

## INORGANIC AND BIOINORGANIC CHEMISTRY

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### Summary

Inorganic chemistry is the discipline which studies the chemistry of the elements of the periodic table. Traditionally, the chemistry of compounds containing several carbon atoms is grouped separately as organic chemistry. Humanity has always tried to use minerals and metals for a variety of purposes but we can define the birth of the discipline with the discovery and classification of a large number of elements around the end of the 18<sup>th</sup> century.

Then the synthesis or analytical characterization of compounds led to the discovery of periodic properties and eventually to the organization of the elements in the periodic table. In the first half of the 20<sup>th</sup> century the basic industrial inorganic chemistry established a big progress in the industrialized countries with the synthesis of NH<sub>3</sub> (and of HNO<sub>3</sub>), Na<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> etc. In the second half of the 20<sup>th</sup> century coordination chemistry developed which broadened the understanding of the chemical bond to transition metal ions. Therefore the characterization of metal ions in biological systems and in particular those bound to proteins has flourished.

After coordination chemistry, metallo-organic chemistry has developed which is characterized by the presence of metal-carbon bonds. All of these advancements have led to the understanding at molecular level of catalysis both in homogeneous and heterogeneous systems. Although bound to the keywords provided by the scientific board we have tried to give a flavor of all of this in the present series of chapters in this theme.

## 1. Introduction

Chemistry is the science concerned with the composition, structure, and properties of matter, as well as the changes that matter undergoes during chemical reactions. Disciplines within chemistry are traditionally grouped by the type of matter being studied or the kind of study. Inorganic chemistry is the discipline that studies the chemistry of the elements of the periodic table. This major branch of chemistry is generally considered to embrace all substances except hydrocarbons and their derivatives, or all substances that are mainly constituted by carbon atoms. Traditionally, the chemistry of compounds containing several carbon atoms is separately considered to be organic chemistry. Inorganic chemistry covers a broad range of subjects, including atomic structures, crystallography, chemical bonding, coordination compounds, acid-base reactions, ceramics, and the various subdivisions of electrochemistry (e.g. electrolysis, battery science, corrosion, and semiconduction).

Humankind has attempted to use minerals and metals for a variety of purposes throughout the centuries, but we can define the birth of the discipline with the discovery and classification of a large number of elements around the end of the 18<sup>th</sup> century. Inorganic chemists have made significant advances in understanding the minute particles that compose our world. These particles, called atoms, make up the elements, which are the building blocks of all the compounds and substances in the world around us. All chemical substances are made from combinations of the 117 chemical elements found in the periodic table. Ninety two elements are known to be naturally occurring, and the rest have been made artificially. In Figure 1 is shown the modern periodic table.

