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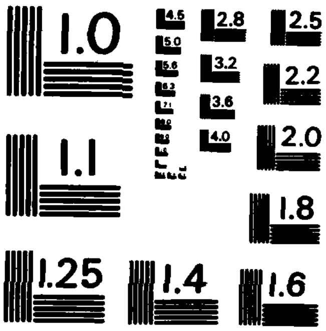

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Binuclear Phthalocyanines as Model Electrocatalysts for the Reduction of Oxygen

BY

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Binuclear cobalt phthalocyanines linked by bridges containing 1,2,4 or 5 atoms are shown to reduce oxygen catalytically, more efficiently than mononuclear cobalt phthalocyanines. The kinetic efficiency for oxygen reduction is related to the degree of electronic coupling between the two halves of the molecule. The Co(II) species disproportionate in non-coordinating solvents, in the presence of hydroxide ion, forming the potentially two-electron redox reagents Co(I) and Co(III)Pc.

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Binuclear Phthalocyanines as Model Electrocatalysts for the Reduction of Oxygen

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Introduction

Since binuclear porphyrins have been shown to be promising electrocatalysts, our recent synthesis of the thermally more stable, soluble, binuclear and trinuclear phthalocyanines has generated considerable interest [1-3]. Until this project was initiated, three years ago, multinuclear phthalocyanines in which two, or more, units are linked together providing the possibility for cofacial conformations, were unknown. Our early advances [4] in preparing soluble mononuclear phthalocyanines led to methods of preparing the world's first covalently linked binuclear and tetranuclear phthalocyanines depicted below (I,II).

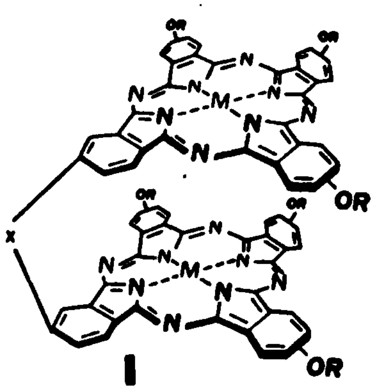
Multinuclear phthalocyanines containing bridges of lengths 0,1,2,4, and 5 have been prepared and fully characterised by elemental analysis, uv/vis/ir/nmr and particularly FAB mass spectroscopy which generally allows direct observation of the very large parent ion. Our synthesis led to metal-free multinuclear phthalocyanines. To date, metal insertion has been carried out with iron, cobalt and copper though, clearly, any metal ion could be incorporated. Uv/vis spectroscopic absorption and emission data permits one to deduce the extent of electronic coupling and the extent of cofacial interaction in these species. All the complexes show evidence for electronic coupling between the two rings, to an extent dependent upon the bridge conformation, metal ion and oxidation state, isomer, temperature and medium. In general, there is some flexibility about the bridge link leading to a range of conformations including cofacial.

The binuclear phthalocyanine complexes have the general formula (tri(neopentoxy)phthalocyanine)$_2$(bridge) where the (bridge) may be absent (direct link between a benzene ring on each phthalocyanine unit), or may contain 1,2,4 or 5 atoms. The three neopentoxy groups are randomly distributed in the 3 or 4 positions of the three unlinked benzene rings and provide for solubility in organic solvents.

Of relevance to this presentation are the following species with their abbreviations and where the number in parenthesis is the number of bridging atoms connecting the two phthalocyanine units:-

PcCo (Tetra(neopentoxy)phthalocyaninato)cobalt. This is the mononuclear control molecule.

Cat(4)(PcCo)$_2$ Bis(tri(neopentoxy)phthalocyanato)cobalt attached via a catechol $-O-C_6H_4-O$ bridge.



