

Stereochemistry of Coordination Compounds. From Alfred Werner to the 21st Century

Alex von Zelewsky*

Abstract: As a contribution to the scientific symposium, November 22nd, 2013, commemorating the Nobel Prize awarded to Alfred Werner in 1913, a presentation of the development of stereochemistry of coordination compounds during the past 120 years was given. Stereochemistry was fundamental to Werner's theory of coordination compounds. After Werner's death in 1919, stereochemistry in this field did not progress much further for almost 20 years, but then developed continuously. It was realized that stereochemical features of elements showing coordination numbers larger than four are responsible for an almost unlimited number of stereochemical possibilities, thus opening a molecular world of new structures. In the beginning of the 21st century, interest in the field rose again considerably, mainly due to the potential of stereoselective catalysis, and the self-assembly of supramolecular structures. An end of these developments is not in sight. Here an abbreviated version of the lecture is given. A PowerPoint® file, or a video of the presentation, can be downloaded.^[1-5]

Keywords: Chirality · Coordination compounds · Stereochemistry · Stereoselectivity · Werner, Alfred

Introduction

20 years after the publication of his fundamental formulation of the coordination concept, Alfred Werner was awarded the Nobel Prize in Chemistry in 1913. Werner's views of the molecular structure of compounds of metallic elements proved to be correct for a vast number of compounds and it is still the basis for contemporary research and development in many branches of chemistry. Werner based his theory to a large part on considerations about the numbers and types of isomers of compounds of transition metals. It is basically a theory exploring the various possibilities to arrange atoms in three-dimensional space and this is nothing else but the subject of stereochemistry.

The coordination theory is one of the unbreakable hard rocks of science that will

probably never be succeeded by a better concept. To commemorate the centenary of the Nobel Prize of Alfred Werner, the Department of Chemistry at the University of Zürich organized a symposium on several aspects of coordination chemistry. I had the privilege to review the development of stereochemistry of coordination compounds from Alfred Werner to the present. Here, only a short excerpt of the presentation in the symposium is given. A first specialized textbook on 'Stereochemistry of Coordination Compounds'^[1] by the present author appeared one hundred years after the basic publication by Alfred Werner.^[2] It is fully referenced and covers also the historical development in some detail. A second, more specialized book by Amouri and Grussile, was published recently.^[3] It covers the topical subject of chirality in transition metal chemistry in great detail. Chirality was already of central interest to Alfred Werner. His experimental proof in metal compounds was the main reason for the Nobel committee to award the Prize in 1913. In addition to these two books, a number of reviews have been published in recent years,^[4-10] proving the revived interest in the subject.

The Development of Stereochemistry of Coordination Compounds since Alfred Werner

After the proposition of the tetrahedral carbon atom by van't Hoff and Le Bel in 1874, stereochemistry of organic com-

pounds developed rapidly during the last quarter of the 19th century, as recognized by the second Nobel Prize in Chemistry awarded to Emil Fischer in 1902. In the beginning of this period, inorganic chemistry was still dominated by the view of the Danish chemist Sophus Mads Jørgensen, who was an excellent experimental chemist. Jørgensen adhered strictly to the chain theory of Blomstrand, one of the leading chemists of the 19th century. The seminal publication of a 27-year-old chemist, Alfred Werner, appeared in 1893.^[11] Werner introduced the octahedron as a coordination center. Most notably, in the same publication, he attributed to Pt(II) compounds the coordination number four in a square planar arrangement. The tetrahedral arrangement for coordination number four, however, was so deeply burned into the mind of chemists during the last quarter of the 19th century that it needed a highly independent mind to dare to propose the planar structure for metal compounds. In 1899 the first mention of the possibility of 'asymmetry' in an octahedral complex followed^[12] and in 1911 the proof of the existence of two separable enantiomers in a cobalt compound was presented.^[13] It was shown in 1914, finally, that optical activity is not necessarily associated with the presence of carbon.^[14] A carbon-free complex, Co(hexol), comprising a central cobalt atom, surrounded by four bidentate ligands that are themselves cobalt-amine complexes, was separated into its enantiomers. After 1914, the activity of the Zürich group ceased rapidly, due to Werner's severe ill-

