

# Recent studies in phthalocyanine chemistry

A.B.P.Lever, M.R.Hempstead, C.C.Leznoff, W.Liu, M.Melnik, W.A.Nevin and P.Seymour

Dept. of Chemistry, York University, North York, Ontario, Canada M3J 1P3

## Abstract

Our recent synthetic studies in polynuclear phthalocyanine chemistry are reviewed. The electronic coupling which occurs between the various phthalocyanine units are probed by electronic absorption and emission spectroscopy. Many of the complexes are effective as oxygen reduction electrocatalysts and these studies, carried out with the catalysts as monolayers on ordinary pyrolytic graphite surfaces, are discussed. Under certain circumstances, the cobalt(II) phthalocyanine species will disproportionate into Co(I) and Co(III) species thereby providing the potential for multi-electron catalysis. The general utility of polynuclear phthalocyanines as multi-electron catalysts is explored.

## A. INTRODUCTION

Since their accidental synthesis in Scotland, by Imperial Chemical Industries, in 1928, phthalocyanines (Pc) have enjoyed considerable industrial importance for use in dyestuffs, paints, colours for metal surfaces, fabrics and plastics. In recent years there has been considerable interest in developing their use in electrochromic devices, organic catalysis, electrocatalysis, photocatalysis, photovoltaic devices, lithium batteries, fuel cells, pollution control (especially desulfurisation) etc.

Many of the uses cited in the preceding sentence involve a redox process in which two or more electrons are exchanged per reaction sequence, e.g. water or hydrogen sulfide oxidation and oxygen or thionyl chloride reduction.

Of especial interest to us has been the design of multi-electron redox catalysts capable of a concerted catalysis of multi-electron processes. Such multi-electron reagents might be facilitated by one or more of several strategies. These include the use of mononuclear species capable of a simultaneous 2 (or more) electron redox process, the use of aggregation to produce a cooperative result between mononuclear molecules, and the design of polynuclear reagents. All three of these approaches have been considered of late [1-21]. In this paper, we shall review our progress towards the multi-electron catalysts.

## B. SPECTRO-ELECTROCHEMISTRY OF IRON AND COBALT TETRASULFONATED PHTHALOCYANINES (TsPc)

These water soluble species were studied by laying down 1 or more monolayers on an ordinary pyrolytic graphite (OPG) surface [11]. The layers remain adherent to the OPG electrode when placed in water, at least within certain positive and negative polarisation limits. Three or four redox waves were seen, with potentials varying with solution pH (varied from 2 to 13) (Table I). The variation of certain redox couples in

Table I Summary of Redox Data for FeTsPc and CoTsPc at Various pH [11]

Couple <sup>a</sup>	Potential range <sup>b</sup> Volts vs SCE	pH range
[TsPc(-2)Fe(IV) <sup>2+</sup> /TsPc(-2)Fe(III) <sup>+</sup> ]	0.8 - 0.4	5-13
[TsPc(-2)Fe(III) <sup>+</sup> /TsPc(-2)Fe(II)]	0.42	2-5
	0.42 - -0.1	5-13
[TsPc(-2)Fe(II)/TsPc(-2)Fe(I) <sup>-</sup> ]	-0.16 - -0.45	2-7
	-0.5	7-13
[TsPc(-2)Fe(I) <sup>-</sup> /TsPc(-3)Fe(I) <sup>2-</sup> ]	-0.38 - -0.56	2-5
	-0.9 - -1.3	6-13
[TsPc(-2)Co(III) <sup>+</sup> /TsPc(-2)Co(II)]	0.8	2-7
	0.8 - 0.5	7-13
[TsPc(-2)Co(II)/TsPc(-2)Co(I) <sup>-</sup> ]	-0.30 - -0.50	2-5
	-0.50	5-13
[TsPc(-2)Co(I) <sup>-</sup> /TsPc(-3)Co(I) <sup>2-</sup> ]	-0.6 - -0.7	2-5
	-1.0 - -1.4	7-13

a) Axial ligands omitted. b) Potential range corresponds with pH range with a slope of approximately 60mV/pH decade. A single number implies constant potential over the pH range indicated.