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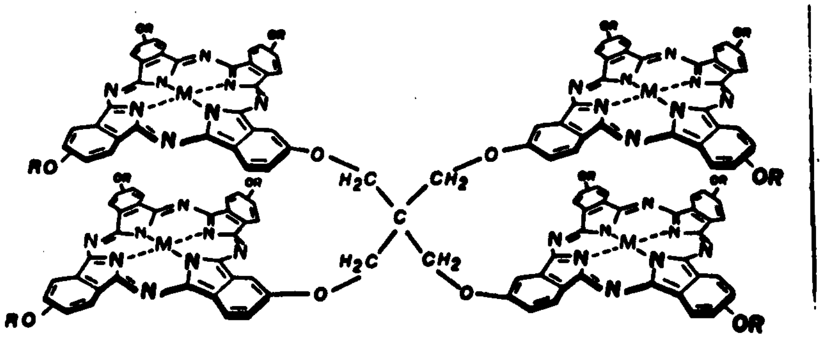

II

t-BuCat(4)$(PcCo)_2$	Bis(tri(neopentoxy)phthalocyanato)cobalt attached via a 3,5-ditertiarybutyl catechol $-O-C_6(C_4H_9)_2H_2-O$ bridge.
O(1)$(PcCo)_2$	Bis(tri(neopentoxy)phthalocyanato)cobalt attached via a single oxygen (ether) bridge.
C(2)$(PcCo)_2$	Bis(tri(neopentoxy)phthalocyanato)cobalt attached via a $-CH_2.CH_2-$ bridge.
EtMeO(5)$(PcCo)_2$	Bis(tri(neopentoxy)phthalocyanato)cobalt attached via a $-OCH_2C(Me)(Et)CH_2O-$ bridge.
Pc-Pc(O)Co_2	Bis(tri(neopentoxy)phthalocyanato)cobalt attached directly.
spiro-$(PcCo)_4$	Tetra(tri(neopentoxy)phthalocyanato)cobalt attached to a $C(CH_2O-)_4$ bridge.

In discussing the metal-free derivatives [5], certain conclusions were drawn which are relevant to the discussion below.

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.

ii) Some binuclear phthalocyanines may close upon themselves ('clamshell' behaviour) to aggregate via cofacial intramolecular aggregation. Specifically, only Cat(4)$(PcH_2)_2$, t-BuCat(4)$(PcH_2)_2$ and EtMeO(5)$(PcH_2)_2$ appear capable of such intramolecular cofacial aggregation. Such species exist in a dynamic equilibrium with 'open' and 'closed' conformations.

iii) The electronic spectra of the metal-free species show evidence of the coupling of the transition moments on each phthalocyanine ring. Thus coupling is expected in the cofacial conformations and gives rise to a blue shift in the Q and Soret absorption. However a blue shift is also observed in the other metal-free binuclear species, as a consequence of coupling through space in 'open' non-aggregated, conformations.

iv) Deprotonated binuclear phthalocyanine species also show evidence for electronic coupling through space in the form of broadening or splitting of the Q band absorption [5]. Note that electronic coupling is more readily detected in the electronic spectra of binuclear phthalocyanine species, relative to comparable porphyrin species, because the visible region transition moments are much larger in the former case.

Many important redox processes, especially the water-oxygen redox system, are multi-electron in nature and are likely to be catalysed more effectively (higher quantum yield, greater catalytic efficiency) by redox catalysts which can participate in a concerted 2 (or more) electron processs with the substrate. One might design such a catalyst arranging, for example that it be stable in two oxidation states separated by two electrons, the intermediate oxidation state being thermodynamically unstable. One might also link two one-electron catalysts together in such a way that coupling between them favours two electron oxidation and reduction rather than sequential one electron processes. Both of these opportunities exist in the cobalt phthalocyanine system and we will present a discussion of the redox chemistry and electronic structure of mononuclear and binuclear cobalt phthalocyanine derivatives. Preliminary data for iron derivatives will also be discussed.

Results and Discussion

In general, Co(II)Pc can be oxidised or reduced according to two alternate pathways depending upon solvent or supporting electrolyte (in its standard redox state, phthalocyanine is represented Pc(-2)) [6]:- (axial ligands omitted)

$$\mathrm{Co(I)Pc(-2)} \overset{e^-}{----} \mathrm{Co(II)Pc(-2)} \overset{e^-}{\underset{e^-}{----}} \mathrm{Co(III)Pc(-2)} \overset{e^-}{----} \mathrm{Co(III)Pc(-1)} \ldots (1a)$$

$$\mathrm{Co(II)Pc(-1)} \overset{e^-}{----} \mathrm{Co(III)Pc(-1)} .. \ (1b)$$

Pathway (1b) is effective in the absence of a solvent which can coordinate 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, dichlorobenzene (DCB) plus a perchlorate supporting electrolyte follow (1b), while pyridine or an anion such as chloride facilitate six coordination with Co(III) and favour pathway (1a).

