APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 10, 549–556 (1996)

DEDICATION
To Professor A. B. P. Lever on the Occasion of his 60th Birthday

This issue of *Applied Organometallic Chemistry* is dedicated to Professor A. B. P. Lever of York University, Toronto, Canada.

Manuscripts were assembled and edited by Dr H. S. Nalwa of the Hitachi Research Laboratory, Ibaraki, Japan.

BIOGRAPHICAL SUMMARY

Barry Lever, born in London, UK, in 1936, graduated from the Imperial College of Science and Technology with a Ph.D. in 1960. After several years of post-doctoral experience with Ron Nyholm and Jack Lewis he moved to a Lectureship at the University of Manchester Institute of Science and Technology and subsequently to York University in Canada, in 1967, after a brief 'visiting' sojourn at Ohio State University. He has remained at York since then but has held various sabbatical and visiting teaching appointments, especially at the Californian Institute of Technology (1976/77) and at several Italian universities.

He has been very involved with the International Conferences on Coordination Chemistry (ICCC), being on the planning committee for over 20 years, and having been program chairman at the XIV ICCC in Toronto in 1972, and on the International Advisory Boards of the XXIV ICCC (Athens, 1986) and XXXII ICCC (Santiago, 1997). Lever was also Program Chair and co-organiser of the combined ACS/CIC Biennial Inorganic Chemistry Conference (BICS) at York University in 1985. He also initiated the Ontario Inorganic Discussion Weekend, in 1967, and this has taken place without a break every year since then at sites around Ontario and has spawned similar weekend conferences across Canada.

Space precludes listing of invited lectures, but these include Session and Plenary lectures at Conferences in China, Canada, USA, Italy, Chile, Portugal, Switzerland, Germany and Japan.

Lever is the founding editor of *Coordination Chemistry Reviews* (*CCR*) with over 150 volumes now published. He has also been on the Editorial Boards of *Inorganica Chimica Acta* and *Inorganic Chemistry*. Lever is a co-editor of several series of monographs—with Harry B. Gray, a five-volume set entitled *Physical Bioinorganic Chemistry*, with Cliff Leznoff, a four-volume set entitled *Phthalocyanines—Properties and Applications*—plus several other individual volumes. He is the author of *Inorganic Electronic Spectroscopy* (*IES*) (Elsevier, 1968 and 2nd edition 1984, and Russian edition 1987). *IES* is a 'Citation Classic' of the Institute of Scientific Information (Philadelphia), as is an early article dealing with the electronic spectra of tetragonal metal complexes (*CCR*, 1968).

Professor A. B. P. Lever

Lever is a recipient of the Alcan Lecture award (CIC, 1981), a Japan Society for Promotion of Science Fellowship (1983), the Walter Gordon Fellowship award (York, 1988) and the 1996

CCC 0268–2605/96/080549–08

Gerhard Herzberg Award for outstanding achievements in spectroscopy (Spectroscopy Society of Canada).

RESEARCH ON PHTHALOCYANINES

The phthalocyanines were among the first macrocyclic species ever synthesized. They were first noted in 1907 by Braun and Tcherniac, in the process of heating *o*-cyanamide to a high temperature, and were then re-discovered by accident during an industrial preparation of a phthalic derivative. R. P. Linstead, at Imperial college, characterized them in the 1930s. This investigation laid the basis for an industrial dyestuff industry based upon these species. Lever was a graduate student of John Elvidge, at Imperial College, whilst Elvidge was a student of Linstead, and thus Lever is an academic grandson of the man who began this field.

The first major review of phthalocyanine chemistry ever published, written by Lever, appeared in 1965 in the hard-cover journal *Advances in Inorganic Chemistry and Radiochemistry.* It stimulated activity in the field by summarizing, comprehensively, what was then known about these species. Despite its age, this article is still frequently cited by those wishing to reference general phthalocyanine chemistry.

While initially regarded simply as important colorants, it was soon recognized that the phthalocyanines had many other important properties, especially the fact that they were photoconductive and that they could be prepared in a range of different oxidation states. Currently they are commercially used, not only in the dyestuff industry, but also in photocopying machines and in some newly developed read–write compact disks. Titanyl phthalocyanine, a very important and commercially applied metallophthalocyanine (MPc), was first synthesized by Lever [Ph.D. Thesis, 1960].