**IUPAC Periodic Table of the Elements**

1 H hydrogen (1.007 84)																	2 He helium (4.002 602)																														
3 Li lithium (6.941)	4 Be beryllium (9.012 182)	Atomic Number Symbol (name)										5 B boron (10.811)	6 C carbon (12.0107)	7 N nitrogen (14.006 42)	8 O oxygen (15.999 4)	9 F fluorine (18.998 4032)	10 Ne neon (20.179 7)																														
11 Na sodium (22.989 76928)	12 Mg magnesium (24.304)											13 Al aluminium (26.981 5386)	14 Si silicon (28.085 5)	15 P phosphorus (30.973 762)	16 S sulfur (32.06)	17 Cl chlorine (35.453)	18 Ar argon (39.948)																														
19 K potassium (39.098 3)	20 Ca calcium (40.078)	21 Sc scandium (44.955 912)	22 Ti titanium (47.88)	23 V vanadium (50.9415)	24 Cr chromium (51.9961)	25 Mn manganese (54.938)	26 Fe iron (55.845)	27 Co cobalt (58.933 195)	28 Ni nickel (58.6934)	29 Cu copper (63.546)	30 Zn zinc (65.38)	31 Ga gallium (69.723)	32 Ge germanium (72.64)	33 As arsenic (74.921 6)	34 Se selenium (78.96)	35 Br bromine (79.904)	36 Kr krypton (83.795)																														
37 Rb rubidium (85.4678)	38 Sr strontium (87.62)	39 Y yttrium (88.905 842)	40 Zr zirconium (91.224)	41 Nb niobium (92.906 38)	42 Mo molybdenum (95.94)	43 Tc technetium (98)	44 Ru ruthenium (101.07)	45 Rh rhodium (102.905 5)	46 Pd palladium (106.42)	47 Ag silver (107.8682)	48 Cd cadmium (112.411)	49 In indium (114.818)	50 Sn tin (118.710)	51 Sb antimony (121.757)	52 Te tellurium (127.603)	53 I iodine (126.905 47)	54 Xe xenon (131.29)																														
55 Cs cesium (132.905 451)	56 Ba barium (137.327)	57-71 lanthanoids	72 Hf hafnium (178.49)	73 Ta tantalum (180.947 88)	74 W tungsten (183.84)	75 Re rhenium (186.207)	76 Os osmium (190.23)	77 Ir iridium (192.222)	78 Pt platinum (195.084)	79 Au gold (196.966 57)	80 Hg mercury (200.59)	81 Tl thallium (204.3833)	82 Pb lead (207.2)	83 Bi bismuth (208.980 4)	84 Po polonium (209)	85 At astatine (210)	86 Rn radon (222)																														
87 Fr francium (223)	88 Ra radium (226)	89-102 actinoids	103 Rf rutherfordium (261)	104 Db dubnium (262)	105 Sg seaborgium (266)	106 Bh bohrium (264)	107 Hs hassium (277)	108 Mt meitnerium (268)	109 Ds darmstadtium (271)	110 Rg roentgenium (272)																																					
<table border="1"> <tr> <td style="text-align: center;">89 La lanthanum (138.905 47)</td> <td style="text-align: center;">90 Ce cerium (140.12)</td> <td style="text-align: center;">91 Pr praseodymium (140.907 65)</td> <td style="text-align: center;">92 Nd neodymium (144.242)</td> <td style="text-align: center;">93 Pm promethium (145)</td> <td style="text-align: center;">94 Sm samarium (150.36)</td> <td style="text-align: center;">95 Eu europium (151.964)</td> <td style="text-align: center;">96 Gd gadolinium (157.25)</td> <td style="text-align: center;">97 Tb terbium (158.925 3)</td> <td style="text-align: center;">98 Dy dysprosium (162.500)</td> <td style="text-align: center;">99 Ho holmium (164.930 32)</td> <td style="text-align: center;">100 Er erbium (167.259)</td> <td style="text-align: center;">101 Tm thulium (168.934 2)</td> <td style="text-align: center;">102 Yb ytterbium (173.054)</td> <td style="text-align: center;">103 Lu lutetium (174.967)</td> </tr> <tr> <td style="text-align: center;">104 Ac actinium (227)</td> <td style="text-align: center;">105 Th thorium (232.037 7)</td> <td style="text-align: center;">106 Pa protactinium (231.036 89)</td> <td style="text-align: center;">107 U uranium (238.028 91)</td> <td style="text-align: center;">108 Np neptunium (237)</td> <td style="text-align: center;">109 Pu plutonium (244)</td> <td style="text-align: center;">110 Am americium (243)</td> <td style="text-align: center;">111 Cm curium (247)</td> <td style="text-align: center;">112 Bk berkelium (247)</td> <td style="text-align: center;">113 Cf californium (251)</td> <td style="text-align: center;">114 Es einsteinium (252)</td> <td style="text-align: center;">115 Fm fermium (257)</td> <td style="text-align: center;">116 Md mendelevium (258)</td> <td style="text-align: center;">117 No nobelium (259)</td> <td style="text-align: center;">118 Lr lawrencium (260)</td> </tr> </table>																		89 La lanthanum (138.905 47)	90 Ce cerium (140.12)	91 Pr praseodymium (140.907 65)	92 Nd neodymium (144.242)	93 Pm promethium (145)	94 Sm samarium (150.36)	95 Eu europium (151.964)	96 Gd gadolinium (157.25)	97 Tb terbium (158.925 3)	98 Dy dysprosium (162.500)	99 Ho holmium (164.930 32)	100 Er erbium (167.259)	101 Tm thulium (168.934 2)	102 Yb ytterbium (173.054)	103 Lu lutetium (174.967)	104 Ac actinium (227)	105 Th thorium (232.037 7)	106 Pa protactinium (231.036 89)	107 U uranium (238.028 91)	108 Np neptunium (237)	109 Pu plutonium (244)	110 Am americium (243)	111 Cm curium (247)	112 Bk berkelium (247)	113 Cf californium (251)	114 Es einsteinium (252)	115 Fm fermium (257)	116 Md mendelevium (258)	117 No nobelium (259)	118 Lr lawrencium (260)
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**Notes**

