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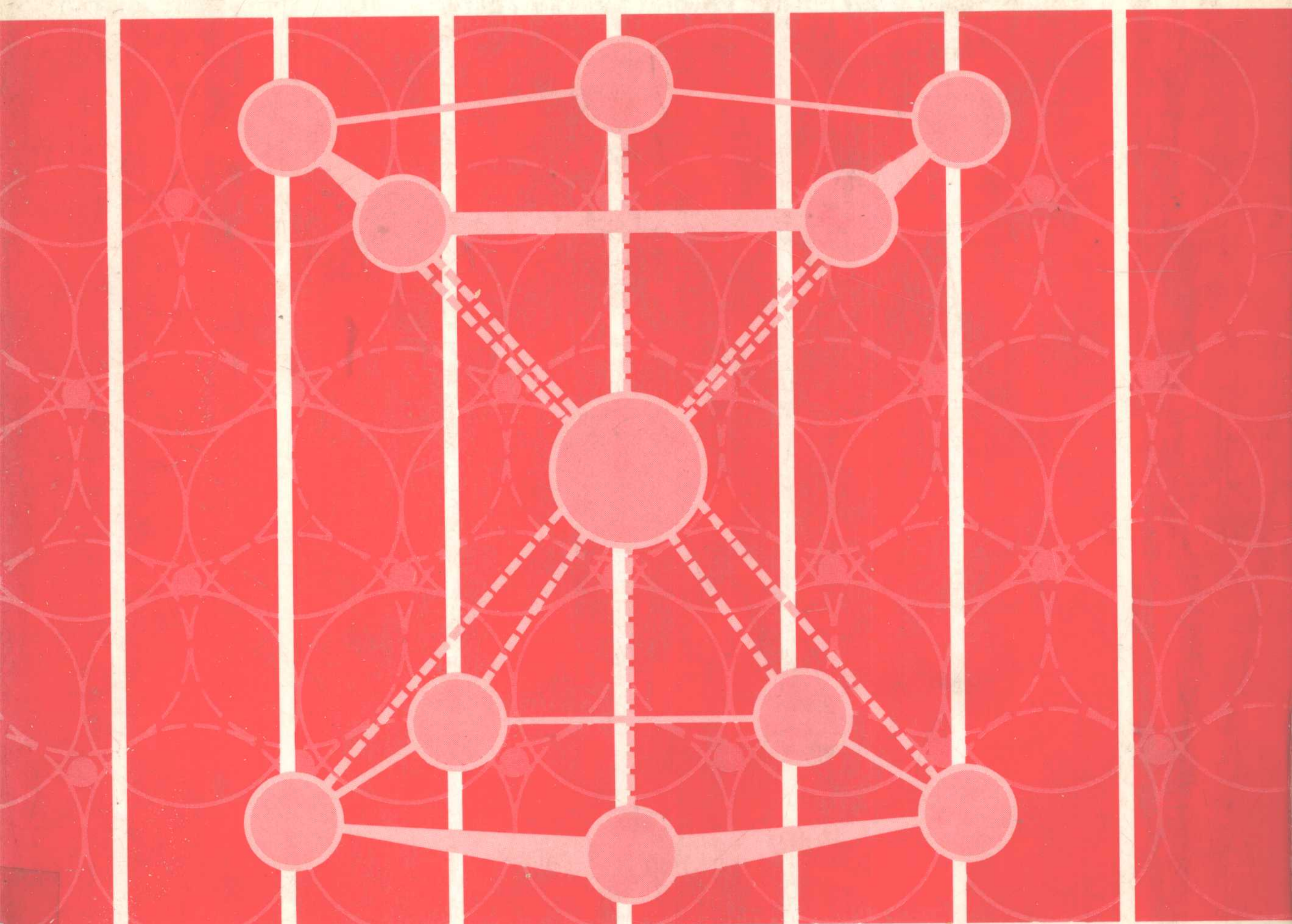
An Introduction to Inorganic Chemistry



