

Preface

When I heard in August 2010 that Carl Ballhausen had died at the age of 84, I was very sad because he had played such an important part in the development of my interests in coordination and theoretical inorganic chemistry in the 1960s. Indeed lectures given by Carl, Al Cotton, Dick Fenske, and Harry Gray at a NATO Summer School held at Selsdon Park Hotel near London in 1967 did much to stimulate my interest in theoretical inorganic chemistry. Later, when I embarked on my first semiempirical molecular orbital calculations to understand why nitrosyl complexes adopted linear and bent geometries, I was greatly assisted by “Molecular Orbital Theory,” which Carl coauthored with Harry Gray (W.A. Benjamin New York, 1965). My sense of loss must have been small when compared with those of the many graduate students and postdoctoral fellows who had been supervised by him. His many international collaborators would also have missed his profound theoretical insights and friendly, jovial manner. Therefore, I was pleased when Peter Day after consulting with Jens Peder Dahl proposed a volume of *Structure and Bonding* dedicated to Carl’s life and his seminal contributions to quantum chemistry. The large number of Carl’s co-workers who have gone on to occupy senior academic positions made it relatively easy to propose a list of authors for the volume. Their response to invitations to contribute has been so enthusiastic that it proved necessary to expand the project into two volumes. The first one deals with the application of Carl’s Ligand Field Theory to spectroscopic and chemical properties of transition metal complexes. The second volume concentrates on more theoretical topics and reviews the development of modern ab initio theoretical methods and discusses the broader implications of fundamental theoretical concepts.

Jens Peder Dahl was closely associated with Carl’s research group for many years, and his introductory chapter summarizes his scientific achievements and in particular his contributions to the inorganic renaissance which unfolded from 1950. Harry Gray recounts his very fruitful collaboration with Carl which resulted in a general molecular orbital description of the metal-oxo bond, and he and Jay Winkler review more recent experimental and spectroscopic data on metal-oxo complexes of the later transition metals. Colin Flint also provides a brief review of

his work with Carl in 1967–1968, and then describes his subsequent research on the assignments of the vibronic sidebands in the emission spectra of chromium ammine complexes. He also comments on the Jahn–Teller effect in the emissive state.

Joshua Palmer discusses the transition metal complexes of the noninnocent, electron-rich corrole macrocycle. This includes a detailed summary of investigations to determine the physical oxidation states of formally copper(III), iron(IV), and cobalt(IV) corroles. The electronic structures and reactivities of other metallo-corroles are also discussed, and comparisons made between corrole and porphyrin complexes. William Trogler reviews thin film conductivity sensors that use metal phthalocyanine semiconductors which offer properties distinct from those of organic thin film transistor sensors. Phthalocyanines (Pc) are planar ligands that are closely related to porphyrins (Por), as both can be deprotonated to form dianions that yield a wide variety of square planar metal(II) chelate complexes MPc and MPor. Porphyrins are crucial redox active metalloenzymes that play key roles in metabolism, oxygen storage, photosynthesis, and other biological processes. Phthalocyanines are also important dye and paint pigments, as well as having electronic device applications in CD-recordable media, xerography, photovoltaics, and organic light-emitting devices. Kyle Lancaster reviews the concept of outer-sphere coordination (OSC) in the context of bioinorganic chemistry. A distinction is made between electronic and structural OSC, which arises from the interaction of the protein matrix with inner sphere ligands. Electronic OSC entails the electronic interaction between the polypeptide and inner-sphere ligands. These effects principally arise from hydrogen-bonding interactions, though through-space dipolar interactions are also encountered.

Rosalie Hocking and Ed Solomon in the next chapter note that Carl Ballhausen taught them how to interpret ground and low lying excited state spectral features in terms of ligand field and covalency effects. With the availability and development of synchrotron radiation, this has been extended to the X-ray region where ligand field and covalency effects have an impact on the metal K and L-edges. The L-edge intensity and its distribution over the multiplets are particularly powerful in experimentally determining the bonding in highly covalent systems, where ligand spectral features can obscure the use of more traditional methods. Klaus Møller and Niels Henriksen in their review discuss how time-resolved X-ray diffraction may lead to important insights into the dynamics of the chemical bond. The focus of the review is the underlying theoretical concepts which are required in order to extract the dynamics of the chemical bond from the time-resolved X-ray diffraction data.

