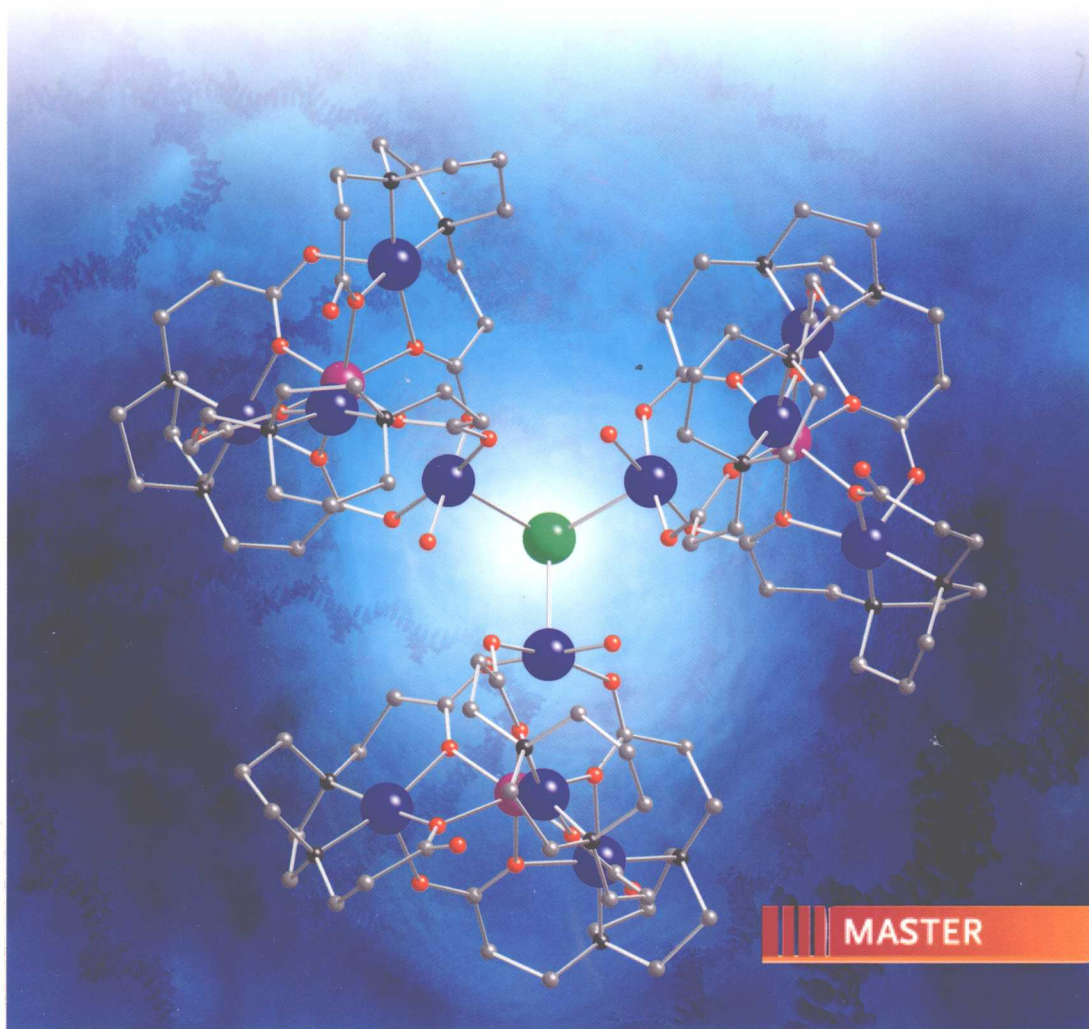


Joan Ribas Gispert

 WILEY-VCH

Coordination Chemistry



Joan Ribas Gispe

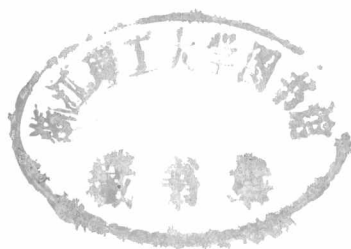


30806105

Coordination Chemistry



WILEY-
VCH



WILEY-VCH Verlag GmbH & Co. KGaA

3012000

The Author

Prof. Joan Ribas Gispert
Department of Inorganic Chemistry
University of Barcelona
Av. Diagonal 647
08028 Barcelona
Spain

■ All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.:

applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

Die Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition SNP Best-set Typesetter Ltd.,
Hong Kong

Printing Betz-Druck GmbH, Darmstadt

Bookbinding Litges & Dopf GmbH,
Heppenheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-31802-5

Preface

During my academic life at the Department of Inorganic Chemistry of the University of Barcelona, I have taught Coordination Chemistry for several years. In my University, this course is optional, and offered to those students that, having passed the general (and essential) topics of Chemistry (Inorganic, Organic, Analytical and Physical Chemistry), decide to deepen in this field of Inorganic Chemistry. Since the beginning of my career as a Professor I missed a textbook for students on this topic that would help them both, on the theoretical aspects as well as on the more descriptive ones. A revision of the relatively modern text books reveals the presence of only one book written in English that may be useful for students in this respect. Its title is “*Physical Inorganic Chemistry. A Coordination Chemistry Approach*”, by S.F.A. Kettle (1996). This is indeed a very good book, however, – as may be inferred from the title – it fails to treat many important aspects of Coordination Chemistry.