Table II Summary of Redox Species and Aggregation Effects [15]

Acidic and basic regions		
	$[\text{Co(II)TsPc(-3)}]^{2-}$	Non-aggregated
	$[\text{Fe(II)TsPc(-3)}]^{2-}$	Non-aggregated
	$[\text{Co(II)TsPc(-2)}]^{1-}$	Non-aggregated
	$[\text{Fe(II)TsPc(-2)}]^{1-}$	Non-aggregated
	$\text{Co(II)TsPc(-2)}$	Aggregated
	$\text{Fe(II)TsPc(-2)}$	Partially aggregated
Acidic region		
	$[\text{Co(III)TsPc(-2)}]^+$	Non-aggregated
	$[\text{Fe(III)TsPc(-2)}]^+$	Aggregated
Basic region		
	$[\text{Co(III)TsPc(-2)}]^+$	Non-aggregated
and	$[\text{TsPc(-2)Co(III)-OH-Co(III)TsPc(-2)}]^+$	in equilibrium
	$[\text{Fe(III)TsPc(-2)}]^+$	Aggregated
and	$[\text{TsPc(-2)Fe(III)-O-Fe(III)TsPc(-2)}]$	in equilibrium

only specific pH ranges, provides evidence to identify the nature of the redox process and its involvement with protons. Such studies are necessary prior to a more detailed analysis of the mechanism of oxygen reduction by these species, also as a function of pH. Of especial interest was the observation, with  $\text{FeTsPc}$  in alkaline solution, of a wave with four times the charge of the other one-electron waves, apparently corresponding to four molecules being reduced by one electron each.

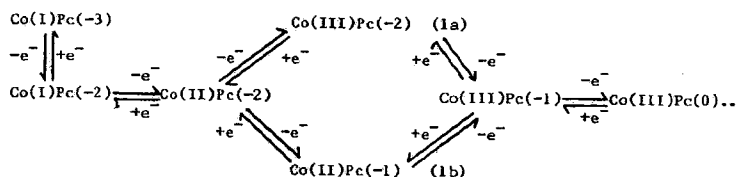
Spectro-electrochemistry [15] provided a means not only of confirming the nature of the various redox waves observed with Fe and CoTsPc, but also of learning something of the degree of aggregation as a function both of pH and oxidation state, it having been intimated that binuclear aggregated species might be the active species on the electrode in some cases. Indeed there was spectroelectrochemical evidence for binuclear complexes being formed with the M(III) species in alkaline media, and it was possible to determine which oxidation states were subject to aggregation in the various pH ranges (Table II). Thus, mechanistically, oxygen reduction may be facilitated by interaction of the oxygen with a binuclear aggregated form of the catalyst.

Trends in the pH dependencies of the various redox species are due, in part, to differences in axial coordination of the central metal atoms. Aggregation of  $\text{Co(II)TsPc(-2)}$  is a result of its very labile axial water molecules. However, the  $d^6$   $\text{Fe(II)TsPc(-2)}$  species is not expected to have such labile axial water, and thus is only partially aggregated in solution.  $\text{Co(III)}$  is also  $d^6$ , and  $[\text{Co(III)TsPc(-2)}]^+$  is found to be non-aggregated (in acid solution) as a result of the non-lability of its axially coordinated water molecules. In contrast,  $\text{Fe(III)TsPc(-2)}$  is fully aggregated in acid solution due to the lability of its axial ligands [15].

In base, the tendencies of  $\text{Co(III)}$  and  $\text{Fe(III)}$  to form hydroxy- and  $\mu$ -oxo-bridged species, respectively, are manifested in the spectro-electrochemistry of  $[\text{Co(III)TsPc(-2)}]^+$  and  $[\text{Fe(III)TsPc(-2)}]^+$  at pH 7-10, which is markedly different from that found in acid solution. In base, an equilibrium exists between monomeric and dimeric forms of  $[\text{Co(III)TsPc(-2)}]^+$ , whose relative concentration depends upon concentration of CoTsPc, ionic strength, pH and temperature.

### C. ELECTROCHEMISTRY OF MONONUCLEAR CoPc AND ITS DISPROPORTIONATION

$\text{Co(II)Pc}$  can be oxidised or reduced according to two alternate pathways:-



depending upon solvent or supporting electrolyte [16-18] (axial ligands are omitted).

Pathway (1b) is effective in the absence of a solvent coordinating axially to the cobalt atom, and in the absence of a strongly axially binding supporting electrolyte anion. When this is not true, pathway (1a) is followed. Thus, for example, CoPc in o-dichlorobenzene (DCB) plus a perchlorate supporting electrolyte follows (1b), while dimethylformamide (DMF) or an anion such as chloride facilitates six coordination with  $\text{Co(III)}$  and favour pathway (1a).