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an introduction to INORGANIC CHEMISTRY

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An Introduction to Inorganic Chemistry

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This book is dedicated to the many students and colleagues with whom we have worked over the years, but most especially it is dedicated to those who have had the greatest impact upon our careers:

Ken	*Shirley*
Marge	*Syd*
Susan	*Katie*
Russ	*Lauby*
	Mike
	Riley

PREFACE

TO THE STUDENT:

Inorganic chemistry is an exciting field! We wish to share with you the fact that inorganic chemistry has reached a point where an attack can begin on problems of considerable scientific and social significance. For example, watch for significant developments in the communications, electronics, and energy industries in the near future. These advances will derive from current inorganic research on metal catalysts for production of hydrogen and organic fuels, on solid-state, one-dimensional conductors and solid-state batteries, and on metal catalysts for solar energy conversion. These problems, and many others like them, require a broad knowledge of inorganic chemistry.

Inorganic chemistry—contrary to the belief of some students after taking general chemistry—is more than sulfuric acid and sodium chloride. It is understanding molecular topology and its relation to the reactivities of non-metal and metal compounds and the mechanisms of their reactions. Our goal in this text is to provide a firm foundation in these principles and to lead you to new insight into the chemistry of the elements other than carbon. We have attempted to write a book that is, above all, correct and clear, but one that is also insightful and illustrative of the discoveries that lie just ahead. An important goal is to help you share the enthusiasm of the international community of scholars in our field. We hope that you come away from your course in inorganic chemistry with this feeling, confident that the principles discussed will be of value to you throughout your career in chemistry.

TO THE INSTRUCTOR:

"Introduction to Inorganic Chemistry" is intended for use by college junior and senior chemistry majors; we assume that the student possesses the background of a first year, college level course and some knowledge of organic chemistry.

The present book is clearly an outgrowth of our previous book, "Inorganic Chemistry" (W.B. Saunders Co., 1977). Our goal in both texts is to promote the unification of descriptive chemistry with structure, bonding, and reaction mechanism concepts. In both instances, we attempted to write books that are correct and clear, but which also illustrate the excitement of modern inorganic chemistry and our pleasure in being involved with this field and with the world-wide community of inorganic chemists.

How do the two texts differ? First of all, the 40% reduction in size comes at the expense of the higher level theoretical and descriptive material. Comments on special items of interest follow:

The atomic structure chapter has been written at a lower level. Our students report that this material clarifies many of their misconceptions about atomic orbitals and gives them new insights into their importance in chemistry.

In the second chapter, the symmetry properties of molecules are described, but group theory has been omitted; solid-state topics and contemporary applications appear in this chapter.

The third chapter (hybrid orbital concepts and spectroscopy applications) has been shortened and rewritten to some extent, as has the molecular orbital chapter. We have removed from the latter the discussions of polyhedral molecules, forecasting fewer applications of orbital concepts to descriptive chemistry in the remainder of the text.

Chapters 5 to 17 have been shortened by eliminating the more difficult descriptive and interpretive sections.

Instructors seeking to give coverage of, but not emphasis to, descriptive non-metal chemistry can utilize the first part of Chapter 5 and one of the three succeeding chapters; the selection of the latter should derive from one's own convictions regarding the importance of thermochemistry, kinetics, or rational synthesis.

Catalysis has become such an important topic that it has been made into a separate chapter (Chapter 18). This chapter could be used without first covering the previous chapters on organometallic chemistry if the students are first introduced to the 16-18 electron rule (Chapter 15) and then to some common classes of organometallic compounds (*e.g.*, metal carbonyls and metal-olefin complexes) as well as to some standard reaction types (oxidative addition and reductive elimination, carbonylation).