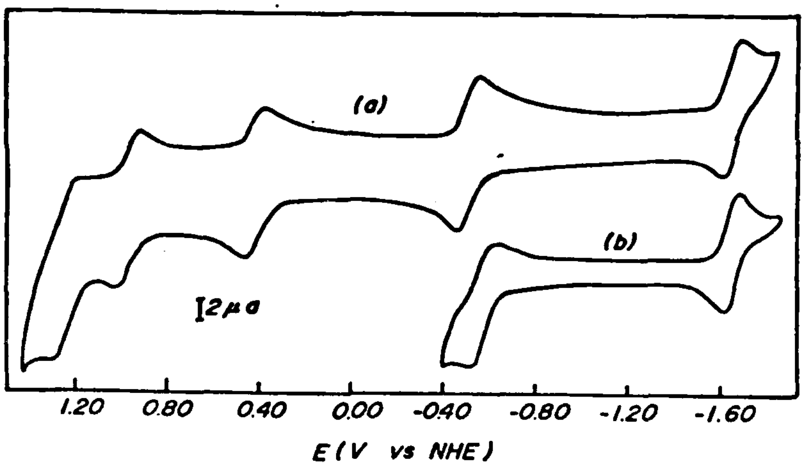

Fig.1 a) Cyclic voltammetry (0.1V/s) of PcCo in DCB/Bu_4NClO_4. b) a section of the voltammogram as it appears after addition of Bu_4NOH (80:1).

Co(II)Pc (Pc = tetraneopentoxyphthalocyanine) dissolved in DCB, exhibits redox series (1b) when tetrabutylammonium perchlorate is the supporting electrolyte. A series of one-electron redox couples are observed with (Fig.1a):-

E[Co(III)Pc(-0)/Co(III)Pc(-1)] = 1.27
E[(Co(III)Pc(-1)/Co(II)Pc(-1) = 0.99
E[Co(II)Pc(-1)/Co(II)Pc(-2)] = 0.43
E[Co(II)Pc(-2)/Co(I)Pc(-2)] = -0.51
E[Co(I)Pc(-2)/Co(I)Pc(-3)] = -1.67V vs NHE

With the exception of the first most positive couple, these one-electron processes are diffusion controlled and quasi-reversible ($i \propto v^{1/2}$ (v = scan rate), $i_a/i_b \simeq 1$). The Co(III)/Co(II) couple is observed at a relatively high potential and its position is very sensitive to traces of coordinating anions which would stabilise Co(III)Pc. We restrict our discussion to the special case where hydroxide ion is added to the solution.

If hydroxide ion (e.g. tetrabutylammonium hydroxide (TBAOH) in methanol) is added to a DCB solution of Co(II)Pc, then the voltammetry changes (Fig.1b). The couple near -0.50 (vs NHE) (couple A) is now characterised as a **two-electron** quasi-reversible couple most definitively by controlled potential spectro-electrochemistry. Using an optically thin cell with a gold mini-grid electrode, polarisation some 200mV more negative than couple A generates a spectrum characteristic of a Co(I)Pc species [7,8] (Fig.2). Thus the addition of hydroxide ion shifts the reduction potential for Co(III)Pc nearly 2V negatively and changes the process from one-electron to two-electron.

When the gold mini-grid is polarised some 200 mV more positive than couple A, the 475nm absorption is lost and the spectrum becomes characteristic of a Co(III)Pc, probably $[(HO)_2Co(III)Pc]^-$ [9].

The appearance of the two-electron Co(III)/Co(I) couple at the same potential as the one-electron Co(II)/Co(I) couple in the absence of added hydroxide ion implies that we are observing an ECE redox mechanism. Consider a solution containing OH^- ion and Co(I)Pc. There would be no interaction between these species, i.e. the polariser, Co(I), would oxidise at a potential almost independent of the added OH^- ion, i.e. -0.50V. However once oxidised to Co(II), process E_1, the species would recognise the OH^- ion by participating in an equilibrium with $[HOCo(II)Pc]^-$ and $[(HO)_2Co(II)Pc]^{2-}$ (chemical reaction C). The latter is likely to exist in only trace amounts but we conclude that its Co(III)/Co(II) redox potential is more negative than -0.5v (vs NHE). Oxidation to Co(III) must then occur, process E_2, driving all the CoPc to Co(III)Pc, in this E_1CE_2 mechanism.