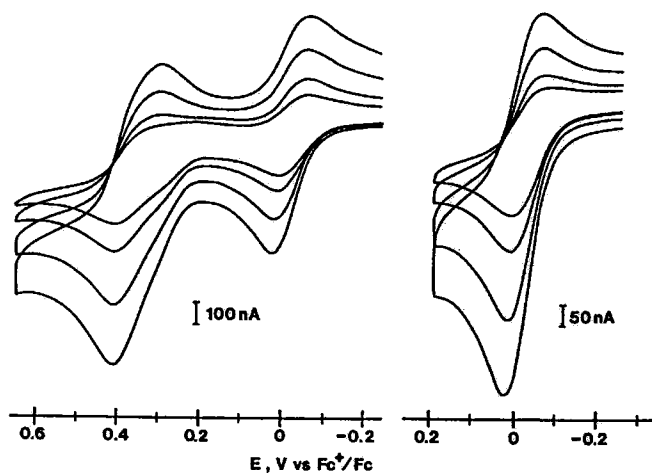


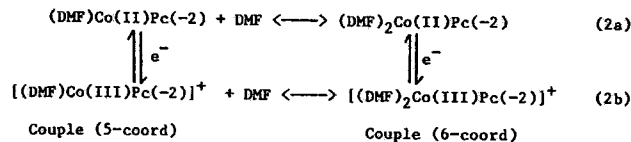
Fig.1 The cyclic voltammetry of Co(II)TNPc dissolved in DMF with tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. Scan rates are 10, 20, 50 and 100 mV/s [19].

Co(II)TNPc (TNPc=tetraneopentoxophthalocyanine) dissolved in DCB exhibits redox series (1b) when TBAP is the supporting electrolyte. A series of redox couples are observed, assigned by spectroelectrochemistry [18]:-

$$\begin{aligned}
 E[\text{Co(III)TNPc(0)}/\text{Co(III)TNPc(-1)}] &= 0.87 \\
 E[(\text{Co(III)TNPc(-1)}/\text{Co(II)TNPc(-1)}] &= 0.59 \\
 E[\text{Co(II)TNPc(-1)}/\text{Co(II)TNPc(-2)}] &= 0.03 \\
 E[\text{Co(II)TNPc(-2)}/\text{Co(I)TNPc(-2)}] &= -0.91 \\
 E[\text{Co(I)TNPc(-2)}/\text{Co(I)TNPc(-3)}] &= -2.07 \text{ V vs } \text{Fc}^+/\text{Fc}
 \end{aligned}$$

All of these processes are one-electron, diffusion controlled and quasi-reversible or reversible ( $i_p \propto v^{1/2}$  ( $v$  = scan rate)). In DMF/TBAP the Co(III)/Co(II) and Pc(-1)/Pc(-2) couples shift negatively and positively to values of -0.02V and +0.38V vs  $\text{Fc}^+/\text{Fc}$  respectively, so that the first oxidation now occurs on the cobalt atom (pathway 1a). When scanned over a limited potential range (Fig.1, right), this couple shows irreversible behaviour with  $i_c/i_a$  approaching zero with slow scan rates ( $i_c$  and  $i_a$  are the cathodic and anodic currents).

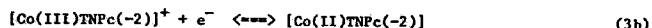
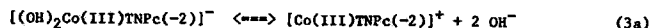
The bulk solution is 5-coordinate  $(\text{DMF})\text{Co(II)Pc(-2)}$  [14,18,22], but the species being oxidised is the 6-coordinate  $(\text{DMF})_2\text{Co(II)Pc(-2)}$  with which it is in equilibrium (see (2a)).



The potential of couple (6-coord) is more negative than couple (5-coord) because of the strong predilection of Co(III) for 6-coordination. Thus  $(\text{DMF})_2\text{Co(II)Pc(-2)}$  (2a, right-hand side) is oxidised first (anodic wave). During the cathodic scan, in the limited scan in Fig.1(right), there is time to establish a little five coordinate  $(\text{DMF})\text{Co(III)Pc(-2)}$  (left-hand side of 2b) which is now at a potential for reduction. Thus some Co(III) on the electrode is 'lost' before it reaches the potential for reduction of 6-coordinate Co(III)Pc - hence the return wave diminishes in current with decreasing scan rate. If the potential sweep is continued beyond the Co(III)Pc(-1)/Co(III)Pc(-2) wave (Fig.1, left), the Co(III)/Co(II) wave is apparently reversible even at very slow scan rates. This is possibly due to the formation of  $[(\text{DMF})(\text{ClO}_4)\text{Co(III)Pc(-1)}]^+$  which reduces to  $(\text{DMF})(\text{ClO}_4)\text{Co(III)Pc(-2)}$  and where, presumably, the loss of a ligand to form a five coordinate  $(\text{DMF})\text{Co(III)Pc(-2)}$  species is too slow to be recorded [18].