Phthalocyanines are now being investigated actively for many other potential applications, including photodynamic therapy (cancer treatment), chemical sensors, molecular metals, effluent analysis and control, smart windows, electrochromic display devices, redox electrocatalysts, photovoltaic devices, optical limiting switches, molecular electronics and so on. Over the past 30 years Lever has contributed to the basic understanding of these species and laid down much of the foundation which would be incorporated, implicitly, into these commercial applications. These contributions include the following aspects, discussed here roughly chronologically. Lever carried out some of the early magnetic studies culminating in an important paper which both contributed to the field, and reviewed its then-current status. The phthalocyanines species are synthetic analogues of the biologically important porphyrins and offer reactivity similar to the porphyrins, yet are more resistant to chemical decomposition. Oxygen reactivity is a major aspect of porphryin chemistry, so it was especially important that in 1959 Lever demonstrated, in a brief Communication, that manganese phthalocyanine would carry oxgen reversibly; at the time this was the first known reversible oxygen-carring species based upon a manganese porphryin or analogue.

During the 1970s, and continuing even now, there had been great interest in how oxygen-carrying molecules bind oxygen and transfer it. It was important therefore to learn how manganese phthalocyanine functioned in this respect. This turned out to be very difficult to solve, but in the late 1970s Lever's group characterised an oxygen adduct of manganese phthalocyanine and reported its chemistry; today, this is still a unique system. After publishing a major contribution on chromium phthalocyanines, Lever moved his attention away from phthalocyanine chemistry to develop interests in spectroscopy and coordination chemistry. However, around 1972 he returned to phthalocyanine chemistry and since then has published over 60 papers developing the field, in which he remains a leader.

A major characteristic of MPc species is their redox activity, their ability to form a range of stable complexes in different oxidation states. This important feature guarantees their utility in future molecular electronic devices. Redox activity had been addressed briefly in a number of papers by Calvin and by Clack and Yandle, but it was Lever who first brought together a combined treatment of syntheses, electronic spectra and structure, magnetism, ESR, etc., of higher oxidation-state, first-row transition-metal MPcs.

The mid-1970s also saw the Lever group turn to the detailed electrochemical properties of the phthalocyanines, an interest which remains very active today. There followed a series of important papers which explored the basic electrochemistry of simple first-row-transition-metal MPcs in non-aqueous media, touching especially upon solvent dependence and upon the characterization (energetics, structure, ESR, etc.) of the accessible oxidation states. These paralleled the studies on porphyrin electrochemistry being carried out by Kadish, Fenton and others, but revealed characteristic differences therefrom, which will be exploited in the molecular devices of the future. These electrochemistry papers are not limited to simple presentations of electrochemical potentials for oxidation and reduction of the metallophthalocyanine species, but are analysed in detail to show the chemical reactions which are often coupled to the electrochemical process, and to explore, where relevant, their kinetic and structural aspects.

The papers on iron and cobalt phthalocyanines are especially noteworthy, as is the analysis of the very complex electrochemistry of a binuclear oxide-bridged manganese phthalocyanine species. The recent analysis of the solution electrochemistry of rhodium phthalocyanine is arguably the single most intensive analysis of the electrochemical behaviour of an MPc species ever undertaken. No less than 14 redox-active species were identified during the oxidation and reduction of ClRh(III)Pc. Cyclic and differential pulse voltammetry at ambient and low temperature, spectroelectrochemistry, ESR spectroscopy and digital simulation were necessary to elucidate this extremely complex system.

A recent electrochemical study of a charge-transfer adduct between zinc tetraneopentoxyphthalocyanine and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone is a novel study of a charge-transfer complex studied as a redox series. This early work provided the basis for modern studies of phthalocyanine electrochemistry around the world; it culminated in a major review of phthalocyanine electrochemistry. [Lever *et al.*, *The Phthalocyanines*, Vol. 3; see Bibliography, Ref. 56], the first such review ever published.

Given the intense colour of MPc species, it was clearly of great interest to study their electronic spectra in their various oxidation states (and including mixed-valence species), and to seek some theoretical linkage between these spectroscopic energies and the electrochemical potentials. This led to a seminal paper showing how redox-active metals incorporated into MPc species exhibited charge-transfer transitions whose energies could be readily derived from their electrochemical potentials. Such transitions had never been identified in phthalocyanine species; the paper is critically important in directing all subsequent studies of the charge-transfer spectroscopy of phthalocyanines, such as, for example, the work of Stillman. This paper also had many ramifications outside the field of metallophthalocyanine chemistry. It demonstrated a simple 1:1 relationship between a charge-transfer energy and a difference in electrochemical potentials. In a sense it was too simple; the Lever group then demonstrated that such a relationship should exist but only if one takes into account reorganization energies and differential solvation free energies. In fact, for good reason, these extra terms vanish in MPc species to leave the simple 1:1 relationship. This led however to a series of critical papers (outside metallophthalocyanine chemistry) exploring the more general relationship which exists between the electronic spectra and electrochemical properties of a coordination complex and how this can be used to derive reorganization energies, solvation energies, etc. The Lever group also turned briefly to looking at the redox potentials and photoactivity of MPc excited states.