The absence of a region of existence of Co(II)Pc in these hydroxide containing solutions requires that addition of hydroxide ion to a DCB solution of Co(II)Pc must result in disproportionation to a solution containing 50:50 Co(I)Pc + Co(III)Pc (when carried out under n inert atmosphere). This is exactly the case as shown in Fig.2. Further experiments revealed that disproportionation will occur in a range of non-coordinating or very weakly coordinating solvents such as toluene and dimethylformamide, but not in coordinating solvents such as pyridine or ethanol wherein the species remain Co(II)Pc. Disproportionation is encouraged under conditions where the hydroxide ion can contact the Co(II) atom in an axial site, but is discouraged when a solvent occupies the axial sites.

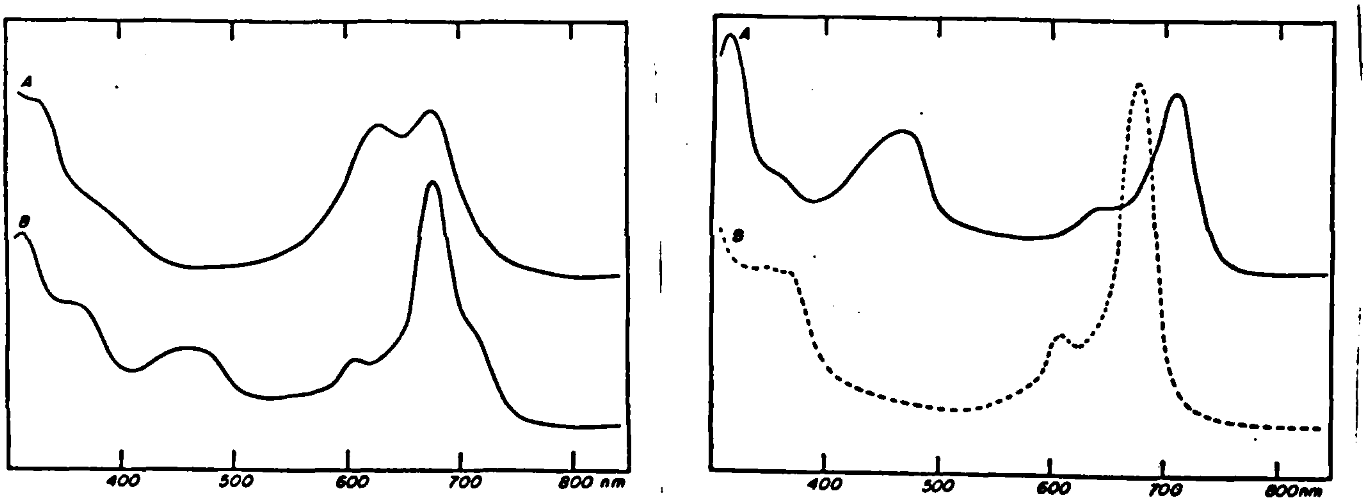

Fig.2 (Left) A: PcCo(II) in DCB; B Disproportionated PcCo(I) + $PcCo(III)(OH)_2$ in DCB/TBAOH. (Right) A: PcCo(I) in DCB/TBAOH/vacuo; B $PcCo(III)(OH)_2$ in DCB/TBAOH/air.

When air (oxygen) is present, the Co(I)Pc will oxidise directly to Co(III)Pc such that the final solution contains only Co(III), presumably $[(HO)_2Co(III)Pc]^-$. Reduction to Co(I)Pc occurs if a DCB solution of the Co(III)Pc species is left under an inert atmosphere (slow reduction) or is irradiated with red light (into the Q band,in vacuo) (rapid reduction). The two-electron photoreduction is unusual but is of low quantum yield (<1ô). The system may be cycled by re-oxidising the Co(I)Pc species with oxygen, de-gassing and re-irradiating. Such cycles occur with some loss of phthalocyanine pigmentation. Thus although it is not clear what is being oxidised when the Co(III)Pc is photoreduced to Co(I)Pc, the phthalocyanine ring itself is partially involved (see below).