The potential of the Co(III)/Co(II) couple is very sensitive to the presence of anions. Discussion here is restricted to the special case where hydroxide ion is added to the solution. If hydroxide ion (e.g. TBAOH in methanol) is added to a DCB solution of Co(II)TNPC, then the electronic spectrum changes instantly forming a mixture of 50:50 Co(I)TNPC and Co(III)TNPC [17]. This is of special interest in that a potential 2-electron reducing agent, and a potential 2-electron oxidising agent are produced. The disproportionated solution can be converted to 100% Co(I)TNPC by irradiation into the Q band, in the absence of oxygen, or completely into 100% Co(III) by aeration. Disproportionation will occur in a range of solvents provided they do not bind too strongly to Co and inhibit attack of OH<sup>-</sup>.

This chemistry is based upon the equilibria:-



where (3a) lies very much to the left, and Co(II)TNPC does not bind hydroxide ion. Under these conditions, the electrode potential for  $[(OH)_2Co(III)TNPC(-2)]^-/Co(II)TNPC(-2)]$  lies more negative than the  $[Co(II)TNPC(-2)]/[Co(I)TNPC(-2)]$  redox process, and, as a consequence, Co(II)TNPC(-2) will disproportionate. This situation leads to some interesting features in the potentiodynamic behaviour of Co(I) and Co(III)TNPC, which are discussed elsewhere [17]. Note that this chemistry is not exclusive to TNPC, but is expected to be general for any Co(II)Pc which is soluble and stable in hydroxide-containing non-donor organic solvents.

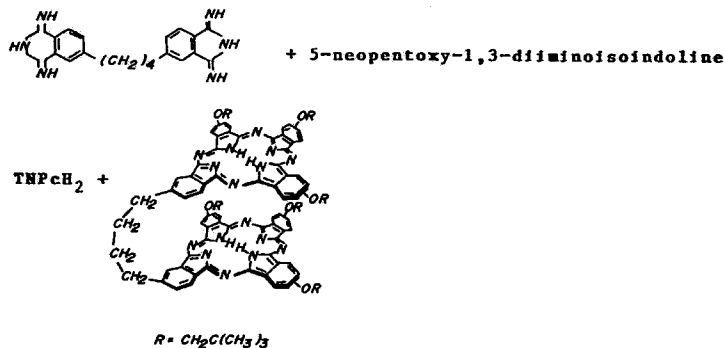
Some preliminary experiments were undertaken to probe the possible catalytic utility of this system [17]. In view of the inability to study this system in homogenous aqueous solution, polymer films containing CoTNPC were prepared. These could be produced to contain 100% Co(I)TNPC or 100% Co(III)TNPC. Indeed if a Co(III)TNPC film is exposed to white light, or to monochromatic light corresponding to the Q band absorption (red), photoreduction of the film from Co(III)TNPC to Co(I)TNPC occurs, a rare example of a two-electron photoreduction. The film is probably being oxidised in the process.

When contacted with various reagents the resulting chemistry was monitored by electronic spectroscopy. A film of Co(I)TNPC will reduce protons (dilute acid), and alkaline carbonate rapidly and alkaline sulfite very slowly. The oxidation product in the film, however, is Co(II)Pc not Co(III)Pc.

#### D. SYNTHESIS OF POLYNUCLEAR PHTHALOCYANINES

Phthalocyanines may be prepared by self-condensation of 1:3-diiminoisoindoline [25]. While dimeric species have been prepared in the past [26,27] their insolubility precluded adequate purification and characterisation. The basis of the successful design of characterisable binuclear, and polynuclear, phthalocyanines lies in two strategies.