- "Lanthanoid" and "actinoid" are commonly used alternative spellings for "lanthanum" and "actinium".
- IUPAC 2005 standard atomic weights (mean relative atomic masses) are listed with uncertainties in the last figure in parentheses (J. E. Seaw, *Pure Appl. Chem.* 78, 2051 (2006)). These values correspond to current best knowledge of the elements in natural terrestrial sources. For elements that have no stable or long-lived isotopes, the mass number of the nuclide with the longest confirmed half-life is listed between square brackets.
- Elements with atomic numbers 112 and above have been reported but not fully synthesized.

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Figure 1. IUPAC Periodic table of the elements

The synthesis or analytical characterization of compounds then led to the discovery of

periodic properties and eventually to the organization of the elements in the periodic table.

Basic industrial inorganic chemistry provided a basis for extensive progress in industrialized nations in the first half of the 20<sup>th</sup> century with the synthesis of compounds such as NH<sub>3</sub> (and HNO<sub>3</sub>), Na<sub>2</sub>CO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>. In the second half of the 20<sup>th</sup> century, coordination chemistry was developed, broadening the understanding of the chemical bond to transition metal ions. The characterization of metal ions in biological systems, particularly those bound to proteins, has therefore flourished. Following coordination chemistry, metallo-organic chemistry was developed, characterized by the presence of metal-carbon bonds. All of these advancements have led to an understanding at the molecular level of catalysis both in homogeneous and heterogeneous systems.

Bioinorganic chemistry is a specialized field that spans the chemistry of metal-containing molecules within biological systems. This field is concerned with the control and use of metal ions in biochemical processes. Although bioinorganic chemistry includes the study of artificially introduced metals (e.g. medicinally), many naturally occurring biological processes (such as respiration) depend upon molecules containing inorganic elements, such as metalloproteins; these natural processes are also studied by bioinorganic chemistry. Bioinorganic chemistry is important for the realization of the implications of electron-transfer proteins, substrate bindings and activation, atom and group transfer chemistry, as well as metal properties in biological chemistry.

Although bound to the keywords provided by the scientific board, we have tried to provide a flavor of these topics in the series of chapters in the theme.

## 2. Chemical Elements and their Discovery

All chemical elements are substances, all of whose atoms are alike in that they have the same positive charge on the nucleus and the same number of extra-nuclear electrons. Chemical elements show a wide diversity, some of these elements are known even in antiquity, others having been discovered within the past several hundred years and still others having been synthesized since the 1950s via nuclear reactions on heavy elements, as these elements are unstable and radioactive and do not exist in nature. In Table 1 are shown the chemical elements with the date of discovery and their discoverer.

