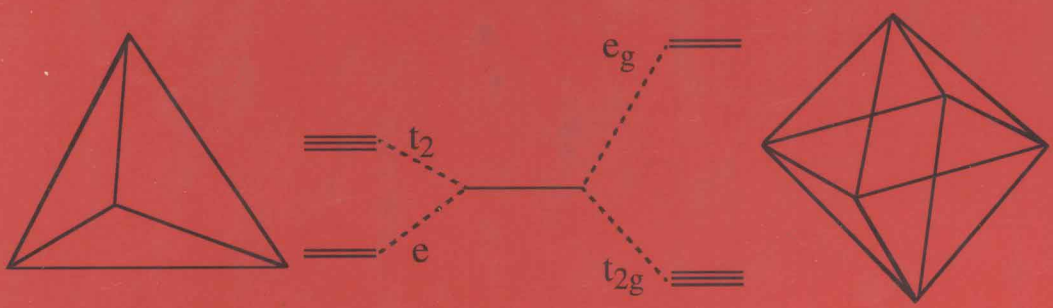
SPECIAL TOPICS IN INORGANIC CHEMISTRY

Ligand Field Theory and Its Applications

Brian N. Figgis
Michael A. Hitchman



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LIGAND FIELD THEORY AND ITS APPLICATIONS

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LIGAND FIELD THEORY AND ITS APPLICATIONS

To our wives, Jane and Annette, and children, Benjamin, Honor, Martin, Peter, and Ruth, who said it would never get done!

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SPECIAL TOPICS IN INORGANIC CHEMISTRY
INTRODUCTION TO THE SERIES

This text represents the first in a series of one-volume introductions to major areas of inorganic chemistry written by leaders in the field. Inorganic chemistry covers a variety of diverse substances including molecular, coordination, organometallic, and nonmolecular compounds as well as special materials such as metallobiomolecules, semiconductors, ceramics, and minerals. The great structural diversity of inorganic compounds makes them vitally important as industrial feedstocks, fine chemicals, catalysts, and advanced materials. Inorganic compounds such as metalloenzymes also play a key role in life processes. This series will provide valuable, concise graduate texts for use in survey courses covering diverse areas of inorganic chemistry.

Department of Chemistry
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R. BRUCE KING, Series Editor

PREFACE

In the 30 years since the publication of *Introduction to Ligand Fields* the subject has undergone considerable change in its conceptual basis and in some aspects of its applications, while retaining its unrivaled usefulness despite advances in theoretical chemistry as applied to transition metal complexes. The origins of ligand field theory's basic premise, i.e., the "splitting" of the d orbitals, is now recognized to be largely in chemical bonding effects, including covalency, rather than the purely electrostatic perturbations produced by the charges of surrounding ligands. A new parameterization scheme that is chemically more transparent has been made available through the introduction of the angular overlap model. Although rigorous ab-initio and density functional calculations can now be carried out successfully on transition metal complexes, in practice they have not significantly reduced the need for ligand field treatments for interpreting, for example, experimental spectral and magnetic properties.

The subject has also matured. At the time of *Introduction to Ligand Fields*, ligand field theory was a subject in its own right, with the major emphasis being on the nature of the metal–ligand interaction and how it influenced experimental observations. Those investigations are now largely complete: It is understood how, why, and under what conditions ligand field theory can be successfully applied. Ligand field theory has become a valuable tool in the armories of inorganic chemistry and chemical physics and is widely used to interpret the properties of transition-metal ions in biologically important molecules. As such, there is a place for an updated version of *Introduction to Ligand Fields*, but one that emphasizes a different relationship between theory and application. This volume, under an appropriately modified title, addresses that need.

The chapters "Group Theory" and "Molecular Orbital Theory" have been deleted because these topics are now adequately covered in standard undergraduate textbooks. Two new chapters—"The Angular Overlap Model"

and "The Origin and Calculation of Δ"—have been introduced. The chapters on the influence of weak, medium, and strong crystal fields have been merged and that on complexes of non-cubic stereochemistry has been subsumed into other parts of the book. In response to the changes in emphasis that have occurred, the chapter "Thermodynamic Aspects of Crystal Fields" has been replaced with "Influence of the d Configuration on the Geometry and Stability of Complexes." Finally, the chapters on the electronic spectra, magnetochemistry, and electronic paramagnetic resonance of transition metal complexes have been considerably expanded and updated, so that the theory and the applications of ligand field theory receive approximately equal weighting.