The lack of a formal, more comprehensive, textbook, gave me the idea to do the effort to write a systematic book fulfilling the purposes stated above, in Spanish language. This book, with the title “*Química de Coordinación*” was published in 2000 (Ed. Omega-Universitat de Barcelona). The present new book is not a translation from the Spanish language to English of the above mentioned work, but rather a complete and updated revision. I have deliberately omitted some chapters (such as that devoted to Coordination Chemistry of lanthanides) and reduced some of the more complicated aspects related to Quantum Chemistry. For example, in the Spanish book, I wrote a separate Chapter on Spin-Orbit coupling, which I have now included in the Chapter on Crystal (Ligand) Field. Also, a very different perspective is now given in the Chapter devoted to Supramolecular Chemistry. I have now adopted a more restricted vision owing to the tendency of many authors (including myself) to use the term Supramolecular in our research papers in such a manner that the first meaning (from J.M. Lehn) has been completely changed and lost. Some other issues have been added in this English version; chapters devoted to polynuclear complexes, clusters with metal-metal bond, biocoordination chemistry or metal-organic frameworks (MOFs) have been included.

The present book – like the parent Spanish book – is addressed to students who already have a background in Inorganic Chemistry, Organic Chemistry, and Fundamentals of Spectroscopy, Quantum Chemistry and Group Theory. This book

has been, thus, thought for graduate students or for advanced undergraduate students.

An important aspect to be considered when trying to write a modern book on Coordination Chemistry is the treatment of this field made by almost all textbooks of general Inorganic Chemistry. Important concepts such as bonding, thermodynamic stability, kinetics and mechanisms, are generally well treated in graduate Inorganic textbooks. Thus, this new book is thought for readers that already have a minimum background on these subjects. However, there are some issues of modern Coordination Chemistry that are scarcely treated in textbooks of Inorganic Chemistry, such as Photochemistry, Magnetic properties of complexes (polynuclear systems are generally ignored), applications of Electronic Paramagnetic Resonance, Mixed-Valence compounds, Supramolecular Coordination Chemistry, the so-called Metal-Organic Frameworks (MOFs, of increasing importance), etc. All these issues are treated in this book in separated Chapters.

With this book I have, thus, tried to fill in many gaps that are currently empty in related books for graduate and undergraduate students. This needed to be accomplished keeping in mind unavoidable space restrictions. Neither the editor nor the author can propose to the students an excessive number of pages. For this reason, the more “classical” aspects of Coordination Chemistry have been relatively shortened, trying, however, to emphasize the most important ones. For example, I decided to join in a Chapter the part devoted to the thermodynamics and non-redox mechanisms. These subjects are well known by many students. On the contrary, I have emphasized the redox mechanisms in a separated Chapter, because they are a preliminary requirement for understanding the Mixed-Valence compounds.

In the spirit expressed above, I propose at the end of many chapters selected references to help readers interested in a particular topic, to find additional information. My honest advice is that the reader should explore these references to complete the discussion given in the text, mainly for some descriptive and graphical aspects, for which the original paper will always be the best source. I am thinking, for example, about the Chapters devoted to Polynuclear complexes, Clusters, Photochemistry, Supramolecular Coordination Chemistry or Metal-Organic Frameworks. In these Chapters the help of the referenced literature is of paramount importance. With this idea in mind I have tried to choose, when possible, the most recent literature, because the reader usually can find there other references to similar papers published previously. In my opinion this task is very pedagogical for the student. Furthermore, when possible, I have indicated references to Reviews, very useful for the reader to acquire a larger vision of a particular issue.

Finally, this book is not intended to encompass all aspects that are related to Coordination Chemistry, in its more general and wide sense. In many Universities around the world, some parts that can be “formally” considered as derived from Coordination Chemistry are separated matters in the curriculum proposed to students, such as Organometallic Chemistry and Bioinorganic Chemistry. I have embraced in this book the same general tendency.

Acknowledgments

A number of colleagues have read either chapters or parts of different chapters of the manuscript or have given me their opinion about the meaning of some problematic terms, ideas, papers published by them, etc. I can assure that their suggestions and criticisms have been invaluable. Of course all the errors and obscure passages that remain after all revisions have to be attributed to the author.