Elements	Symbols	Dates	Discoverers
Gold, Silver, Copper, Iron, Lead, Tin, Mercury, Sulfur, Carbon, Antimony	Au, Ag, Cu, Fe, Pb, Sn, Hg, S, C, Sb	Ancient times: prior to 1 A.D.	-
Arsenic	As	~1250	Magnus
Phosphorus	P	1669	Brand
Cobalt	Co	~1735	Brandt
Platinum	Pt	1735	Ulloa
Zinc	Zn	1746	Margraf
Nickel	Ni	1751	Cronstedt

Bismuth	Bi	1753	Geoffroy
Hydrogen	H	1766	Cavendish
Nitrogen	N	1772	Rutherford
Oxygen	O	1774	Priestley, Scheele
Chlorine	Cl	1774	Scheele
Manganese	Mn	1774	Gahn, Scheele, Bergman
Molybdenum	Mo	1778	Scheele
Tellurium	Te	1782	von Reichenstein
Tungsten	W	1783	J. and F. d'Elhuyar
Zirconium	Zr	1789	Klaproth
Titanium	Ti	1791	Gregor
Yttrium	Y	1794	Gadolin
Chromium	Cr	1797	Vauquelin
Beryllium	Be	1798	Vauquelin
Niobium	Nb	1801	Hatchett
Tantalum	Ta	1802	Ekeberg
Strontium	Sr	1808	Davey
Uranium	U	1841	Peligo
Cerium	Ce	1803	Berzelius, Hisinger, Klaproth
Palladium	Pd	1803	Wollaston
Osmium	Os	1803	Tennant
Iridium	Ir	1803	Tennant
Rhodium	Rh	1803-1804	Wollaston
Sodium	Na	1807	Davy
Potassium	K	1807	Davy
Barium	Ba	1808	Davy
Calcium	Ca	1808	Davy
Magnesium	Mg	1808	Davy
Boron	B	1808	Davy, Gay-Lussac, Thenard
Iodine	I	1811	Courtois
Lithium	Li	1817	Arfvedson
Cadmium	Cd	1817	Stromeyer
Selenium	Se	1817	Berzelius
Silicon	Si	1824	Berzelius
Bromine	Br	1826	Balard
Aluminum	Al	1827	Wohler
Thorium	Th	1828	Berzelius
Vanadium	V	1830	Sefstrom
Lanthanum	La	1839	Mosander
Erbium	Er	1842-1843	Mosander
Terbium	Tb	1843	Mosander
Ruthenium	Ru	1844	Klaus
Cesium	Cs	1860	Bunsen, Kirchoff

Rubidium	Rb	1861	Bunsen, Kirchoff
Thallium	Tl	1861	Crookes
Indium	In	1863	Riech, Richter
Fluorine	F	1866	Moissan
Helium	He	1868	Ramsay
Gallium	Ga	1875	Boisbaudran
Ytterbium	Yb	1878	Marignac
Scandium	Sc	1878	Nilson
Holmium	Ho	1878	Delafontaine
Thulium	Tm	1879	Cleve
Samarium	Sm	1879	Boisbaudran
Gadolinium	Gd	1880	Marignac
Praseodymium	Pr	1885	von Weisbach
Neodymium	Nd	1885	von Weisbach
Dysprosium	Dy	1886	Boisbaudran
Germanium	Ge	1886	Winkler
Argon	Ar	1894	Rayleigh, Ramsay
Europium	Eu	1896	Demarcay
Krypton	Kr	1898	Ramsey, Travers
Neon	Ne	1898	Ramsey, Travers
Xenon	Xe	1898	Ramsey, Travers
Polonium	Po	1898	Curie
Radium	Ra	1898	P. and M. Curie
Actinium	Ac	1899	Debiere
Radon	Rn	1900	Dorn
Lutetium	Lu	1907	Urbain
Protactinium	Pa	1917	Hahn,
Hafnium	Hf	1923	Conster
Rhenium	Re	1925	Noddack, Berg, Tacke
Technetium	Tc	1937	Segre
Francium	Fr	1939	Perey
Neptunium	Np	1940	McMillan, Abelson
Astatine	At	1940	Segre
Plutonium	Pu	1940	Seaborg
Curium	Cm	1944	Seaborg
Americium	Am	1944	Seaborg
Promethium	Pm	1945	Marinsky
Berkelium	Bk	1949	Seaborg
Californium	Cf	1950	Thompson, Street, Ghiorso, Seaborg
Fermium	Fm	1952	Ghiorso
Einsteinium	Es	1952	Ghiorso
Mendelevium	Md	1955	Ghiorso, Harvey, Choppin, Thompson, Seaborg

