Metallophthalocyanines: Dependence of Oxygen Reactivity and Redox Energies upon Solvent

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Metallophthalocyanines are structurally analogous to the porphyrins which play a dominant role in biological redox processes. Such processes may involve electron transfer, oxygen activation and/or oxygen transfer. In recent years we have been undertaking a detailed investigation of the redox behaviour and oxygen binding capability of metallophthalocyanines as a means of improving our understanding of the redox role played by square macrocyclic MN_4 species. We find that solvent interactions are extremely important whenever the solvent can bind to the axial site of the molecule. In such conditions redox couples may shift by as much as 700 mV and systems which are oxygen insensitive in one solvent can react readily with oxygen in another. Such studies are clearly relevant to biological processes where changes in the conformation of the protein resulting in a modification of the axial interactions, paly a role similar to that of changing the solvent. In this paper we review progress in understanding these phenomena.

Large differences in redox energies are frequently observed when a weakly or non-donating solvent is replaced by a strong donor solvent. Redox potentials can be 'tuned' by suitable choice of a solvent intermediate between these two extremes. Not all metallophthalocyanines (MPc) show such sensitivity, and the factors which determine such sensitivity will be explored. Oxygen sensitivity may occur when a redox couple has a potential ($E^{\circ}_{1/2}$) near or more negative than 0 volts (*vs.* s.c.e.), provided a kinetic pathway is available. For example PcFe(II)/pyridine/ $Et_4N^+ ClO_4^-$ ($E^{\circ}_{1/2}$ = 0.66 V) is air stable but PcFe(II)/$HCON(CH_3)_2$/$Et_4N^+ Cl^-$ ($E^{\circ}_{1/2}$ = −0.15 V) oxidises rapidly in air [1], to PcFe(III) species. In these cases no oxygen adduct of PcFe is observed. However in dimethylsulphoxide [2], dimethylacetamide [3] or conc. H_2SO_4 [4], oxygen complexes of PcFe are detected. In DMSO and H_2SO_4, the species PcFe–O_2–FePc is presumed to occur. On the other hand oxygenation of PcCr(II) is reported [5] to yield PcCr(IV)O, whilst PcMn(II) yields PcMn(III) (O_2^-) in DMA but not in pure pyridine [6]. Both cobalt [7] and vanadyl Pcs [8] also reportedly form oxygen adducts. We shall review these systems and show how their oxygen reactivity is related to their redox behaviour and stereochemistry in various solvents. Finally the binding of oxygen to a metal phthalocyanine is of critical importance in the use of such systems to reduce oxygen electrocatalytically. Aspects of this problem, important in fuel cell development, will be briefly discussed.

References

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Metal Ligand Complexing in Biological Systems

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Life chemistry spans a wide range of science subjects including inorganic, organic, physical and biological chemistry. To the uninitiated these may embody a bewildering collection of unrelated scientific facts from which it is difficult to extract the basic concepts. Some of these difficulties can be overcome by mounting more courses in bio-inorganic chemistry, by setting up a framework to encourage dialogues between scientists from the various disciplines, and by introducing mathematical models or schemes which simplify the *in vivo* chemistry but which nevertheless give an overview to nucleate hypotheses.

The challenge facing researchers may be subdivided into two sections: the chemistry of coordination complexes is considerably more sophisticated *in vivo* because, compared to normal laboratory bench experiments, the ligands are very much more complicated and there is also the presence of a multitude of metal ions and ligands. Secondly, many complexing reactions occur at concentrations considerably more dilute than those normally experienced in the laboratory. Thus, means of studying such highly complicated but very dilute solutions are necessary.

To offset these substantial problems, there is the powerful attraction that an understanding of bio-inorganic solution chemistry can lead to successes in many areas of pharmacology and of dietetics. Although solution chemists may not become professional medical researchers *per se,* nevertheless, they