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Elements Of Stereochemistry With A Section On Coordination Compounds

Ana de Bettencourt-Dias



Elements Of Stereochemistry With A Section On Coordination Compounds:

Stereochemistry of Coordination Compounds Alexander von Zelewsky, 1996-06-03 This well illustrated and well referenced book provides a systematic introduction to the modern aspects of the topographical stereochemistry of coordination compounds which are made up of metal ions surrounded by other non metal atoms ions and molecules **The Chemistry of Coordination Complexes and Transition Metals** P.L. Soni, Vandna Soni, 2021-05-14 This book covers all important nomenclature theories of bonding and stereochemistry of coordination complexes The authors have made an effort to inscribe the ideas knowledge clearly and in an interesting way to benefit the readers The complexities of Molecular Orbital theory have been explained in a very simple and easy manner It also deals with transition and inner transition metals Conceptually all transition and inner transition elements form complexes which have definite geometry and show interesting properties General and specific methods of preparation physical and chemical properties of each element has been discussed at length Group wise study of elements in d block series have been explained Important compounds complexes and organometallic compounds of metals in different oxidation states have been given explicitly Note T F does not sell or distribute the Hardback in India Pakistan Nepal Bhutan Bangladesh and Sri Lanka **Electronic Structure and Properties of Transition Metal Compounds** Isaac B. Bersuker, 2010-12-01 With more than 40% new and revised materials this second edition offers researchers and students in the field a comprehensive understanding of fundamental molecular properties amidst cutting edge applications Including 70 Example Boxes and summary notes questions exercises problem sets and illustrations in each chapter this publication is also suitable for use as a textbook for advanced undergraduate and graduate students Novel material is introduced in description of multi orbital chemical bonding spectroscopic and magnetic properties methods of electronic structure calculation and quantum classical modeling for organometallic and metallobiochemical systems This is an excellent reference for chemists researchers and teachers and advanced undergraduate and graduate students in inorganic coordination and organometallic chemistry World Directory of Crystallographers Allan L. Bednowitz, Armin P. Segmüller, 2013-04-17 A brief historical account of the background leading to the publication of the first four editions of the World Directory of Crystallographers was presented by G Boom in his preface to the Fourth Edition published late in 1971 That edition was produced by traditional typesetting methods from compilations of biographical data prepared by national Sub Editors The major effort required to produce a directory by manual methods provided the impetus to use computer techniques for the Fifth Edition The account of the production of the first computer assisted Directory was described by S C Abrahams in the preface of the Fifth Edition Computer composition which required a machine readable data base offered several major advantages The choice of typeface and range of characters was flexible Corrections and additions to the data base were rapid and once established it was hoped updating for future editions would be simple and inexpensive The data base was put to other Union uses such as preparation of mailing labels and formulation

of lists of crystallographers with specified common fields of interest The Fifth Edition of the World Directory of Crystallographers was published in June of 1977 the Sixth in May of 1981 The Subject Indexes for the Fifth and Sixth Editions were printed in 1978 and 1981 respectively both having a limited distribution

Progress in Inorganic Chemistry, Volume 16 Stephen J. Lippard, 2009-09-17 This comprehensive series of volumes on inorganic chemistry provides inorganic chemists with a forum for critical authoritative evaluations of advances in every area of the discipline Every volume reports recent progress with a significant up to date selection of papers by internationally recognized researchers complemented by detailed discussions and complete documentation Each volume features a complete subject index and the series includes a cumulative index as well

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Pyridine Metal Complexes, Part 6A Desmond J. Brown, 2009-09-15 The Chemistry of Heterocyclic Compounds since its inception has been recognized as a cornerstone of heterocyclic chemistry Each volume attempts to discuss all aspects properties synthesis reactions physiological and industrial significance of a specific ring system To keep the series up to date supplementary volumes covering the recent literature on each individual ring system have been published Many ring systems such as pyridines and oxazoles are treated in distinct books each consisting of separate volumes or parts dealing with different individual topics With all authors are recognized authorities the Chemistry of Heterocyclic Chemistry is considered worldwide as the indispensable resource for organic bioorganic and medicinal chemists