These colleagues and friends are (in alphabetical order):

Dr. Guillem Aromí, Departament de Química Inorgànica, Universitat de Barcelona (Spain)

Dr. Stuart R. Batten, School of Chemistry, Monash University (Australia)

Dr. Roman Boca, Department of Inorganic Chemistry, Slovak Technical University, Bratislava, (Slovakia)

Dr. Jaume Casabó, Departament de Química, Universitat Autònoma de Barcelona (Spain)

Mr. Jordi Casabó, Departament of Mathematics, Universitat Politècnica de Catalunya, Barcelona (Spain)

Dr. Montserrat Corbella, Departament de Química Inorgànica, Universitat de Barcelona (Spain)

Dr. Dante Gatteschi, Laboratory of Molecular Magnetism, Polo Scientifico Universitario; Dipartimento di Chimica, Università di Firenze, Firenze (Italy)

Dr. Xavier Giménez, Departament de Química-Física, Universitat de Barcelona (Spain)

Dr. Thorfinnur Gunnlaugsson, School of Chemistry, University of Dublin, Trinity College, Dublin (Ireland)

Dr. Andreas Hauser, Department de Chimie Physique, Université de Genève, Genève (Switzerland)

Dr. Richard M. Hartshorn, University of Canterbury, Christchurch (New Zealand)

Dr. Carlos Lodeiro, CQFB-REQUIMTE, Departamento de Quimica, Universidade Nova de Lisboa (Portugal)

Dr. Miguel Julve, Departament de Química Inorgànica/Instituto de Ciencia Molecular (ICMol). Universitat de Valencia, Paterna (Valencia, Spain)

Dr. Robert J. Lancashire, Department of Chemistry, University of the West Indies, Kingston (Jamaica)

Dr. Francisco Lloret, Departament de Química Inorgànica/Instituto de Ciencia Molecular (ICMol). Universitat de Valencia, Paterna (Valencia, Spain)

Dr. Manel Martínez, Departament de Química Inorgànica, Universitat de Barcelona (Spain)

Dr. Jane Nelson, Department of Chemistry, Loughborough University, Loughborough. (United Kingdom)

Dr. Juan Carlos Paniagua, Departament de Química-Física, Universitat de Barcelona (Spain)

Dr. Mark Pedersen, Center for Computational Materials Science, Naval Research Laboratory, Washington, D.C. (USA)

Dr. Spiros Perlepes, Department of Chemistry, University of Patras, Patras (Greece)

Dr. José Antonio Real, Departament de Química Inorgànica/Instituto de Ciencia Molecular (ICMol). Universitat de Valencia, Paterna (Valencia, Spain)

Dr. Jan Reedijk, Coordination and Bioinorganic Chemistry, Leiden Institute of Chemistry, Leiden (The Netherlands)

Dr. Jordi Ribas-Ariño, Departament de Química-Física, Universitat de Barcelona (Spain)

Dr. Néstor E. Katz, Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán (Argentina)

Dr. Pascual Román, Departamento. Química Inorgánica, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Bilbao (Spain)

Dr. Jean-Pierre Sauvage, Laboratoire de Chimie Organo-Minérale, Université Louis Pasteur-CNRS, Institut Le Bel, Strasbourg (France)

Dr. Vassilis Tangoulis, Department of Chemistry, University of Thessaloniki (Greece)

Dr. Boris Tsukerblat, Department of Chemistry, Faculty of Natural Sciences, Ben-Gurion University of the Negev, Beer-Sheva (Israel)

Dr. Margherita Venturi, Dipartimento di Chimica "G. Ciamician", Università di Bologna (Italy)

Dr. Michel Verdaguer, Professeur Emèrite, Université Pierre et Marie Curie, Paris (France)

I also acknowledge Drs. Guillem Aromí, E.Carolina Sañudo and Nuria Aliaga (Department of Inorganic Chemistry, University of Barcelona) for their continuous help in many questions concerning the English language. Their help has been unforgettable.

Most of the 3-D-structural diagrams in the book have been drawn using Crystal Maker 1.2.1 for Windows XP, with coordinates accessed from the Cambridge Crystallographic Base. However, Prof. S.R. Batten has gently supplied some very complicated structures on interpenetrated networks. An special mention to him, as well as another special mention and acknowledgment to Ms. Adelaida Pàmies, a very good friend, who designed and drew the most beautiful Figures (Borromean rings, Catenanes, etc) impossible to do – at least for me – with ChemDraw or Crystal Maker.

Special Acknowledgments

I would like to express, finally, a very particular acknowledgment to some special colleagues and friends. First I would like to invoke my first-cousin, Prof. Jaume Casabó, now emeritus Professor at the Universitat Autònoma of Barcelona. He gave me (at the early 1970s) a modern vision on Coordination Chemistry in a moment when in Spain, for political reasons, Science (in capital letters) was in urgent need of a renaissance. Jaume, with his pedagogical attitude, opened a new and different world of Coordination Chemistry to me.

During my life as a researcher I had the opportunity to work with many expert scientists, in different fields, but always related to Coordination Chemistry: Dr. René Poilblanc and Dr. Patrick Cassoux, in the Laboratoire de Chimie de Coordination, CNRS, Toulouse (France) (1980); Dr. Olivier Kahn (*in memoriam*) in the Université of Paris-Sud, Orsay (France) (1986). I would like to make a special mention of Olivier (with his colleagues in Orsay in the early 1986, Michel Verdaguer, Jean-Jacques Girerd and Yves Journaux) who helped me to enter in the not always easy field of molecular magnetism. I remember Olivier as a great scientist, friend and pedagogue, with enthusiasm and passion for spreading the science.

