Metallophthalocyanines: Dependence of Oxygen Reactivity and Redox Energies upon Solvent

A. B. P. LEVER

Department of Chemistry, York University, Downsview, Toronto, Ont., M3J 1P3, Canada

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.

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Metal Ligand Complexing in Biological Systems

PETER M. MAY and DAVID R. WILLIAMS

Department of Chemistry, University of Wales, Institute of Science and Technology, Cardiff CF1 3NU, U.K.

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

can help bring about considerable improvements in the quality of life for their colleagues and themselves.

Our approach to unravelling some of these problems has been to introduce the use of computerised mathematical models based upon equilibrium calculations of these multiple-metal/multiple-ligand solutions. The model is, of course, an oversimplification but we must realise that a good simplification is a big advantage. Just as a map should not show all of the details of the terrain, our models aim to include only those biological and chemical features concerning low molecular weight complexes *in vivo*, the liberation of metal ions from metallo-proteins, the bioavailability and membrane permeability of metal ligand complexes, and strategies for encouraging metal ion complex excretion. The object is to imitate reality with such models and to make predictions based upon hypotheses. Scientific method demands that we use such an approach since the human mind cannot understand and remember the millions of biochemical facts at one and the same time.

Through defining objectives, setting up equilibrium models, and then designing experiments to try and answer the questions raised by such model computations, we have been able to tackle a large variety of problems. Details concerning the charges, stoichiometry, and some structural aspects of the low molecular weight complexes present in biofluids are thus obtainable permitting us to manipulate metal ions through a variety of *in vivo* reactions.

Upon the basis of these computerised analyses, we are able to construct correlations with known biological data (half lives, rates of excretion, response to medication, *etc.*). Examples of these features will be described in respect of adriamycin metal complexes *in vivo*, copper and rheumatoid arthritis, and chelating ligands designed to remove toxic metal ions.

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On the Interpretation of Thermodynamic Quantities in Complexation Reactions

A. BRAIBANTI

Institute of Pharmaceutical Chemitry, University of Parma, Italy

Schwarzenbach presented a physico-chemical model of the complexation reaction, useful for the interpretation of entropy, ΔS° and enthalpy, ΔH° changes.

The main observations of Schwarzenbach concerning the thermodynamics of complexation between a ligand and a metal can be summarized as follows:

(*i*) complexes formed by metals with A-character show $T\Delta S^\circ \gg 0$ and $\Delta H^\circ \sim 0$ and complexes by metals with B-character show $T\Delta S^\circ \sim 0$ and $\Delta H^\circ \ll 0$;

(*ii*) the entropy term $\Delta S^\circ > 0$ is independent of A or B character and *it must be connected with the compensation of charges and be caused by structural changes occurring within the solvent*;

(*iii*) the enthalpy term ΔH° is not suited to measure bond energies, because *thermodynamic quantities are also influenced by the environment of the reacting species.*

The two classes of thermodynamic changes indicates in (*i*) can be found in the protonation of acids and bases, respectively. In every case the paramount importance of the processes at the solute–solvent interface is apparent.

The distinction between the internal processes (bond formation or bond cleavage) and the external ones (solute–solvent interactions) have been put by Hepler by stating that

$$\Delta S^\circ = \Delta S_{int} + \Delta S_{ext}$$

$$\Delta H^\circ = \Delta H_{int} + \Delta H_{ext}$$

In most cases in solution, $\Delta S_{int} \approx 0$ and $\Delta S^\circ \sim \Delta S_{ext}$. ΔS_{ext} can be therefore calorimetrically determined.

Other methods, *e.g.* relaxation experiments, can be used to enlight the properties of the solute–solvent zone and hopefully help to calculate ΔS_{ext} and ΔH_{ext}.

Computer-Assisted Methods for the Investigation of Solution Equilibria

PETER GANS

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, U.K.

The computer is now widely used as an instrument for studying solution equilibria. The most complete description of a solution system consists of the values of the formation constants of all the species present, and the computer programs available for this calculation will be discussed and compared. However, a computer program that permits calculation of formation constants in complex systems must be supplied with the stoichiometries of all species believed to be