The disproportionation process provides a facile mechanism for generating a two-electron oxidant (Co(III)) and a two-electron reductant (Co(I)) simultaneously. Although in the presence of hydroxide ion, the Co(III) is only very weakly oxidising (in its ground state), removal of the hydroxide ion would lead to a powerful one-electron Co(III)Pc oxidant since we would return to the hydroxide-free situation. We return to this discussion below.

Binuclear Phthalocyanine species

It is evident that if, potentially, a two-electron oxidant and a two-electron reductant are generated, via disproportionation of the mononuclear Co(II)Pc species, there is the opportunity to obtain, formally, a four electron oxidant and a four electron reductant, via disproportionation of binuclear Co(II)Pc species.

There are observed with the binuclear complexes, a series of one-electron redox processes which directly parallel those of the mononuclear species and appear at essentially the same potentials. The coupling between the two halves of the molecule is evidently not important enough to cause a marked change in these potentials and the molecule behaves as though it were two essentially uncoupled mononuclear species. The Cat(5)$(PcCo)_2$ and EtMeO(5)$(PcCo)_2$ species also behave as mononuclear species electrochemically implying that any co-facial conformational contribution (see below) must uncouple prior to electrochemical redox.

The addition of hydroxide ion (t-Bu_4NOH, TBAOH, at least 80:1 molar excess) to the binuclear (and tetranuclear) species in DCB also promotes rapid disproportionation to a 50:50 mixture of binuclear Co(I)Pc and binuclear Co(III) species. Degassing or irradiation in vacuo provides total conversion to the binuclear $(PcCo(I))_2$ species, while air oxidation yields the fully oxidised binuclear $(PcCo(III))_2$ species.

Chemistry of Co(I) and Co(III)Pc species

Aerial oxidation of Co(I)Pc leads directly to Co(III)Pc with no intervening Co(II)Pc. Degassing a solution of Co(III)Pc in DCB/OH^- results in reduction to Co(I)Pc, a process greatly facilitated by irradiation (white light or red light into Q band). In principle the degas/irradiation and aerial oxidation processes can be cycled to generate each oxidation state in sequence. However in practice, there is a few percent loss of phthalocyanine during each reduction cycle. During successive cycles it becomes rather more difficult to affect reduction of Co(III) to Co(I)Pc, i.e. a longer time is needed. These processes are monitored in cuvettes by electronic spectroscopy. Thus only some 10^{-7} moles of material are present. It is likely that trace organic material in the solvent, and to some degree the phthalocyanine ring itself, are the reductants in the Co(III)Pc to Co(I)Pc conversion.

Obviously one may add specific oxidising or reducing reagents to a solution of Co(I) or Co(III)Pc. Some preliminary experiments were carried out (in a cuvette) to seek possibly useful redox processes. Thus the addition of ascorbic acid to a Co(III)Pc solution results in ready formation of Co(I)Pc unless the ascorbic acid is in sufficient excess to neutralise the hydroxide content of the solution, in which case the final product is Co(II)Pc. Aqueous acid addition (under nitrogen) to Co(I)Pc (in DCB/OH^-) yields Co(II)Pc and presumably hydrogen (see below). There are obvious problems involved in using dichlorobenzene solutions with aqueous reagents and for this reason and to provide more ready access to separated Co(I)Pc and Co(III)Pc species, transparent films were generated.

Chemistry of the Disproportionated Cobalt Phthalocyanines in Polymer Films

The cobalt-containing species, either prior (to obtain Co(II)Pc) or subsequent to disproportionation (to obtain Co(I) and/or Co(III)Pc) could be incorporated into a film by dissolving the cobalt species and the polymer powder into dichlorobenzene or toluene and evaporating off the solvent. In this fashion transparent films were prepared from polystyrene, hydroxy methylmethacrylate, polyethylene, poly-2- and poly-4-vinylpyridine.

The disproportionated solutions which contain both Co(I) and Co(III)Pc, yielded a Co(III)Pc film when processed with polymer in air. Production of the films in vacuo yielded mixtures which tended to favour one oxidation state, depending upon the polymer used. Co(III)Pc films could be converted to Co(I)Pc films by irradiation under vacuo, or indeed even by heating. In the latter case, cooling the film restored Co(III)Pc. Again cycling does not fully reproduce the original quantity of phthalocyanine material; some degradation occurs.