In Orsay, I met Dante Gatteschi, deeply Italian, but also universal. I have always liked very much to speak to Dante in Italian language. How many times we have spoken not only about magnetism and e.p.r., but also about football!

Later, I met Dr. Marc Drillon (Strasbourg, France), and Dr. George Christou (University of Indiana, Bloomington (USA) (1992). With them I learned many important issues on molecular magnetism.

I am indebted to my closer collaborators in the Department and, mainly, to my colleague and friend, Dr. Montserrat Corbella. She was my graduate and undergraduate student some years ago. I taught her the fundamentals of Inorganic Chemistry. Then, she became specialist in Bioinorganic Chemistry, mainly in Models on Biocoordination and she helped me with extraordinary kindness to write the Chapter devoted to Biocoordination Chemistry. Her clear ideas and enthusiasm were invaluable to me.

I am indebted to my wife, Maria Rosa, and my son, Jordi, who demonstrated great patience when finding me often – may be too often – busy with the writing of this manuscript.

Last but not least, I am also indebted to great musicians who “accompanied” me in the writing of the manuscript. The “Missa Solemnis”, the piano and violin concerts of Beethoven, the operas “Norma” and “I Puritani” of V. Bellini, “Tannhauser” and the final part of “Tristan und Isolde” etc, have filled my mind during the hard task of giving form, writing, revising, changing, abbreviating, drawing, etc, the manuscript. It is a good experience to be alone, trying to understand the “mystery” of the spin-orbit coupling, with the music of Beethoven or Mozart filling the ambient. You can try ... good luck!

Barcelona, January 2008

Joan Ribas

Introduction: Definitions, History, Nomenclature

Definitions: Complexes, Coordination Compounds

The compounds studied in this context will be called “coordination compounds”, or “complexes”. The term “complex” dates from the end of the 19th century. By that time, a distinction was made between first order compounds, formed by atoms, and higher order compounds, formed by a combination of molecules (these are sometimes also called “molecular compounds”).

A special class of higher order complexes was the historically important cobalt and platinum ammine complexes. These complexes formed the archetypes of Werner’s coordination theory. Werner called them coordination compounds, consisting of a central metal atom (or central ion) and a certain number of coordinated molecules or ions. In the context of the compounds he studied, Werner already used the terms complex and coordination compound (exactly: *coordination unit*), mostly as synonyms, although strictly speaking, the term “complex” was the more general one. In those coordination compounds which were studied at the turn of the century, ‘*ligands*’ were stable, even in their dissociated form [1]. Therefore Werner’s complexes were higher order compounds also in the original meaning of the term. Today, other ligand systems are gaining importance for which no dissociation equilibria in solution should be formulated as these ligands are unstable when dissociated from the metal. There is, however, no reason not to call these compounds “complexes” or “coordination compounds”!

Summary In modern coordination chemistry, the terms “complex” and “coordination compound (unit)” are largely used as synonyms and are applied to almost any molecular compound of transition metals (*although not necessarily*), formed by a central metal atom and its coordinated set of ligands. It may be a cation, an anion or non-ionic.

IUPAC Recommendations (2005): *Each coordination compound either is, or contains, a coordination entity (or complex) that consists of a central atom to which other groups are bonded. A coordination compound is any compound that contains a coordination entity. A coordination entity is an ion or neutral molecule that is composed of a central atom, usually that of a metal, to which is attached a surrounding array of other atoms or groups of atoms, each of which is called a ligand.* [2].

The Historical Development of Coordination Chemistry

Any attempt to summarize the history of coordination chemistry is complicated by the fact that there is no clearly defined beginning. It was not until the middle of the 19th century that coordination compounds began to be the object of chemical investigation. Coordination chemistry became an independent discipline by the end of the 19th century through Alfred Werner's work. Therefore we will start by trying to trace the history of coordination chemistry up to Alfred Werner by highlighting several individual compounds which were fundamental for the early scientific development.

The Development of Coordination Chemistry Before Alfred Werner's Theory

Perhaps the earliest known of all coordination compounds is the bright red alizarin dye, a calcium aluminum chelate compound of hydroxyanthraquinone. It was first used in India and known to the ancient Persians and Egyptians long before it was used by the Greeks and Romans. Alizarin was mentioned by Herodoto in ca. 450 B.C.

The first scientifically documented proof of the formation of a coordination compound (1597) is the description of the tetramminecopper(II) complex, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, by the physician and alchemist Andreas Libavius. He observed a blue color caused by the effect of a solution of $\text{Ca}(\text{OH})_2$ and NH_4Cl on bronze (copper–tin alloy).

In the case of “Prussian blue”, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, for the first time a complex compound was isolated and used as a color pigment (Diesbach and Dippel, 1704). Its preparation was kept secret for 20 years, until in 1724 it was published by John Woodward (based on Diesbach's instructions). The preparation required a mixture of potassium hydrogen tartrate, potassium nitrate and charcoal, as well as dried and carefully pulverized bovine blood, calcinated iron(II)sulfate, potassium alum and hydrochloric acid, and the preparation was extremely laborious. A closer revision of Diesbach's prescription soon showed that the use of potassium alum was unnecessary, but not, however, the use of an iron salt, which was recognized rather early as a basic ingredient of the color-giving component.

