# INORGANIC AND BIOINORGANIC CHEMISTRY

**Ivano Bertini**
*Magnetic Resonance Center (CERM), University of Florence, Italy*
*Department of Chemistry, University of Florence, Italy*

**Mirko Mori**
*Magnetic Resonance Center (CERM), University of Florence, Italy*

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## Contents





## 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 the18$^{th}$ 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 20th century the basic industrial inorganic chemistry established a big progress in the industrialized countries with the synthesis of $NH_3$ (and of $HNO_3$), $Na_2CO_3$, $H_2SO_4$ etc.

In the second half of the 20th 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 the18th 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.

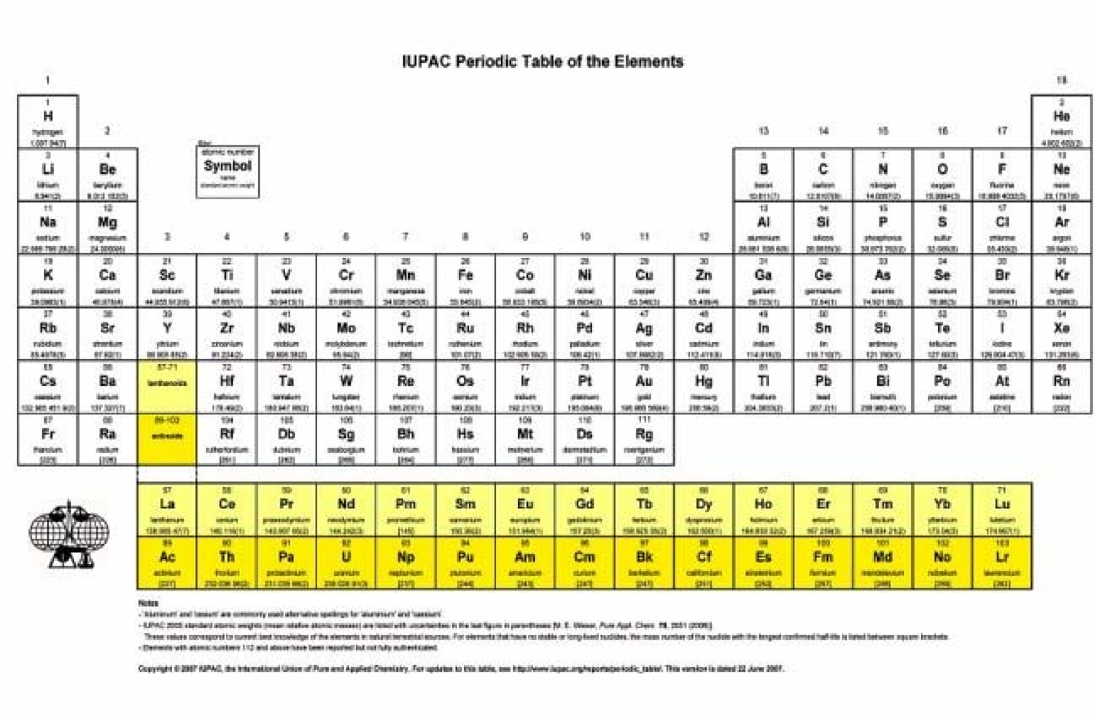


Figure 1. IUPAC Periodic table of the elements

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$^{th}$ century with the synthesis of compounds such as $NH_3$ (and $HNO_3$), $Na_2CO_3$, and $H_2SO_4$. In the second half of the 20$^{th}$ 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 |
| Titanuim | 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 | Peligot |
| Cerium | Ce | 1803 | Berzelius, Hisinger, Klaproth |
| Palladium | Pd | 1803 | Wollaston |
| Osmium | Os | 1803 | Tennant |

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|---|---|---|---|
| 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 |

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|---|---|---|---|
| Actinium | Ac | 1899 | Debierne |
| 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 $^{13}C$ and amide $^{15}N$ nuclei.