Scheme I



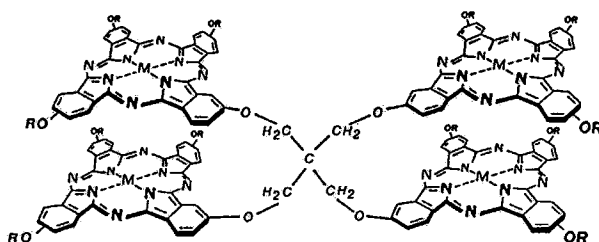
Firstly, two 1:3-diiminoisoindoline units are linked together via a variety of bridges including direct linkage (zero bridge) and using a common benzene ring (so-called -1 link). These are then condensed with 5-neopentoxyl-1,3-diiminoisoindoline to generate mononuclear tetra-neopentoxylphthalocyanine (by self-condensation of the latter molecules) and the new binuclear system (scheme I) [8,9,12,21]. The neopentoxyl groups on six of the benzene rings of the binuclear molecule, confer organic solvent solubility, and allow purification by chromatographic techniques. The products were characterised by microanalysis, electronic and nmr spectroscopy, and FAB mass spectroscopy which always showed parent peaks. The six neopentoxyl groups are randomly distributed in the 4 or 5

positions of the pair of three unlinked benzene rings. They provide for solubility in organic solvents, but the presence of inseparable isomers precludes proper crystallisation and crystal structure analysis. They will also assure the presence of various conformational forms of the various isomeric species.

The binuclear species include, using cobalt derivatives as example, (the number in parenthesis is the number of bridging atoms connecting the two phthalocyanine units):-

- CoINPc [Tetra(neopentoxy)phthalocyanato]cobalt. This is the mononuclear control molecule.
- Pc-Pc(-1) Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a common benzene ring
- Pc-Pc(0) Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a single bond between the benzene rings.
- O(1)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a single oxygen (ether) bridge.
- C(2)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a -CH<sub>2</sub>CH<sub>2</sub>- bridge.
- C(4)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a -(CH<sub>2</sub>)<sub>4</sub>- bridge.
- Cat(4)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a catechol -O-C<sub>6</sub>H<sub>4</sub>-O- bridge.
- tBuCat(4)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a 4-t-butylcatechol -O-C<sub>6</sub>H<sub>4</sub>-O- bridge.
- EtMeO(5)[CoTrPc]<sub>2</sub> : Bis[tri(neopentoxy)phthalocyanato]cobalt attached via a -OCH<sub>2</sub>C(Me)(Et)CH<sub>2</sub>O- bridge.

The use of pentaerythritol as a template for connecting four 1,3-diiminoisoindoline groups, led to the successful synthesis of the remarkable tetranuclear species (II), being tetra[tri(neopentoxy)phthalocyanato]cobalt attached via a C(CH<sub>2</sub>O)<sub>4</sub> core [19]. This species (tetra) also showed a parent ion in the FAB mass spectrum !



II

In studying the metal-free and cobalt complexes of these various species, certain features were evident.

- i) In condensed phases (frozen solution glass, crystal, Nujol mull etc), these complexes may exhibit intermolecular aggregation. In dilute solution,  $< 5 \times 10^{-5} M$ , intermolecular aggregation is generally absent (but not in the tetranuclear species).
- ii) Some binuclear phthalocyanines may close upon themselves ('clamshell' behaviour) via cofacial intramolecular aggregation. Specifically, only Cat(4), t-BuCat(4) and EtMeO(5) exhibit intramolecular cofacial aggregation. Such species exist in a dynamic equilibrium with 'open' conformations.
- iii) The electronic spectra of the metal-free species show evidence of the coupling of the transition moments on each phthalocyanine ring, expected to be more important here than in the porphyrins, because of the larger visible region transition moments of the former [28]. In the cofacial conformations coupling gives rise to a blue shift in the Q and Soret absorption, and a specific emission peak near 750nm. A blue shift is also observed in the other metal-free binuclear species, as a consequence of coupling through space (or through the bridge) in 'open' non-aggregated, conformations.
- iv) Deprotonated and cobalt polynuclear phthalocyanine species show evidence for electronic coupling through space in the form of broadening or splitting of the Q band absorption. Some aspects of the above will now be dealt with in more detail.

## E. ELECTRONIC COUPLING IN POLYNUCLEAR METAL-FREE DERIVATIVES

Mononuclear metal-free phthalocyanines emit from the Q band  $\pi-\pi^*$  state, near 700nm [28,29]. In the polynuclear complexes this is significantly quenched with intensities of this emission commonly being about 1-35% of the mononuclear intensity (under parallel conditions, in toluene/ethanol solvent). If the relative intensity of

this emission is taken as a qualitative measure of the degree of intra-ring coupling, then the sequence of coupling in very dilute ( $1 \times 10^{-6} \text{M}$ ) solution is [percentage in square brackets, 100% is fully uncoupled]:-

Monomer [100%] < t-BuCat(4) [35%] < C(4) [26%] < (-1) [18%] = EtMeO(5) [16%] = Cat(4) [16%] = O(1) [15%] = Pc-Pc(O) [14%] < C2 [4%] < tetra [1%]

(4)

Some variation in this sequence can be expected to occur with the isomer mix isolated during column chromatography of these species.