At the time of the French Revolution a certain “Citoyen Tassaert” (1798), reported the formation of a brown solution after reaction of cobalt nitrate or chloride with an excess of aqueous ammonia, although he was not able to explain this observation. As is known today, this was the hexaammine cobalt(III) complex $[\text{Co}(\text{NH}_3)_6]^{3+}$, which is why Tassaert is considered by some historians to be the discoverer of this substance class.

At the beginning of the 19th century, a whole series of complexes was synthesized, and for the first time a purposeful, preparative methodology was established. Louis-Nicholas Vauquelin (1763–1829) discovered $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$ (Vauquelin's salt). The corresponding platinum compound, $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ was discovered by Heinrich Gustav Magnus (1802–1870) and is known as Magnus' Green

salt. William Christoffer Zeise discovered the first organometallic compound, $K[Pt(\eta^2-C_2H_4)Cl_3] \cdot H_2O$, (Zeise's salt) in 1825. According to some authorities, the first metal ammine to be isolated in the solid state was the reddish yellow $[Co(NH_3)_6]_2(C_2O_4)_3$, described in 1822 by Leopold Gmelin. Gmelin also discovered several cyano derivatives, such as $K_3[Fe(CN)_6]$, $M_3[Co(CN)_6]$ and $M_2[Pt(CN)_4]$.

Two extremely important platinum(II) compounds were discovered in 1844: *cis*- and *trans*- $[PtCl_2(NH_3)_2]$. Werner, in his first paper on the coordination theory, discussed these compounds and considered them to be geometric isomers with a square-planar coordination. The explanation was finally given by I.I. Chernyaev in his famous *trans*-effect (1926).

In 1852 Oliver W. Gibbss began to collaborate with Frederick A. Genth on an investigation which has since become famous in the annals of coordination chemistry. In 1856 they reported the preparation, properties, analytical data and reactions of 35 salts of some cobalt-ammine cations. Since many of the compounds were colored, the next step was to name these compounds on the basis of color: $CoCl_3 \cdot 6NH_3$ (yellow, *Luteo* complex); $CoCl_3 \cdot 5NH_3$ (purple, *Purpureo* complex); $CoCl_3 \cdot 4NH_3$ (green, *Praseo* complex), $CoCl_3 \cdot 4NH_3$ (violet, *Violeo* complex), $CoCl_3 \cdot 5NH_3 \cdot H_2O$ (red, *Roseo* complex). Addition of $AgNO_3$ to a freshly prepared solution of these salts, resulted in different amounts of precipitated $AgCl$ (3 for *Luteo*, 2 for *Purpureo*, and 1 for *Praseo* and *Violeo*). Another kind of experiment provided useful information about the number of ions present in a solution of these different complexes. One early observation was that two or more complexes having the same chemical composition but different chemical and physical properties sometimes existed. These compounds were called *isomers*.

Early Theories of Coordination Compounds [3]

Several hypotheses and theories were proposed to account for all these experimental facts. The development of a structural theory for organic compounds predated that for coordination compounds. At the time people began to consider the structure of complexes, the concept of the tetravalency of carbon and the formation of carbon-carbon bond chains in organic compounds was already well recognized. This concept had a marked influence on the chemists of that time. No doubt it influenced Blomstrand and his student Jorgensen. Therefore a chain structure was used to account for the additional six ammonia molecules in $CoCl_3 \cdot 6NH_3$.

Amongst chemists preparing complexes in the 19th century, Sophus Mads Jorgensen was probably the most productive. He systematically synthesized a large number of complexes, introduced, with others, the chelate ligand ethylenediamine into coordination chemistry and created the basis for Alfred Werner's theory of coordination chemistry. For a long time, both scientists were opponents on conceptual questions and originated a scientific dispute which turned out to be extremely fertile.

Werner

Werner was the first inorganic chemist to be awarded the Nobel Prize in Chemistry (1913), at the age of 26. His greatest contribution to coordination chemistry came as an inspiration in 1893 [4]. Three of his most important postulates are:

- The number of groups attached to an atom (something that he referred to as its *secondary valency*) need not equal its oxidation number (*primary valency*). The chemistry of the cobalt(III)-ammonia compounds could be rationalized if in them cobalt had a primary valency of three, as in CoCl_3 , but a secondary valency of six, as in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$. The term secondary valency has now been replaced by *coordination number* and primary valency by *oxidation state* but Werner's ideas otherwise stand largely unchanged.
- Every element tends to satisfy both its primary and secondary valencies. Werner postulated that in the series of cobalt-ammonia-chloride compounds, the cobalt exhibits a constant coordination number of 6 and, as ammonia molecules are removed, they are replaced by chloride ions which tend to act as covalently bound to the cobalt rather than as free chloride ion. For Werner, to describe the complex chemistry of cobalt, one must therefore consider not only the oxidation state but also its coordination number. Werner thus formulated these salts as $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$, and $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$.