Biological Chemistry K. E. Suckling, C. J. Suckling, 1980-10-23 *Stereochemical and Stereophysical Behaviour of Macrocycles* Bozzano G Luisa, 2012-12-02 Stereochemical and Stereophysical Behavior of Macrocycles deals with the stereochemical and stereophysical properties of macrocyclic ligands and their coordination compounds More specifically the stereochemistry of metallic macrocyclics is discussed along with the relationship between the thermodynamics and stereochemistry of macrocyclics and cryptates The stereochemical aspects of the macrocycles of second and third row transition elements are

also examined Comprised of three chapters this volume begins with an introduction to the stereochemistry of metallic macrocyclics as well as their structure together with the conformation of their chemical rings and the steric effects of their coordination geometry The next chapter considers the relationship between the thermodynamics and stereochemistry of macrocyclics and cryptates with particular reference to the macrocyclic and cryptate effect Cation ligand interactions and solvent effects upon complex formation are described along with macrocyclic and macrobicyclic ligands having different donor atoms The final chapter is devoted to the stereochemical aspects of the macrocycles of transition metal ions with additional comments on the stereochemistry of copper and nickel in unusual oxidation states This book will be of interest to inorganic chemists Shriver and Atkins' Inorganic Chemistry Peter Atkins, 2010 Inorganic Chemistry fifth edition represents an integral part of a student's chemistry education Basic chemical principles are set out clearly in Foundations and are fully developed throughout the text culminating in the cutting edge research topics of the Frontiers which illustrate the dynamic nature of inorganic chemistry **Chemistry Of P-Block Elements** M. Satake & S.A. Iqbal, 2003 Many developments have occurred in the chemistry of elements during the recent past New theories of bonding and structure have contributed to the growth of the subject leading to a more clear understanding of the structural aspects in particular The present volume deals with the chemistry of p Block elements A general treatment of the properties of the elements in relation to their electronic configuration and other periodic trends is a major feature of the book The text has been well illustrated The text is intended for undergraduate students majoring in chemistry It will also serve as a handy reference

Environmental Health Perspectives, 1993 **Synthetic Coordination and Organometallic Chemistry** Alexander D. Garnovskii, Boris I. Kharissov, 2003-04-25 This reference describes standard and nonstandard coordination modes of ligands in complexes the intricacies of polyhedron programmed and regioselective synthesis and the controlled creation of coordination compounds such as molecular and hnp complexes chelates and homo and hetero nuclear compounds It offers a clear and concise review of modern synthetic techniques of metal complexes as well as lesser known gas and solid phase synthesis electrosynthesis and microwave and ultrasonic treatment of the reaction system The authors pay special attention to o hydroxyazomethines and their S Se containing analogues b diketones and quinines among others and examine the immediate interaction of ligands and metal salts or carbonyls Introduction to Coordination Chemistry Paul V. Bernhardt, Geoffrey A. Lawrance, 2024-12-20 INTRODUCTION TO COORDINATION CHEMISTRY An accessible introduction to one of the primary fields of study in Inorganic Chemistry revised to incorporate contemporary topics and applications Written in a highly readable descriptive and accessible style Introduction to Coordination Chemistry examines and explains the interaction between metals and molecules that bind as ligands and the consequences of this assembly process The book describes the chemical and physical properties and behavior of these complex assemblies and their applications The contents of this book tell a story taking the reader from fundamentals including metal ions ligands metal ligand bonding and structure

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Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials Ana de Bettencourt-Dias,2014-11-17 This comprehensive book presents the theoretical principles current applications and latest research developments in the field of luminescent lanthanide complexes a rapidly developing area of research which is attracting increasing interest amongst the scientific community Luminescence of Lanthanide Ions in Coordination Compounds and Nanomaterials begins with an introduction to the basic theoretical and practical aspects of lanthanide ion luminescence and the spectroscopic techniques used to evaluate the efficiency of luminescence Subsequent chapters introduce a variety of different applications including Circularly polarized luminescence Luminescence bioimaging with lanthanide complexes Two photon absorption of lanthanide complexes

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