The basic organization of "Introduction to Inorganic Chemistry" is:

Part 1: The Tools of Chemical Interpretation

It is in this section that **atomic orbitals** and **electron configurations** of the elements are described. The student is led to discover the factors that determine the **structures** of simple **non-metal compounds** and to describe these structures in terms of their **symmetry properties**. The basic ideas of **solid-state** structures are outlined, and the student is exposed to covalent bonding models **(hybrid orbital** and **molecular orbital)** and examples of their application.

Part 2: Descriptive Non-Metal Chemistry with Interpretations

It is here that we illustrate the power of the concepts of **Lewis acid-base** interactions, **structure**, **bonding**, and **kinetics** to unify **non-metal chemistry**. One entire chapter is devoted to the techniques and systematics of the **synthesis** of non-metal compounds.

Part 3: Descriptive Transition Metal Chemistry with Interpretations

The final portion of the text is devoted to metal chemistry, again with stress on **bonding**, **structure**, and **reaction mechanisms**. Of particular interest today are the topics of **organometallic chemistry**, **catalysis**, and **bio-inorganic chemistry**. The student who is bound for either industry or graduate school should have exposure to at least the first two areas. Some aspects of catalysis are covered in a chapter devoted entirely to that subject.

Since "Inorganic Chemistry" was published in 1977, the adoption of the SI system of units has been rapid. Therefore, this text uses joules, meters, and so on.

And finally, we note that, for those who seek more detailed and extensive coverage, our previous book will continue to be available. The current "Introduction to Inorganic Chemistry" is not intended to supplant the former book.

ACKNOWLEDGMENTS

First, we wish to thank all of our fellow inorganic chemists who have passed on their experiences with our previous book. The compliments were appreciated; more importantly, the criticisms were constructive and invaluable in producing this new book.

We again thank the reviewers of the previous book (Mike Bellema, Bob Fay, Ron Gillespie, Bill Hatfield, Galen Stucky, and Jerry Zuckerman). They contributed to the success of the first book and, as "Introduction to Inorganic Chemistry" is an outgrowth of that first effort, these reviewers have contributed to the present book as well. The same is true of our students and colleagues (Bill Fateley, Bruce Knauer, and Tay Tahk especially) who supported these efforts in a variety of ways. We wish to thank Alberto Romão Dias, Carlos Romão, and the students of the Instituto Superior Tecnico in Lisbon, Portugal for their generous hospitality during a stay in which portions of the current manuscript were completed.

We also acknowledge a very pleasant, continuing association with the W. B. Saunders Company. These projects could not have been completed without the encouragement and assistance of John Vondeling, John's assistants, Kay Dowgun and Jeannie Shoch, and Jay Freedman, the best copy editor in the business.

Finally, our greatest debt of gratitude is to our families (Susan, Kristan, and Karen; Katie, David, and Peter) for being supportive in times of stress and for helping with the duller tasks of manuscript preparation.

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JOHN C. KOTZ

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PROLOGUE
THE COMING OF AGE: PERSPECTIVE

What is modern inorganic chemistry and what direction is it likely to take in the near future? What does one teach undergraduate and graduate students in general, and prospective inorganic chemists in particular, that they gain perspective on the past and are prepared for the future? It is these questions that inorganic chemists ask one another at American Chemical Society meetings, at Gordon Research Conferences, and at other "gatherings of the clan." Not surprisingly, there are nearly as many answers as there are inorganic chemists, and the answers change with time.

From an historical view inorganic chemistry is synonymous with "general" chemistry; in addition to his area of specialization the "inorganic" chemist was expected to be conversant, if not knowledgeable, with the chemistries of all the elements. At various times the inorganic chemist has been closely allied with analytical chemistry (both qualitative and quantitative chemical methods), with physical chemistry, and even with organic chemistry. These strong ties are still existent today, but the rapid development of our field since the late fifties has created great depth in research specialties so that the "generalist" posture has waned slightly. Concomitant with this evolution, the field gained formal recognition in this country with the establishment of the journal *Inorganic Chemistry* by the American Chemical Society in 1962; since then the "Division of Inorganic Chemistry of the American Chemical Society" has produced offspring in the form of the "Organometallic" and "Solid State" subdivisions.