The Co(I)Pc films, once prepared were fairly stable towards aerial oxidation; presumably the polymer matrix protects the species against oxygen. Thus addition of degassed water (neutral or basic with NaOH) to a Co(I)Pc film, under nitrogen, yields no reaction. Similarly pure, dry, oxygen has no effect. However wet oxygen does oxidise the Co(I)Pc to Co(II)Pc.

Addition of degassed aqueous acid (0.001M HCl) under vacuo, results in formation of Co(II)Pc. There is little doubt, given the tendency for Co(I) to reduce aqueous acid to hydrogen [10], that hydrogen is produced in this reaction, though it was not proven.

While addition of aq.NaOH to the Co(I)Pc film has no effect, the addition of degassed aq.Na_2CO_3/NaOH results in rapid formation of Co(II)Pc with the presumed reduction of carbonate ion [11] to carbon monoxide. Interestingly, there is also a slow reaction with degassed Na_2SO_3/NaOH, forming Co(II)Pc, presumably with the formation of sulphur.

Note that Co(II)Pc is the end product of oxidation by wet oxygen, protons or carbonate ion. However the wet oxygen product differs from the other products in that irradiation thereof re-generates Co(I)Pc, while irradiation has no effect upon the other Co(II)Pc products or upon a fresh Co(II)Pc film. It is likely that wet oxygen reacts with Co(I)Pc to generate Co(II)Pc + O_2^- and that the superoxide ion is trapped into the polymer lattice close to the Co(II)Pc. Irradiation then causes a reduction because of the greater oxidising power of excited state Co(I)Pc.

Co(III)Pc formed in these reactions in the presence of hydroxide ion, is a poor oxidising agent since the Co(III)/Co(I) couple is so negative. However Co(III)Pc bound to less stabilising anions would be a stronger oxidising agent. Thus addition of perchloric acid should neutralise the hydroxide ion and generate a Co(III)Pc species probably bound axially to water. This is expected [13] to have a Co(III)/Co(II) potential near 1.0-1.5V (vs NHE). Indeed addition of dilute perchloric acid to a Co(III)Pc film results readily in formation of Co(II)Pc. Elucidation of the oxidation products is in progress.

Coupling between Co moieties

The ability to make use of a multi-electron redox catalyst probably depends both upon geometric and electronic constraints. We are therefore interested to know to what extent electronic coupling occurs between each half of these binuclear molecules in their various oxidation states. Such information can be obtained from consideration of the electronic spectra.

The theory has recently been presented [5]. In summary, electronically coupled conformers are expected to show a blue shift in the Q band absorption. Given that these species may exist in several conformational forms in dynamic equilibrium, the electronic spectrum will have the appearance of a mixture of conformers. Red shifted Q band absorption can also be anticipated in lower symmetry species, but the probability (intensity) of such absorption is smaller than for the blue shifted transitions [5]. We should therefore see broad Q band absorption originating from the red edge of the original Q band and generally showing two peaks. The lower energy peak corresponds with conformers with little or no coupling and occurs at a wavelength essentially the same as for the mononuclear species. The higher energy peak corresponds with the dominant conformational form and, from previous experience [5,12], will be seen about 500 - 1500 cm^{-1} to higher energy. The degree of broadening is a rough qualitative measure of the degree of electronic coupling.

A broad double-peaked Q band spectrum is observed for both $EtMeO(5)(PcCo(II))_2$ and $Cat(4)(PcCo(II))_2$ in non-coordinating solvents (Fig.2). Since both these binuclear species are believed to be capable of cofacial conformer formation [1,2] it is reasonable to associate such absorption with the presence of an extensive (but not 100%) contribution from cofacial, or closed 'clamshell' conformation(s) [1]. The cobalt(II) atom is expected to be four coordinate in such an environment so that axial ligation will not inhibit the close approach of the two halves of the molecule.