As indicated above, cofacial metal-free binuclear species additionally emit at 750nm, at liquid nitrogen temperature, with a lifetime of about 50ns compared with about 5ns for the 700nm emission. Coupling of the transition moments on each phthalocyanine ring results in the Q state coupling to yield an upper and lower level. Each level further splits in the lower symmetry of the metal-free derivative [13] (Fig.2). The 750nm emission originates in the lower (forbidden) component of the lower exciton-split Q state. The total exciton splitting is of the order of  $2500 \text{cm}^{-1}$ , much larger than commonly seen in porphyrin species such as chlorophyll.

Interestingly, many of the polynuclear species also exhibit  $S_2$  emission (very short-lived ca 5-10ns), from the Soret region, near 425nm [20]. The quantum yield of such emission is very low (ca  $1 \times 10^{-3}$ ), but appears to increase with the degree of coupling, being a maximum per phthalocyanine ring for the tetranuclear. Such emission may have practical value in that it indicates the existence of a pathway through which photochemistry might be induced. Such photochemistry could take advantage of the significantly large energy associated with this state. Main group complexes of the tetranuclear species are to be explored for this objective.

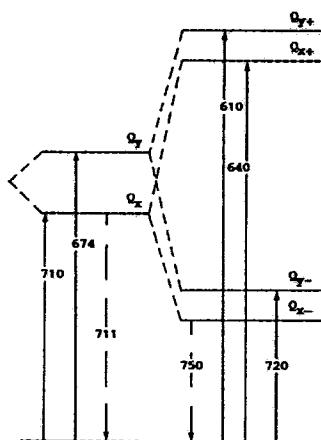


Fig.2 Energy level diagram for metal free mononuclear (left-hand) and binuclear (right-hand) metal-free phthalocyanines. Upward arrows are absorption or excitation, downward arrows are fluorescence. Typical numbers are cited [13].

## F. ELECTRONIC COUPLING IN POLYNUCLEAR COBALT DERIVATIVES

The cobalt complexes do not emit but electronic coupling may be detected through consideration of their absorption spectra. Extensive coupling occurs in many of the cobalt(II) polynuclear phthalocyanine derivatives. This is exemplified by blue shifting of the Q band absorption (Fig.3). The usual sharp Q band is replaced by a broad envelope centered to higher energy. Reduction or oxidation leads to formation of  $[\text{Co(I)Pc}]_2^{2-}$  and  $[\text{X}_2\text{Co(III)Pc}]_2$  species (X=solvent or counterion) respectively. These species have electronic spectra typical of much reduced coupling. Evidently the negative charge in the former will inhibit inter- or intramolecular aggregation, while the necessity of having axially coordinated groups in the Co(III) species performs the same function. However consideration of the bandwidth of the principle Q band absorption, shows that intramolecular coupling is indeed occurring.

One anticipates that such coupling will generate incipient splitting of the  $^1E_u$  state and hence broadening. Bandwidths are shown below, where it is evident that all the polynuclear species are electronically coupled intramolecularly. The tetranuclear and O(1) species are the most coupled.

Co(I) Half-bandwidths [ $\text{cm}^{-1}$ ] [17]

Co(I)TNPc [660] < C(2) [735] < EtMeO(5) [775] = Cat(4) [775] < tetra [890] < O(1) [920]

Co(III) Half-bandwidths (Hydroxo species)

Co(III)TNPc [680] < C(2) [765] < EtMeO(5) [785] < Cat(4) [800] < tetra [1000] = O(1) [1000] (5)