Protonation is an important process in phthalocyanine chemistry. Protonation processes must depend upon the charge distribution on the phthalocyanine unit and this was explored in an elegant paper which showed how protonation of cobalt phthalocyanine depended on the oxidation state of the central cobalt atom and of the phthalocyanine unit, over four net redox states. In the early 1980s, there developed a close and very fruitful collaboration between Professor Clifford Leznoff, an organic chemist at York, and the Lever group. The intention was basically to explore the chemistry of binuclear and polynuclear phthalocyanines. The syntheses were to be carried out in the Leznoff laboratory, while the physical and electronic characteristics would be in Lever's domain. The first combined paper introduced the so-called 'Clamshell' metallophthalocyanine species in which two phthalocyanine units are held fairly closely together in a cofacial or almost cofacial arrangement. A range of such species were synthesized, with varying bridge length between the two halves, and culminating in 1,8-naphthalene and anthracene derivatives, and in the co-planar so-called (− 1) bridge species in which two MPc units share a common benzene ring. In addition to the purely synthetic design interest in these species, there was the fundamental problem of exploring the extent to which these two phthalocyanine halves were coupled. Such coupling could reveal itself, *inter alia*, by electrochemistry and electronic spectroscopy. Moreover, coupled species might react in concert in some fashion, especially with respect to multi-electron redox electrocatalysis. It was these aspects which were of particular importance to the Lever group, and it was the field of redox electrocatalysis which drove the design strategies for further collaborations.

From this period, the Lever/Leznoff collaboration published a series of papers describing the synthesis, chemistry, physical, spectroscopic and electrochemical properties of a range of multi nuclear species which is unique in MPc chemistry. The interest in redox electrocatalysis, and the related area of chemical sensors, spurred studies of the surface electrochemistry of phthalocyanine-modified electrodes (usually graphite electrodes in which the active graphite surface is coated with one or more metallophthalocyanine layers). Such studies can then be carried out in pH-buffered aqueous media where the aqueous insolubility of the MPc species is now an advantage.

These studies have turned out to be very profitable; they began with a collaboration with the Yeager group in Cleveland, in order to learn the techniques which have now been used in many more recent studies. A study of the surface electrochemistry of ClRhPc reveals a complex dynamic interplay of mononuclear and dinuclear species existing on the surface in a fashion controlled by electrochemical polarization. Several papers and a patent deal with the development of a sulphide ion sensor comprising one of several MPc species adsorbed on a graphite surface; this sensor is of broader application than commercially available devices and prompted a reviewer of an Analytical Chemistry publication to comment that the work represented a major breakthrough in Ion-selective Electrode (ISE) design. The Lever group has since characterized phthalocyanine-modified ISE electrodes for oxygen, sulphide, mercaptans, hydrogen sulphide, ascorbate, hydrazine, hydroxylamine and carbon dioxide targets. Oxygen reduction and the possible use of MPc species as electrocatalysts for reducing oxygen in fuel cells prompted a number of studies. These demonstrated that many of the binuclear species were better electrocatalysts than corresponding mononuclear species but the improvement was, disappointingly, not very dramatic. The elusive four-electron reduction of oxygen was demonstrated with a rhodium phthalocyanine derivative and with a cobalt aminophthalocyanine surface.

The electronic structures of the new polynuclear species were studied in some depth, primarily using electrochemistry and electronic spectroscopy as probes. An important outcome of these studies was the first detailed study of mixed-valence metallophthalocyanine species where a binuclear (or tetranuclear) species contained two metals or two phthalocyanine ligands in different oxidation states. These species were best-developed in polynuclear zinc phthalocyanine species and in the aforesaid naphthalene and anthracene species.

Other contributions include a fascinating new molecule in which four crown-ether linkages adorn the four benzene rings, a publication which was soon followed by the preparation of many other crowned phthalocyanines in other laboratories around the world. These species are mononuclear in chloroform but immediately dimerize in the presence of potassium ions (exclusively) to form two different dimeric species depending upon the Pc:K ratio. One of these is the most perfectly *D4h* cofacial metallophthalocyanine species yet synthesized. The possibility exists to use these compounds as quantitative sensors for the potassium ion which can be detected at extremely low levels. These species also catalytically reduce oxygen in a very well-defined fashion. CoPc is known as an electrocatalyst for the reduction of thionyl chloride in lithium batteries but, until a recent study, the mechanism of this process was unknown. It involves a series of two-electron redox processes which have been analysed in considerable detail. Such two-electron processes are comparatively rare and their elucidation here is a useful contribution to redox mechanism in general. A kinetic study of this system has also been completed. This very applied work derives directly from an earlier publication which showed how thionyl chloride provided a facile route to the synthesis of higher oxidation-state MPc species.