Realizing that these formulations implied a precise statement of the number of ions formed in solution, Werner chose, as one of his experimental studies, measurements of the conductivities of a large number of coordination compounds.

- The secondary valence is directed towards a fixed position in space and therefore can be treated by applications of structural principles. By means of the number and properties of the isomers obtained, Werner was able to assign the correct geometric structures to many coordination compounds long before any direct experimental method was available for structural determination. Werner's method was that used previously by organic chemists to elucidate the structure of organic compounds. Werner postulated that the six ligands in a complex such as $[\text{Co}(\text{NH}_3)_6]^{3+}$ were situated in some symmetrical fashion with each NH_3 group equidistant from the central cobalt atom. Three such arrangements are possible: a planar hexagon, the trigonal prism and the octahedron. In every case Werner investigated, the number of isomers found was equal to that expected for an octahedral complex. In spite all possible difficulties in synthesizing some of the isomers, Werner was correct in his conclusion concerning the octahedral geometry of coordination number 6 for cobalt(III). His results furnish negative evidence, not positive proof. However, he was able to prove definitely that the planar and the trigonal prism structures cannot be correct. The proof involved demonstrating that complexes of the type $[\text{M}(\text{AA})_3]$ are optically active. He was also correct in his assignment of square-planar geometry for the four-coordinate complexes of palladium and platinum, from the fact that two isomers had been isolated for compounds of formula $[\text{MA}_2\text{B}_2]$.

It is worth noting that the first crystallographic confirmation of Werner's assignment of octahedral geometry to Pt(IV) complexes, $(\text{NH}_4)_2[\text{Pt}^{\text{IV}}\text{Cl}_6]$, was published in 1921, some 20 years after his theories were completed. The square-planar complexes $(\text{NH}_4)_2[\text{Pd}^{\text{II}}\text{Cl}_4]$, $\text{K}_2[\text{Pd}^{\text{II}}\text{Cl}_4]$, $\text{K}_2[\text{Pt}^{\text{II}}\text{Cl}_4]$ were confirmed the next year, as well as the tetrahedral complex $\text{K}_2[\text{Zn}^{\text{II}}(\text{CN})_4]$.

The ability of Werner and others to assign the correct structures from indirect data and logic was hailed by Henry Eyring, the former American Chemical Society President: *"The ingenuity and effective logic that enabled chemists to determine complex molecular structures from the number of isomers, the reactivity of the molecule and of its fragments, the freezing point, the empirical formula, the molecular weight, etc., is one of the outstanding triumphs of the human mind"* [5].

Note For the reader interested in exploring the historical aspect in depth, one book is essential: *'Werner Centennial'*, published in 1967 by the American Chemical Society as No 62 in their Advances in Chemistry Series [6]. This book contains over 40 chapters on historical and current (in 1967) chemistry, including chapters devoted to the Werner–Jorgensen controversy and so on.

Historical Steps Forward

Following the general theory on the covalent bond of G. N. Lewis (1916), the first attempts to interpret Werner's views on an electronic basis were made in 1923 by N.V. Sidgwick and T.M. Lowry. Sidgwick's initial concern was to explain Werner's coordination number in terms of the sizes of the sub-groups of electrons in the Bohr atom. He soon attempted to systematize coordination numbers using the concept of the 'effective atomic number' (EAN). He considered ligands to be Lewis bases which donated electrons (usually one pair per ligand) to the metal ion, which thus behaves as a Lewis acid. Ions tend to add electrons by this process until the EAN (the sum of the electrons on the metal ion plus the electrons donated by the ligand) of the next noble gas is achieved. Today the EAN rule is of little theoretical importance. Nevertheless, it is extremely useful as a predictive rule in one area of coordination chemistry, that of metal carbonyls and analogs.

In 1927 W. Heitler and F. London proposed the quantum treatment of the H_2 molecule, which was developed by Linus C. Pauling for coordination compounds. Pauling (1931) developed the valence bond theory, with the so-called hybrid orbitals, to explain the bonding in coordination compounds. Some predictions (later verified) were made, such as that the paramagnetic compounds of Ni(II) should show tetrahedral or octahedral coordination and diamagnetic compounds should show square planar coordination.

In 1926 I.I. Chernyaev pointed out the general regularity of what he called the *trans*-effect in order to describe the influence of a coordinated ligand on the practical ease of preparing compounds in which the group *trans* to it had been replaced.

In 1929 Hans Albrecht Bethe proposed the crystal field model for ionic solids. Between 1930 and 1940 several physicists, in particular J. H. Van Vleck, developed new aspects of this theory, the so-called Theory of the Crystal (Ligand) Field. Since 1950, both theories have been developed by chemists to explain the bonding in coordination compounds. In 1938 Ryutaro Tsuchida published the 'spectrochemical series' based on the results of his measurements of the absorption spectra of cobalt complexes.

In 1937 in his Thesis "On the Stereochemistry of metals with coordination number four" Jensen confirmed the suggestion of Werner regarding the planar configuration of a series of Pt(II), Pd(II) and low-spin Ni(II) complexes. He pioneered the use of dipole moment measurements for stereochemical problems in coordination chemistry.