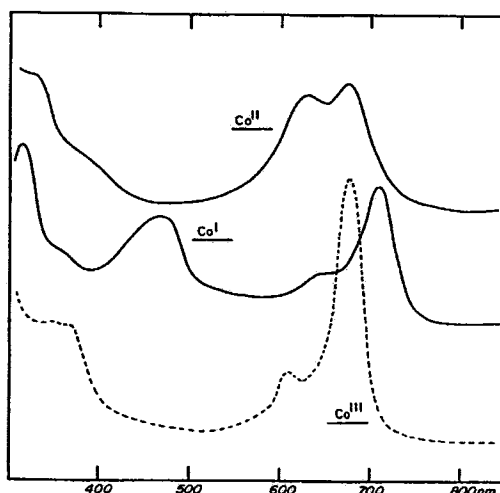


Fig. 3. The electronic spectra of  $\text{EtMeO(5)Co}_2$  in three oxidation states, in *o*-dichlorobenzene [18]. The Co(I) and Co(III) solutions contain tetrabutylammonium hydroxide

Note that whereas in the C(2) and EtMeO(5) species, the two halves of the molecule may rotate to be fairly far apart, there are steric constraints which inhibit this in the Cat(4) and O(1) species. This sequence is therefore reasonable, reflecting increasing coupling in those species where the two halves are constrained to be close even if not cofacial. The broadening in the Co(III) species is generally greater than in the Co(I) species, a consequence of the greater Q band transition moments in the former group.

## G. AGGREGATION PHENOMENA

Aggregation is common in phthalocyanine chemistry. Most of the binuclear phthalocyanines also aggregate in solution in the absence of factors such as axial binding or charged phthalocyanine rings. The tetranuclear species is remarkable in showing aggregation at sub-micromolar concentrations. Given the possible use of a tetranuclear phthalocyanine as a redox catalyst, its aggregative properties may be useful to further extend the multi-electron nature of the species.

Studies of the concentration dependence of the electronic spectrum of  $[\text{Co(II)TrPc}_4]$  (tetra) show that only two of the four rings are involved at concentrations below  $10^{-5} \text{ M}$  and that the aggregation binding constant, in DCB is  $2.3 \times 10^5 \text{ M}^{-1}$  [19], or two orders of magnitude greater than for the mononuclear Co(II)TNPc or binuclear species (e.g.  $K_D = 2.6 \times 10^{-3} \text{ M}^{-1}$ ,  $4.8 \times 10^{-3} \text{ M}^{-1}$  and  $3.3 \times 10^{-1} \text{ M}^{-1}$  for Co(II)TNPc, Co(II) $_2$ C(2) and Co(II) $_2$ EtMeO(5) respectively.)

## H. DISPROPORTIONATION IN POLYNUCLEAR PHTHALOCYANINE SPECIES

Clearly, disproportionation in the binuclear species can potentially provide 4-electron reductants and oxidants via the  $[\text{Co(III)}]_2/[\text{Co(I)}]_2$  redox process and corresponding 8-electron processes using the tetranuclear species. Disproportionation does indeed occur when a polynuclear Co(II)Pc species is treated in a non- or weakly coordinating solvent with hydroxide ion [17]. Studies of such systems are currently in progress. The binuclear species mimic the mononuclear control molecule in reducing protons in acidic media and carbonate and sulphite in sodium hydroxide. However the efficacy does

not appear obviously greater than for the mononuclear species, a disappointing observation. However it is promising that the nitrite ion can be reduced slowly by a film containing the tetranuclear  $[\text{Co(II)TPc}]_4^{8-}$  species, a process not evident with the binuclear or mononuclear species.

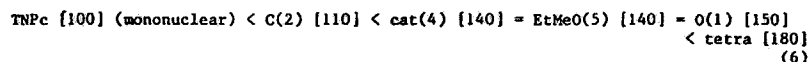
## I. OXYGEN REDUCTION WITH POLYNUCLEAR COBALT DERIVATIVES

Cyclic voltammetry studies on the binuclear cobalt species show redox waves corresponding almost exactly with those observed for the mononuclear control molecule. Evidently the degree of electronic coupling is insufficient to cause a marked departure in redox behaviour, i.e. reduction or oxidation occurs at both rings as though they were unconnected.

This is not quite true of the tetranuclear cobalt species which shows significant aggregation at the concentrations used for voltammetry. In addition to waves due to the unaggregated and mononuclear-like component, additional waves due to the aggregated species occur. Spectroelectrochemistry in the region of these additional waves provides no evidence for any mixed valence species being formed.

Studies have been undertaken by laying down a monolayer or more of a cobalt polynuclear phthalocyanine on an OPG electrode and studying the oxygen reduction chemistry. By using a rotating electrode, it is possible to obtain values for the kinetic current (Koutecky-Levich analysis), being a relative measure of the efficiency of oxygen reduction [16]. Hydrogen peroxide is the product with the cobalt catalysts in alkaline solution, while, under similar conditions, FeTNPC yields the four electron reduction to water [30].