Many substituted metallophthalocyanine species exist. Among these the fully halogenated species are of especial significance since they are even more stably thermally than the unsubstituted species. Moreover, the incorporation of 16 halogen atoms can be expected to have a profound effect upon the electrochemical behaviour. Thus study of the surface electrochemistry of hexadecachloro phthalocyanine species indeed revealed unusual electrochemical behaviour. Not only are some couples shifted dramatically, but some have disappeared, probably due to extreme kinetic sluggishness.

Kinetic problems also inhibit the oxidation of silver(II) TNPc (tetraneopentoxyphthalocyanine) to silver(III) TNPc but this latter species can be obtained by controlled potential electrolysis. This is the first silver phthalocyanine whose electrochemistry has been explored in detail. Reduced Ag(I) and anion radical species can be observed at low temperatures, but these are unstable and lose silver at ambient temperatures. The possibility that the loss (and re-incorporation) of silver could be controlled in a film, led to studies of the Langmuir–Blodgett [LB] film chemistry of AgTNPc, showing the reversible redox chemistry of the surface film. Here Lever reports a new technique for simultaneously probing the electrochemistry, spectroscopy and orientation of a monomolecular film, as a prelude to future studies using Langmuir–Blodgett films in chemical sensors. These early LB studies in the Lever group led to a study of how the orientation of a surface film can be controlled by varying admixture of other species, and how an unaggregated MPc film can be generated (all previous MPc films described in the literature were aggregated). Such studies are critical for the future application of MPc LB films to chemical sensor design and molecular electronics.

Professor Lever has promoted phthalocyanine chemistry through a series of more recent Reviews, following the earlier *Advances* contribution. A summary of current applications appeared in *ChemTech*, under the intriguing title 'the other Periodic Table', to emphasize how ubiquitous MPc species were, and how they themselves formed a periodic group of properties. This was in fact based upon a shorter version published in the *Strem Chemiker*, an organ of the Strem Chemical Company. Just prior to the *ChemTech* publication, a survey article appeared, based upon a Plenary Lecture. The solvent dependence review and the 'Mapping' article were also based upon invited conference presentations. Most recently, Professors Leznoff and Lever have collaborated in publishing, with VCH, an edited series of hard-bound monographs on *The Phthalocyanines; Properties and Applications*. Volumes 1–4 have now appeared. Volume 3 (1993) contains the aforementioned first detailed and comprehensive review of the solution electrochemistry of MPc species. Lever is also the founding Editor of the international journal *Coordination Chemistry Reviews*, which celebrates its 150th volume this year (1996).

Professor Lever and his colleague Professor Leznoff, together with Professors Kobayashi, Shirai and Kenney, were the organizers of a very successful symposium on 'Phthalocyanine Chemistry' held in Hawaii in December 1995 as part of the 1995 International Chemical Congress of Pacific Basin Societies; this brought together many of the world players in the field for the first time. Prompted by Professor Lever, an international conference on Phthalocyanine Chemistry is planned for 1998, probably to be sited in Germany.

Professor Lever has played a crucial role in enriching the research, growth and development of Phthalocyanine Chemistry over a 30-year period, placing him among the foremost macrocycle chemists of our day. The long list of his outstanding scentific publications, remarkably cross-referenced, is a proof of his great imagination, creativity and dedication to science. He has been internationally recognized by maintaining the highest standards of integrity and excellence for scientific research. His unique personality, prudence and leadership have enriched this field of chemistry and will continue to guide and encourage all of us in new scientific endeavours. On the occasion of his 60th birthday, his students, colleagues and friends wish Professor Lever a Happy Birthday and a very long, prosperous, healthy and happy life.

Acknowledgements I am very grateful to Professor Barry Lever for supplying all the details for the preparation of this article. I express my very special thanks to all those who contributed articles to this special 'Phthalocyanines' issue in honour of Professor Lever. I am also indebted to Professor Peter J. Craig for providing me with this unique opportunity to honour Professor Lever. By fortunate chance, Professor Craig, the Editor-in-Chief of *Applied Organometallic Chemistry*, was a student of Professor Lever's at the University of Manchester.

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Professor Lever has published extensively in fields other than phthalocyanine chemistry, especially in coordination chemistry, bonding theory, electronic spectroscopy, inorganic electrochemistry and electroanalytical chemistry. Here we provide a list only of the phthalocyanine-related contributions; in this field alone he has published more than 70 research articles.

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