Important Milestones

In 1957, Sir Ronald S. Nyholm, a reputed researcher in the field of Coordination Chemistry, propagated the concept of "*Renaissance of Inorganic Chemistry*", which stimulated a greater enthusiasm for research in coordination chemistry [7].

Reaction Mechanisms The classical book of F. Basolo and R.G. Pearson, *Mechanisms in Inorganic Reactions* (1967) summarizes all efforts devoted to this subject until that date. In 1983 and 1992, Henry Taube and Rudolph A. Marcus, respectively, were awarded the Nobel Prize for their investigation on the mechanism of redox processes (inner sphere and outer sphere mechanism, respectively; see Chapter 12). Also a crucial area of study has developed over the last few decades, in parallel to the above studies of redox chemistry, in relation to the understanding and applications of mixed-valence complexes (see Chapter 13).

Metal–Metal bond It was not until 1957, with the determination of the structure of $[\text{Mn}_2(\text{CO})_{10}]$, that unequivocal evidence for metal–metal bond formation in metal carbonyls was obtained. However, complexes with a metal–metal bond were not the object of serious studies until 1963, when they became the focus for two different important laboratories (headed by F.A. Cotton and W.I. Robinson, respectively). It is very instructive to read the Introduction of the book *Multiple Bonds Between Metal Atoms*, by Cotton and coworkers, on the history of these very important discoveries [8]. At that time the quadruple M–M bond had reached the category of 'classical'. More than 40 years later, the first metal–metal quintuple bond was discovered and studied theoretically (2005–2006) (see Chapter 6).

Molecular Magnetism Although the concepts describing the magnetic properties of d^n ions had been developing since the first theory on Crystal Field (associated with such as Van Vleck), and these had been exploited by various researchers up to the 1970s, it can be said that the 'renaissance' of molecular magnetism dated from the conference '*Magneto-Structural Correlation in Exchange Coupled Systems*' (1983). At that meeting the different concepts and ideas of physicists and chemists

on the topic were brought together for the first time. The interested reader can consult the book (now a classic) published from this conference, for a quick overview of the ideas existing at that time [9]. The most recent advances in this area are developed in Chapter 10 of this book.

Supramolecular Coordination Chemistry The concept of molecular recognition through crown ethers, cryptands, and similar ligands was introduced by Donald J. Cram, Jean-Marie Lehn and Charles J. Pedersen in the 1960s. They were awarded the Nobel Prize in 1987 for their research on this subject. The term ‘Supramolecular Chemistry’ was coined by Lehn in 1978. The diffuse concept of ‘self-assembly’ lies within this modern term. The issue is discussed briefly in this book (see Chapter 14).

Organometallic Chemistry The discovery of ferrocene (1951) and the Ziegler–Natta catalyst (1953) were crucial milestones in the field of organometallic chemistry (as a part of coordination chemistry). With the discovery and interpretation of the structure of ferrocene (by G. Wilkinson and E. O. Fisher), it can be said that modern organometallic chemistry was born. The arrival of the Ziegler catalyst (in Germany) and its application by G. Natta (in Italy), was followed by more than 200 papers in 5 years. It is a paradigmatic example where basic research, driven sometimes by curiosity, became suddenly part of an industrial process with great worldwide importance.

Biocoordination Chemistry This new branch, born from general coordination chemistry, started with the discovery by A. D. Allen and C. W. Senoff in 1965 of the first dinitrogen complex, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$, which hinted at the important goal of the fixation of N_2 to produce NH_3 . The serendipitous discovery of *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$ (cisplatin) as a powerful anticancer drug by B. Rosenberg in 1965 was another milestone of coordination chemistry and its application to the life sciences. Currently, biocoordination chemistry is one of the most prolific and important areas derived from coordination chemistry (see Chapter 17).

Photochemistry of Coordination Compounds The application of physical chemistry in photochemistry has been known for many decades. It was not, however, until 1970, when V. Balzani and V. Carassiti wrote the first monograph *Photochemistry of Transition Metal Complexes* [10], that the field gained extraordinary relevance and coordination photochemistry and photophysics became a prime topic in Inorganic Chemistry forums. Indeed, this is perhaps the area of coordination chemistry with the most publications in the highest impact journals. The possibility of obtaining, for example, photomolecular machines as well as H_2 production from water and sunlight are top priorities in current research.

Metal–Organic Frameworks (MOFs) Finally, a new strong area has emerged in the current literature (since the beginning of this decade). Study of the so-called MOFs offers almost infinite possibilities and applications.

Although it is undoubtedly still in its infancy, the number of publications in this field has increased exponentially in the past three to four years. This subject will be treated in Chapter 16.