In the first chapter of the second volume, Tom Ziegler reviews the development of electronic structure theories for transition metal complexes from the 1950s to the present day. Jan Linderberg also focuses on the emergence of quantitative means for the study of the electronic properties of complexes and molecules. The development, refinement, and application of the orbital picture have elucidated the electric and magnetic features of molecules and used for the interpretation of electronic transitions, electron spin resonance parameters, rotatory dispersion, nuclear quadrupole couplings, and geometric bonding patterns. In a chapter which addresses some fundamental issues, John and James Avery discuss the theory

of Sturmians and generalized Sturmians. They show that when generalized Sturmians are used as basis functions, calculations on the spectra and physical properties of few electron atoms can be performed with great ease and good accuracy. Brian Sutcliffe considers the implications of Carl Ballhausen's research on vibrational spectra, and it is suggested that his use of the Born–Oppenheimer approximation is capable of some refinement and extension in the light of later developments. A consideration of the potential energy surface in the context of a full Coulomb Schrödinger Hamiltonian in which translational and rotational motions are explicitly considered would seem to require a reformulation of the Born–Oppenheimer approach. The resulting potential surface for vibrational motion allows for the rotational motion and the nuclear permutational symmetry of the molecule. Tony McCaffery considers the role played by angular momentum in chemical physics, an interest which was first aroused by a Carl Ballhausen lecture early in the author's scientific career. Later came a deeper understanding of the fundamental nature of angular momentum and the power of its formal algebraic expression. Spectroscopy using light of precisely defined energy and (z-component of) angular momentum represents a unique experimental probe with the potential to reveal the underlying physics of chemical processes. Experiments using circularly polarized emission of gas phase molecules led to new insights in the field of molecular collision dynamics. Further work, and that of others, has suggested an alternative formulation of the mechanics of bimolecular collisions

Frank Neese and his coauthors summarize recent developments in AI methods for strongly correlated electronic systems, and they discuss their implementation in highly efficient quantum chemistry programs which allow one to calculate – from first principles – the spectroscopic and magnetic properties of transition metal complexes with open d- and f-shells. For a long time, this field was the domain of ligand field theory (LFT), subject to various assumptions and approximations which are solely justified by the success of using this theory for the interpretation of experimental data. Yet the chemical significance of the ligand field parameters, while being under intense debate, remains unclear as far as the roots of LFT in its relation to rigorous quantum chemistry are concerned. In the present review, the authors attempt to answer the question how well ligand field performs from the point of view of state-of-the-art first principle calculations and how to connect the two areas. In his chapter, Steve Berry notes that the Gibbs Phase Rule relating the number of degrees of freedom f of a system to the number of components c and the number of coexisting phases p is a central, universally used relation. However, for small systems, notably atomic clusters the Phase Rule shows the coexistence of two or more phases in thermodynamic equilibrium over *bands* of temperature and pressure (with no other forces acting on them). He demonstrates that it is consistent with the laws of thermodynamics and even allows one to estimate the upper size limit of any particular system for which such apparent violation could be observed.

These two volumes provide a fine endorsement of the way in which Carl's contributions have influenced so many scientists and led them explore important new areas of transition metal chemistry, quantum theory, and spectroscopy. The authors have successfully illuminated the fundamental and broad question which

guided much of Carl's research – "What is a molecule and in particular a transition metal complex?". As an interesting postscript, Carl Ballhausen and Christian Klixbull Jørgenson were both in University of Copenhagen in the early 1950s and did their doctoral theses with Jannik Bjerrum at about the same time. At an early stage they collaborated on a series of papers titled "Studies of Absorption Spectra," but their relationship was not always an easy one. Jorgenson moved from Copenhagen at the age of 29 and did research at Cyanamid and the University of Geneva in Switzerland. He died in 2001 and a pair of commemorative volumes were published as part of the *Structure and Bonding* Series in 2004 (volumes 106 and 107). The four volumes will remind us and future generations the important role played by Danish coordination and theoretical chemists in the renaissance of inorganic chemistry.

Oxford
August 2011

D. Michael P. Mingos

Molecular Electronic Structures of Transition Metal
Complexes I

Mingos, D.M.P.; Day, P.; Dahl, J.P. (Eds.)

2012, XVI, 216 p., Hardcover

ISBN: 978-3-642-27369-8