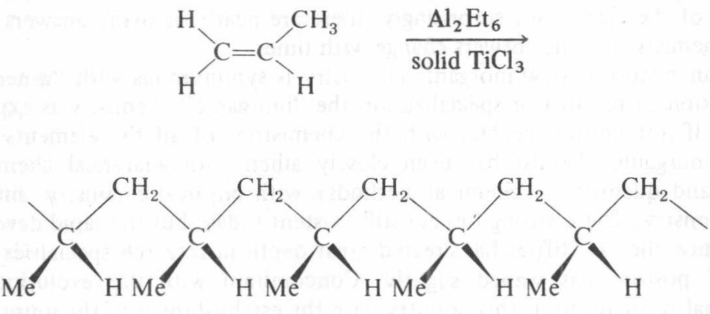
To illustrate what modern inorganic chemistry has become, we surveyed the papers published on topics in the field in *Accounts of Chemical Research* since the inception of the journal in 1968. Such a survey at least partially measures the current status of inorganic chemistry and the probable direction of future work because *Accounts* . . . "publishes concise, critical reviews of research areas currently under active investigation . . . written by scientists personally contributing to the area reviewed." Although our division of papers was perhaps arbitrary at times, the results summarized in Table 1 are quite enlightening. Metals make up about 80% of the Periodic Table, and it is interesting that the fraction of papers on metal chemistry is approximately the same, although all but seven of the papers are concerned with transition metal chemistry. Nonetheless, the results of this crude survey give a fairly clear indication of the current emphasis–the bulk of the papers is on organometallic chemistry, with a bias toward catalysis, while a large number are concerned with coordination chemistry and the biochemical role of metals.

The chemistry of organometallic compounds, especially of the transition metals, has become increasingly important in the past twenty years, as attested to by the fact that the Nobel Prizes in Chemistry in 1963 and 1973 were awarded for work falling in this general area.[1,2] Karl Ziegler of Germany and Giulio Natta of Italy shared the Prize in 1963 for their finding that the stereospecific polymerization of olefins was catalyzed by alkyl aluminum–transition metal halide mixtures.[3-5]

TABLE 1

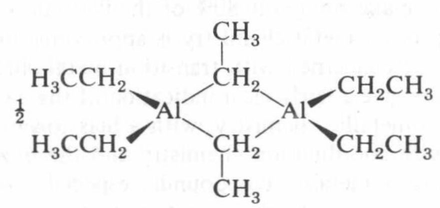
REVIEWS ON INORGANIC CHEMISTRY IN *ACCOUNTS OF CHEMICAL RESEARCH*, 1968–1978

General Area and Sub-area	Number of Reviews
Metal chemistry	Total = 104
Transition metals	Total = 97
Organometallic chemistry (incl. catalysis)	47
Coordination chemistry	13
Bioinorganic chemistry	19
Theoretical and physical papers	18
Non-transition metals: Organometallic chemistry	7
Non-metal chemistry	Total = 27
Boron chemistry (5 with significant metal chemistry)	10
Silicon chemistry	5
Theoretical papers	4
Other (chiefly halogen compounds)	8
TOTAL REVIEWS	131



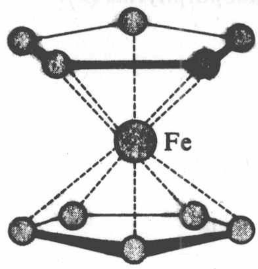
(polypropylene)

This example serves to illustrate much of the fascination of inorganic chemistry. For example, why is the alkylating agent, triethylaluminum (**1**), a dimeric species under normal conditions, whereas triethylborane, $B(CH_2CH_3)_3$, is monomeric? How is one AlR_3 unit bound to the other? In what way is an olefin bound to a metal, and why do metals form kinetically stable olefin complexes only when the metal is in a low oxidation state?