Nobelium	No	1958	Ghiorso, Sikkeland, Walton, Seaborg
Lawrencium	Lw	1961	Ghiorso
Rutherfordium	Rf	1964	Berkeley Lab (USA), Dubna Lab (Russia)
Dubnium	Db	1967	Berkeley Lab (USA), Dubna Lab (Russia)
Seaborgium	Sg	1974	Berkeley Lab (USA), Dubna Lab (Russia)
Bohrium	Bh	1975	Dubna Lab (Russia)
Meitnerium	Mt	1982	Armbruster, Munzenber
Hassium	Hs	1984	Armbruster, Munzenber
Darmstadtium	Ds	1994	Hofmann, Nivov et al. GSI-Germany
Roentgenium	Rg	1994	Hofmann, Nivov et al. GSI-Germany
Ununbium	Uub	1996	Hofmann, Nivov et al. GSI-Germany
Ununquadium	Uuq	1998	Dubna Lab (Russia)
Ununhexium	Uuh	2000	Dubna Lab (Russia)
Ununtrium	Uut	2004	Dubna Lab (Russia)
Ununpuntium	Uup	2004	Dubna Lab (Russia)
Ununoctium	Uuo	2006	Dubna Lab (Russia)
Unseptium	Uus	It has not been synthesized	-

Table 1. Elements, date of discovery and discoverer. The elements are sort by date of discovery

The criteria for claiming the discovery of an element has varied over the centuries. Methods of chemical element discovery in the late eighteenth and early nineteenth centuries were based on the properties of new substances, their separability, the color of their compounds, the shape of their crystals and their reactivity to determine the existence of new elements. In those early days, atomic weight values were not available, and there were no spectral analyses that would later be supplied by arc, spark, absorption, phosphorescent or X-ray spectra. Also in those days, there were many claims, e.g., the discovery of certain rare earth elements of the lanthanide series, which involved the discovery of a mineral ore, from which an element was later extracted. The honor of discovery has often been accorded not to the person who first isolated the element but to the person who discovered the original mineral itself, even when the ore was impure and that ore actually contained many elements. The reason for this is that in the case of these rare earth elements, the “earth” now refers to oxides of a metal not to the metal itself. This fact was not realized at the time of their discovery, until the English chemist Humphry Davy showed that earths were compounds of oxygen and metals in 1808.

Although the atomic weight and a spectral analysis of an element were not available in the early days, both of these elemental properties would be required before the discovery of the element would be accepted, which occurred in the latter part of the nineteenth century. In general, the requirements for claims of discovery have become stricter throughout the years and claims that were previously accepted would no longer meet the minimum constraints now imposed. There are also cases where the credit for discovery was not given to the first person who actually discovered the element, but to the first person to claim the discovery in print. If a publication was delayed, the discoverer was historically often “scooped” by another scientist.

This leads to the question of who should be considered the actual discoverer of a chemical element. Should it be the first person to describe the initial properties, the one who found the oxide or the metal, the one who separated the element or the first one to publish their results? On the matter of publication, the Swedish chemist Jons Jacob Berzelius published an annual review (equivalent to our present abstract service) during the early nineteenth century. Berzelius usually cited articles published in other journals, but he also reported work in his laboratory that had not yet been published. This enabled his assistant Carl-Gustav Mosander to receive early credit for work that Mosander chose not to formally publish until many years later, after he had worked out all of the details.

### **2.1. Determining the Name of Chemical Elements**

The names of the various chemical elements come from many sources including mythological concepts or characters; places, areas or countries; properties of the element or its compounds such as color, smell or its inability to combine; and the names of scientists. There are also some miscellaneous or obscure names for particular elements. Chemical element names are dependent upon acceptance of the chemical community, the priority rights of the discoverer notwithstanding. We shall see long-standing disputes for a number of elements, often involving national pride and rivalry between French and German scientists for some of the older elements, and Russian and American scientists in more recent times.