Nomenclature of Inorganic Chemistry (Coordination Compounds). Extract from IUPAC recommendations 2005

Names of Ligands in Coordination Entities

Anionic Ligands The rule now used, without exception, is that anion names ending in 'ide', 'ite' and 'ate' respectively are changed to end in 'ido', 'ito' and 'ato', respectively, when modifying the ligand name for use in additive nomenclature. *All anionic ligands, upon coordination to a metal, have the simple change in the ending from e to o.*

Certain simple ligands have historically been represented in names by abbreviated forms: fluoro, chloro, bromo, iodo, hydroxo, hydro, cyano, oxo, etc. Following the rule stated above, these are now fluorido, chlorido, bromido, iodido, hydroxido, hydrido, cyanido, oxido.

Neutral Ligands They are used without modification (even if they carry the ending 'ide', 'ite' or 'ate'). Examples: MeCONH_2 = acetamide (*not* acetamido).

Charge Numbers, Oxidation Numbers and Ionic Properties

The key point is: *Arabic numerals are used to designate charge on an atom or groups of atoms, while Roman numerals are used to indicate the (formal) oxidation state of an atom.*

It is also important to distinguish between names and formulae: In formulae the (formal) oxidation state is given as a roman number *in superscript*, e.g. $[\text{Co}^{\text{II}}\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{42}]^{7-}$; $[\text{Mn}^{\text{VII}}\text{O}_4]^-$; $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}^4$. In names the formal charge can be given at the end, e.g. $[\text{CuCl}_4]^{2-}$ = tetrachloridocuprate(II).

The charge can also be used e.g. sodium tetranitratoborate(III) can also be written as sodium tetranitratoborate(1-); $\text{K}_4[\text{Fe}(\text{CN})_6]$ as potassium hexacyanidoferrate(II) or potassium hexacyanidoferrate(4-) or tetrapotassium hexacyanidoferrate; $\text{Na}[\text{PtBrCl}(\text{NH}_3)(\text{NO}_2)]$ is sodium amminebromidochloridonitrito-κN-platinate(1-).

"Naked" Ions

In speech and in line formulae iron(2+) and iron(II), and even $\text{Fe}(\text{II})$ or Fe^{2+} can be used. It is not totally correct, for these ions with *definite charge*, to write Fe^{II} , Cr^{III} , etc. When it is used (such as occurs in many journals) it indicates not a naked

ion, but an ion in a chemical formula: it is more a formal oxidation state than a charge.

It is important to note that for certain atoms, when written as naked but without true ionic charge (such as molybdenum(VI) or similar), it is possible to write: molybdenum(VI), Mo(VI) or even Mo^{VI} (with a preference for the full element name, molybdenum(VI)), and indeed many journals do this. In such cases, Mo⁶⁺, V⁵⁺, etc. would be required if the ion is naked but, since there is a definite implication that it is part of a complex, that does not necessarily apply.

The name of a monoatomic cation is that of the element with an appropriate charge number appended in parentheses: Na⁺ = sodium(1+); Cu²⁺ = copper(2+); Cr³⁺ = chromium(3+).

For anions the rule is the same: homopolyatomic anions are named by adding the charge number to the stoichiometric name of the corresponding neutral species: O₂⁻ = dioxide(1-) (superoxide accepted); C₂²⁻ = dicarbide(2-) (acetylide accepted); N₃⁻ = trinitride(1-) (azide accepted), S₂²⁻ = disulfide, Pb₄⁴⁻ = nonaplumbide(4-).

Summary Arabic numerals are crucially important in nomenclature and their placement in a formula or name is especially significant. As right subscripts they indicate the number of individual constituents (atoms or group of atoms), unity is not indicated, e.g. [Co(NH₃)₆]Cl₃. As right superscripts they indicate the charge, unity is not indicated, e.g. NO⁺, Cu²⁺, etc.

Roman numerals are used in formulae as right superscripts to designate the formal oxidation state, e.g. Fe^{II}Fe^{III}O₄, [Mn^{VII}O₄]⁻. In names they indicate the formal oxidation state of an atom, and are enclosed in parentheses immediately following the name of the atom being qualified, e.g. [Fe(H₂O)₆]²⁺ = hexaaquairon(II); [FeO₄]²⁻ = tetraoxido ferrate(VI).

Plus and minus signs, + and -, are used to indicate the charge of an ion in a formula or name, e.g. Cl⁻, Fe³⁺, Cu⁺, Cu²⁺, As³⁻, [Co(CO)₄]⁻.

Ionic charge is indicated by means of a *right upper index*, as in Aⁿ⁺ or Aⁿ⁻ (not A⁺n or A⁻n). If the formula is placed in enclosing marks, the right upper index is placed outside the enclosing marks.

Ordering of Metal and Ligands in Coordination Entities

Ligands are listed in *alphabetical order* (multiplicative prefixes indicating the number of ligands are not considered in determining that order): [CoCl(NH₃)₅]Cl₂ is pentaamminechloridocobalt(2+) chloride.

In the formulae, ligands are ordered alphabetically according to the abbreviation or formula used for the ligand, irrespective of charge. Thus, CH₃CN, MeCN would be ordered under C and M, respectively. Single letter symbols precede two letter symbols: CO precedes Cl.

In the Recommendation of 1990, charged ligands were cited before neutral ligands. The currently recommended formula for the anion of Zeise's salt is now