, 21, 3606. (c) idem. ibid 1985, 24 3253.


14) The cavity size of 15-crown-5 is estimated from CPK models to be
The ionic diameters of the cations used in this paper are
\[ \text{Mg}^{2+} \ 1.60, \ \text{Na}^+ \ 1.90, \ \text{Ca}^{2+} \ 1.98, \ \text{K}^+ \ 2.66, \ \text{Ba}^{2+} \ 2.70, \ \text{NH}_4^+ \ 2.84, \ \text{Cs}^+ \ 3.34\AA. \]

15) The shift in the position of the isosbestic points were most clearly observed for the CuCRPc and NiCRPc system. For the CuCRPc system, the isosbestic points of the 1st and 2nd stages appeared at 370 and 641nm, while those for the 2nd and 3rd emerged at ca. 418 and 665nm. For NiCRPc, isosbestic points were similarly observed at 378 and 632nm, and at 404 and 672nm respectively.


17) Judging from the previously accumulated data, spectra of MtCRFs in CHCl\(_3\) are clearly those of monomer at [MtCRPc] < 2 \times 10^{-5}M.


25) It is possible to estimate the Cu-Cu distance from the ratio of the 
intensity of the forbidden half-field transition \((\Delta M = \pm 2)\) to the 
intensity of the allowed transitions \((\Delta M = \pm 1)\). In our 
case, this ratio is \(4.1 \times 10^{-3}\), which corresponds to \(r = 4.15 \text{Å}\).

26) The crystal structure of benzo-15-crown-5 reveals that the plane 
containing ether oxygens makes an angle of 31° with the benzene 


1960, 33, 1523.

4131.

Zaleski, I.E.; Kotlo, V.M.; Sevchenko, A.N.; Solovev, L.N.; 
Aaviksoo, J.; Freiberg, A.; Savikhin, S.; Steimakh, G.F.; Tsvirko, 

33) In the porphyrin system, cofacial dimer units emit more weakly than


Table I. Elemental Analytical Data of MtCRPcs.a

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>N</th>
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<tr>
<td></td>
<td>Found</td>
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<tr>
<td>H₂CRPc</td>
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<td>57.54</td>
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a Theoretical values are calculated for C₆₄H₇₂N₈O₂₀H₄ except for H₂CRPc (C₆₄H₇₂N₈O₂₀H₂).
Table II  Characteristic Absorption Bands of MtCRPcs$^a$, nm($\epsilon$)

<table>
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<tr>
<th>Compound</th>
<th>Monomeric Species</th>
<th>$f_{b,c}$</th>
<th>Half-Bandwidth cm$^{-1}$</th>
<th>Dimeric Cofacial Species</th>
<th>$f$</th>
<th>Half-Bandwidth cm$^{-1}$</th>
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</thead>
<tbody>
<tr>
<td>H$_2$CRPc</td>
<td>700(33400)</td>
<td>662(27500)</td>
<td>645(11800)</td>
<td>601(6200)</td>
<td>421(8100)</td>
<td>347(30800)</td>
</tr>
<tr>
<td>ZnCRPc</td>
<td>677(96700)</td>
<td>0.16</td>
<td>350</td>
<td>635(51000)</td>
<td>0.17</td>
<td>730</td>
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<tr>
<td>CuCRPc</td>
<td>676(129400)</td>
<td>0.29</td>
<td>480</td>
<td>635(74000)</td>
<td>0.35</td>
<td>1050</td>
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<tr>
<td>NiCRPc</td>
<td>667(70000)</td>
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<td>520</td>
<td>630(47000)</td>
<td>0.18</td>
<td>845</td>
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</table>

$^a$ Refers to the MtCRPcs compound.
$^b$ Monomeric species.
$^c$ Cofacial species.
Monomer spectra were collected in CHCl₃, while those of dimer were in CHCl₃ containing ca 0.1% MeOH and in the presence of K⁺(CH₃COOK). [K⁺]/[MtCRPc]=4. Extinction coefficient (ε) is per phthalocyanine unit.

Oscillator strength. Oscillator strengths for the monomeric species are lower limits excluding higher energy vibrational satellites.

sh means shoulder.
Table III. Magnetic Parameters\textsuperscript{24} of Cation-Induced CuCRPc Cofacial Dimers\textsuperscript{a}

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g_1$</th>
<th>$g_2$</th>
<th>$A_1$</th>
<th>$A_2$</th>
<th>$D_1$</th>
<th>$D_2$</th>
<th>Frequency Cu–Cu\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>(gauss)</td>
<td>(MHz)</td>
<td>distance/Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[CuCRPc]\textsubscript{2}(K\textsuperscript{+}) \textsubscript{4}</td>
<td>2.050</td>
<td>2.152</td>
<td>107</td>
<td>103</td>
<td>371</td>
<td>407</td>
<td>9093</td>
</tr>
<tr>
<td>[CuCRPc]\textsubscript{2}(Ca\textsuperscript{2+}) \textsubscript{4}</td>
<td>2.047</td>
<td>2.141</td>
<td>105</td>
<td>104</td>
<td>375</td>
<td>425</td>
<td>9096</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Fig. 5 for definition of parameters.

\textsuperscript{b} Calculated via $r^3 = 1.39 \times 10^4 \times g_2/D_2$, where $D$ is in gauss and $r$ is in Ångstroms.\textsuperscript{24}
Fig 2
Uncorrected Relative Fluorescence Intensity

- : Emission
- - : Excitation

Wavelength/nm

Fig 8
Fig 10