Reduction to cobalt(I) generates broad structured absorption near 475nm due to $Co(I)---\pi^*Pc$ charge transfer and a single Q band with associated vibrational structure. The double Q band of the cobalt(II) species is not present. Cobalt(I) phthalocyanine species are expected to be four coordinate [13] and can therefore be expected, from a stereochemical viewpoint, to form a cofacial conformation. That they do not appear to do so, is probably a consequence of the net negative charge residing on each phthalocyanine ring causing repulsion between the two halves of the binuclear molecule.

Similarly oxidation to $(PcCo(III))_2$ Pc derivatives generally yields only a single Q band. In this case we anticipate that the normal requirement for cobalt(III) to be six coordinate, will ensure the presence of axial ligands which will inhibit formation of the cofacial conformer.

Nevertheless coupling is anticipated between the two halves of each binuclear molecule in both the Co(I) and Co(III) species. This is reflected in the half-bandwidths for the Q band which follow the same sequence, viz:-

Co(I) Half-bandwidths (cm^{-1})

PcCo(I) [658] < C(2) [736] < EtMeO(5) [774] = Cat(4) [776] < O(1) [920]

Co(III) Half-bandwidths (Hydroxo species)

PcCo(I) [678] < C(2) [764] < EtMeO(5) [787] < Cat(4) [800] < O(1) [1080]

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.

Background Information on Electrocatalyst Design.

Oxygen reduction occurs in water by a 2-electron process to hydrogen peroxide or a 4-electron process to water. This latter process must be catalysed on a cathode. The multi-electron nature of the reduction is best facilitated by an electrocatalyst itself capable of being involved in a concerted multi-electron redox reaction. Many mononuclear metal porphyrins act as electrocatalysts but the work of Collman and Anson has revealed that certain binuclear cofacial porphyrins are much more effective [14-16]. Similarly, mononuclear iron and cobalt phthalocyanines [17-19] are effective, but Savy and co-workers report that 'dimeric' and polymeric (both ill-characterised) iron phthalocyanines were more effective. The catalyst embedded in the fuel cell carbon cathode serves to accelerate the reduction of oxygen gas. It must resist fuel cell operating conditions (strong acid or base, fairly high temperatures), for long periods of time, without loss of activity. Platinum is commonly used today; however it is expensive representing some 10δ of the total fuel cell cost. Catalysts which are more effective, and less expensive, are needed for the high power fuel cells of the future.

Electrocatalysis with Binuclear Phthalocyanines

One (or two) monomolecular layers of the catalyst were laid down upon a clean ordinary pyrolytic graphite (OPG) electrode. This is accomplished by cycling the electrode in an organic phase solution of the catalyst (ca 1 x 10^{-5}M). The amount of material on the electrode can be deduced via the amount of charge under a redox peak (in the absence of oxygen) using the Frumkin isotherm [20,21].

A detailed analysis of the electrocatalytic behaviour of the binuclear complexes under an oxygen atmosphere, relative to the mononuclear tetraneopentoxyphthalocyaninecobalt(II) as a control molecule, shows that some binuclear cobalt species electrocatalytically reduce oxygen more efficiently than the control species, and much more efficiently than bare carbon, e.g.

	Relative Rate	Halfbandwidth [Co(III)]
Bare carbon	1	
Mononuclear Co(II)Pc	3.6	678cm^{-1}
$C(2)(PcCo)_2$	3.8	764
$O(1)(PcCo)_2$	5.5	1080
$EtMeO(5)(PcCo)_2$	5.5	787
$Cat(4)(PcCo)_2$	4.4	800

To date, the reduction process with the cobalt catalysts is 2-electron (to hydrogen peroxide) rather than the desired 4-electron process to water. However the current work with iron derivatives is showing 4-electron reduction in basic solution. There is a rough correlation between the ability to reduce oxygen, as indicated by the kinetic current, and the degree of electronic coupling as indicated by Q-band half-bandwidths. Catalysts which can exist in a cofacial conformation appear more effective than those which cannot, the latter behaving essentially as mononuclear species 'strung' together. However the $O(1)(PcCo)_2$ species which cannot form a cofacial conformation, but is strongly coupled through space, is one of the best electrocatalysts of this group.

Summary

These binuclear phthalocyanines represent a fascinating new class of complex which have great promise both in electrocatalysis and in photocatalysis. There are also obvious possibilities for these species in related fields such as electrochremism. We are currently very active in exploring their properties and will report further in due course.

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