To avoid this, at the beginning of the twentieth century, the International Committee on Atomic Weights (ICAW) was formed. Although the ICAW did not set internationally approved names, a name with an atomic weight value in their table lent support for the adoption of that name by the chemical community. Twenty years later, the ICAW became a part of the International Union of Pure and Applied Chemistry (IUPAC) upon its formation. IUPAC was called the International Union of Chemistry between 1930 and 1950. When the IUPAC Commission on Atoms officially disbanded in 1949, the responsibility for acceptance of a chemical element name was given by IUPAC to its Commission on Nomenclature of Inorganic Chemistry (CNIC).

The CNIC does not deny the right of a discoverer to propose a name for a new chemical element. However, the approved names of the elements should differ as little as possible in different languages; the names should be based on practicality and prevailing usage and finally the choice of the name carries no implication at all about the circumstances of discovery.

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### Biographical Sketches

**Ivano Bertini** born in Pisa in 1940, he received his doctorate in Chemistry at the University of Florence in 1964 and became full professor of Chemistry there in 1975. He is the Director of the Magnetic Resonance Center (CERM) a Center of Excellence at the University of Florence and a European-funded research infrastructure. His main research interests are nuclear magnetic resonance spectroscopy (NMR), the expression and preparation of metalloproteins, their structural characterization, and the investigation of their interactions with an emphasis on understanding cellular processes at the molecular level. He has written over 600 papers and many books. He received the Chugaev Diploma from the Kurnakov Institute

of the Academy of Science, USSR, in 1981; the Golden Medal of the Magnetic Resonance Group of the Italian Chemical Society in 1991; the Accademia dei Lincei Prize, Italy, in 1993; the Bijvoet Medal, Utrecht, NL, in 1998; the Sapio NMR Prize, Italy, in 1999; the Cannizzaro Medal of the Italian Chemical Society in 2006; and the Basolo Medal, Northwestern University, USA, in 2006. His special lectures include: A.D. Little Lecturer at MIT, Cambridge, MS, USA, in 1997; E.L. Mütterties Lecturer at Berkeley, CA, USA, in 1997; FECS lecturer, Athens, in 2002 and Swift Lecture, CALTECH, Pasadena, USA, in 2007. He has received three honorary doctorates: *Laurea Honoris Causa* in Chemistry University of Stockholm, Sweden, 1998; *Laurea Honoris Causa* in Chemistry, University of Ioannina, Greece, 2002;+ *Laurea Honoris Causa* in Biological Sciences, University of Siena, Italy, 2003. He is a member of the Accademia Nazionale dei Lincei and the Academia Europaea.

**Mirko Mori** was born in Florence, Italy, in 1979. He is a PhD student of the PhD Program in Chemistry of the University of Florence, since January 2007. Graduated in Chemistry of Biological Molecules in September 2006 at the same University, he is, in his quality of PhD student in the Centre of Magnetic Resonance (CERM), an active researcher in the field of NMR spectroscopy of biological molecules. His research interest focus on: a) methodological aspect of NMR spectroscopy, with a specific interest in study of paramagnetic system and in cross correlated relaxation rates; b) solution structure calculations on metalloproteins. To date, he has one published article on Biomolecular NMR Assignment and one submitted article on Journal of Biological Chemistry dealing with the solution structure of a novel monomeric form of Superoxide Dismutase. Actually, his research revolves around two field: a) The potential of using a lanthanide-binding protein tags as an NMR approach for monitoring interdomain phenomena in biological systems; b) The slow internal dynamics on time scales in the range of micro- to milliseconds of the protein backbone by measuring the relaxation rates of zero- and double quantum coherences involving neighboring pairs of carbonyl  $^{13}\text{C}$  and amide  $^{15}\text{N}$  nuclei.