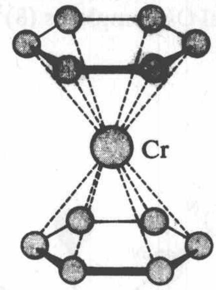


1

Professor Wilkinson at Imperial College, London, and Professor Fischer at Munich earned the Nobel Prize in 1973 for the impetus they provided to the study of metallocenes, or "metal sandwiches" as they are often called. Ferrocene (**2**) in particular has been widely studied, as it is readily synthesized or can be purchased inexpensively. The compound is electron-rich and has an extensive chemistry based on electrophilic substitution reactions.[8] As prototypes of many other similar complexes, 2 and 3 have been thoroughly studied to uncover the reasons for the tremendous stability achieved when a low-valence metal interacts with the π electrons of an unsaturated or aromatic molecule.

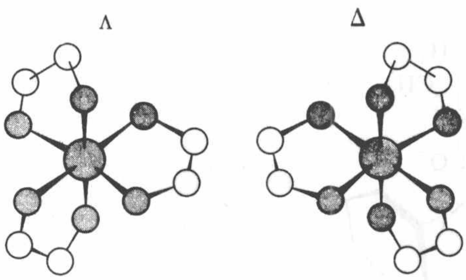


2 ferrocene[6]
[*bis(η^5-cyclopentadienyl)iron*
orange, sublimable solid (mp, 173°)]

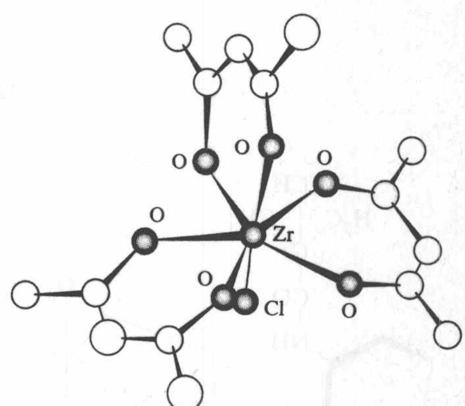


3 dibenzenechromium[7]
[*bis(η^6-benzene)chromium*
black-brown, sublimable solid (mp, 284°)]

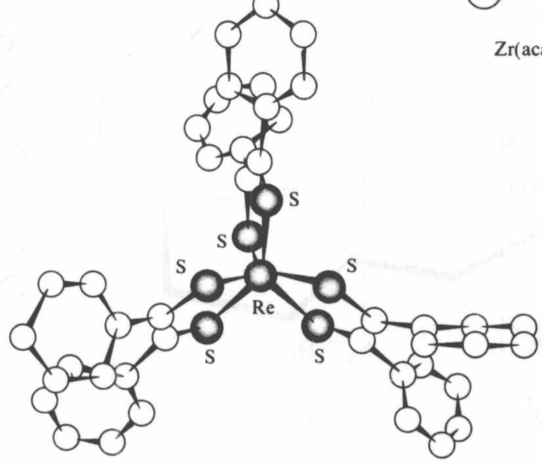
Perhaps the most active area of inorganic chemistry in the 1950's and 1960's was coordination chemistry: the study of complexes of higher valence metals. The most important development during that period was in our understanding of the electronic spectra of these complexes, and many excellent books have been published on "ligand field theory" as a result.[9-11] Another area of special activity in coordination chemistry has been the study of the stereochemistry of chiral complexes **(4)**,[12] or those with high coordination numbers **(5)**[13] or with unusual coordination geometries **(6)**.[14]



4
$M\{C_2H_4(NH_2)_2\}_3^{n+}$



5
$Zr(acac)_3Cl$[15]



6
$Re[S_2C_2(C_6H_5)_2]_3$[16]