A number of people have read through all or part of the book, and we are grateful for their very valuable comments and suggestions. Particular thanks are owed to David Goodgame, David Johnson, Frank Mabbs, Dirk Reinen, and Claus Schäffer as well as to the editor of this series, Bruce King. Thanks are also due to Tim Astley and Horst Stratemeier for help in preparing the figures.

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CHAPTER 1

INTRODUCTION

1.1 THE CONCEPT OF A LIGAND FIELD

The basic notion of a ligand field was first developed by Bethe (1) in 1929 as an application of the newly developed quantum mechanics. In the following few years, the implications of his work for the spectral and magnetic properties of transition-metal complexes were recognized by Penney and Schlapp (2) and van Vleck (3), among others. Bethe undertook the study of the effect of the surrounding ions on the electron distribution within any one of the ions in a NaCl-type lattice. He supposed that the ions were undeformable spheres and the interactions that took place between them were solely the result of the electrostatic potentials set up by their charges. The charges were taken to be located at the centers of the ions. In the specific example of NaCl, the sodium ion was considered to be surrounded by six negative point charges located at the vertices of a regular octahedron. Bethe also took into account ions that were not immediate neighbors of the ion under consideration. It has transpired, however, that little is to be gained by dealing with the influence exerted by any but the immediate neighbors. Each of the six negative charges creates an electrostatic potential:

$$\mathbf{v}_{(i;x,y,z)} = e/r_{(i;x,y,z)} \tag{1.1}$$

at the point (x,y,z), where $\mathbf{v}_i$ is the potential caused by the ith of the six ions, and $r_{(i;x,y,z)}$ is the distance from the ith ion to the point (x,y,z).

Let the origin of the set of Cartesian axes be located on the cation under consideration. The problem resolves itself into summing the potentials from the

individual surrounding ions to give the total potential at any point near the central ion and then finding the effect of such a potential on the electrons of that ion. We have:

$$\mathbf{v}_{(x,y,z)} = \sum_{i=1}^{6} \mathbf{v}_{(i;x,y,z)} \tag{1.2}$$

The process of performing this summation and examining the effect of $\mathbf{v}_{(x,y,z)}$ on the electrons of various central ions is a matter of some mathematical complexity, and its outline occupies much of the first chapters of this book. Before launching into the details of the process, we make some general remarks about the model employed as the starting point.

The facts that the original considerations were made on the potential developed near an ion that was part of a lattice and that such a lattice could occur only in a crystal led to the term *crystal field theory* to cover the subject. It has been found, however, that few of the results of crystal field theory depend on the existence of a lattice. We can therefore carry most of them over to the model that is at the basis of coordination chemistry: that of the *coordination cluster.* By a coordination cluster, of course, we mean a central metal ion associated with a number of attached ligands, the whole forming a distinguishable entity and possibly bearing a net electrical charge. The coordination clusters themselves pack into a lattice in the solid state. This packing is not considered of primary importance, because the principal contribution to the potential at the central metal ion comes from the atoms closest to it—the donor atoms.

In the more general model of a coordination compound, the electrons of the central ion are subject to a potential, not necessarily of simple electrostatic origin, from the ligand atoms. The term *ligand field theory* has been employed to cover all aspects of the manner in which the physical properties an ion or atom is influenced by its nearest neighbors. Ligand field theory, then, contains crystal field theory as a limiting special case.

Defined in the above manner, ligand field theory seems to include all theories of chemical bonding between an atom and its neighbors. Indeed, some authors take such an approach. They include in ligand field considerations subjects such as the strength of the metal–ligand bond and coordination number. Such efforts, however, meet with comparatively little success. We restrict our treatment of the ligand field effects to the results caused by the interactions of ligand atoms with d and f electrons. We do not inquire how the ligands got there, how firmly they are held, nor, too deeply, how the bonds came to possess their particular character.

A great many of the results of ligand field theory depend largely on the approximate symmetry of the ligand distribution around the central metal ion rather than on the particular ligands or the details of their locations. The term *approximate symmetry* needs further clarification. We use the nomenclature *octahedral* and *tetrahedral*, for example, to refer to a coordination cluster in

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