The kinetic currents for the polynuclear cobalt(II) species are greater than that for the mononuclear species (pH 13, NaOH, OPG electrode) according to the sequence (relative numbers in parentheses):-



Thus the binuclear cobalt species are undoubtedly more efficient for oxygen reduction than is the mononuclear control molecule, and the tetranuclear cobalt species is the most efficient. However the improvement over the control molecule, while definite, is not very dramatic.

Of more potential interest, is the observation that the increase in kinetic currents from one species to another parallels, reasonably well, the degree of electronic coupling as indicated by half-bandwidths (5). Thus the premise that the efficiency depends upon electronic coupling seems vindicated. It is evidently true to say that these species exhibit multi-electron redox characteristics and more highly coupled species are now being investigated.

## J. OXYGEN REDUCTION WITH AGGREGATED MIXED PHTHALOCYANINES

During these studies, it became evident that the chemistry of well defined binuclear species, obtained with some synthetic effort, was mimicked, though usually to a lesser degree, by readily obtainable aggregated unattached pairs of molecules. We were interested in synthesizing a mixed binuclear species  $\text{H}_2\text{Pc-PcCo(II)}$  to ascertain whether the presence of hydrogen atoms close to the active cobalt centre would influence its oxygen reduction chemistry in a useful fashion. Such a mixed species is difficult to prepare. However it is possible to lay down two layers of a 50:50 mixture of  $\text{H}_2\text{TNPC}$  and  $\text{Co(II)TNPC}$  on an OPG electrode, and to study the resultant oxygen reduction chemistry. Indeed the mixed system is as efficient as the pure  $\text{Co(II)TNPC}$ , yet  $\text{H}_2\text{TNPC}$  itself shows no oxygen reduction capability [30]. Mixed systems of this type are being explored further.

Zagal and co-workers [31] had previously studied a mixture of  $\text{Co(II)TsPc}$  and  $\text{Fe(II)TsPc}$  on OPG but did not observe any special enhancement of function.

## K. ADVANCES IN OTHER LABORATORIES

There are many exciting advances being made in phthalocyanine chemistry in other laboratories. We survey some of the more interesting areas, but shortage of space prevents detailed discussion and full coverage.

The planarity of the phthalocyanine molecule is well adapted to forming long uni-dimensional chains. The laboratories of Marks and Hoffman, in particular, have made some interesting contributions in the field of molecular metals [32] wherein a phthalocyanine uni-dimensional chain is doped with an electron acceptor such as iodine, forming partially oxidised species such as  $[\text{CoPc}]_3^+ \text{I}_3^-$ . Such studies open up a new class of material with remarkable electrical conductivity for an organic material and which may have value, for example, in super-conducting physics.

Many research groups have probed the utility of metallophthalocyanines as semi-conductor materials in photovoltaic cells. They are potentially a very inexpensive



alternative to silicon. Chloroaluminum phthalocyanine seems to have especial merit [33]. In addition, the photoconductivity of metal-free phthalocyanine, and of some metallophthalocyanines, makes them useful in photocopying machines.

Phthalocyanine films have been shown to have useful electrical properties with respect to the detection of target gases such as oxygen, ammonia, nitrogen dioxide etc [34] and even methane [35]. It is generally the semi-conducting nature of these phthalocyanine films which is of importance and which is modified by the presence of target gases. Recently it has become possible to prepare Langmuir-Blodgett monomolecular films of metallophthalocyanines [36]. The chemical sensor field is an area in which phthalocyanines are likely to excel in the future.

Phthalocyanines may be used as oxygen reduction electrocatalysts [37] for application in fuel cells where usually FePc or CoPc are employed. Metallophthalocyanines may also be employed for carbon dioxide [38] and proton [39] reduction and sulfur dioxide oxidation [40] etc. In primary lithium batteries [41], phthalocyanines electrocatalytically reduce thionyl chloride. In secondary lithium cells, incorporating propylene carbonate, many metallophthalocyanines improve the discharge efficiency [42].

The ability of metallophthalocyanines to change their intense colour by altering the redox level, provides considerable interest in these species in electrochromic display devices [43], the work of Kirin and Nicholson being especially noteworthy. In general this particular area is dominated by lanthanide di-phthalocyanine species.

There is very extensive interest, especially in Russia, in the use of cobalt phthalocyanine as a catalyst for desulfurisation of residues, effluents etc [44].

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