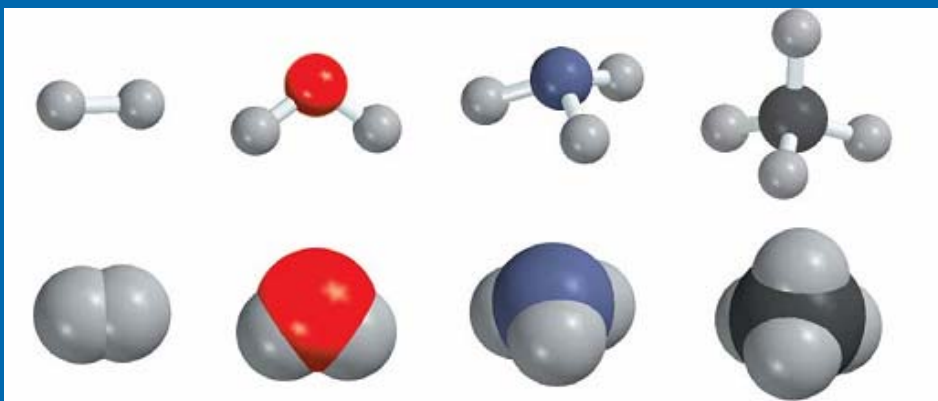# Welcome to Chemistry

If anyone wishes to search out
the truth of things in serious earnest, he
ought not to select one special science;
for all the sciences are conjoined with
each other and interdependent.
Descartes,
Rules for the Direction of the Mind

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Program of course "MEDICAL CHEMISTRY"
for the first-year students of the School of Medicine

Module 1. "Acid-base equilibria and complex formation in biological liquids".
1. Biogenic s- and p- block elements: biological role, application in medicine.
2. Biogenic d- block elements: biological role, application in medicine.
3. Chemical bonding.
4. Solutions. Electrolytic dissociation.
5. Acid-base equilibrium in biological liquids.
6. Dissociation of water, pH scale. Buffer solutions.
7. Colligative properties of solutions.

Practice for Module 1: 4 seminars, 4 tests, 4 praxis and final test.

Module 2. "Equilibrium in biological systems at the phase interface".
1. Chemical thermodynamics. Thermochemistry.
2. Kinetics of biochemical processes.
3. Electrochemical phenomena in biological processes.
4. Colloidal solutions and colloid stability.
5. Electric double layer and electrokinetic phenomena. Adsorption. Chromatography.
6. Properties of polymer solutions.

Practice for Module 2: 4 seminars, 4 tests, 4 praxis and final test.

Grades for Modules

Type of the work	Points
Test	15 4 tests × 15 = 60
Praxis	15 4 praxis × 15 = 60
Final Test	80 1 Final Test × 80 = 80
In total:	**200**

Grading for the Module No. 1 is according to the "Two-level Grade".

Final Graded Credit according to the "Four-level Grade" is calculated as average points of two Modules (No. 1 and No. 2) and placed to the student's Diploma Appendix.

Points	Module No. 1 (Two-level Grade)	Final Graded Credit (Four-level Grade)
200 – 180	credit	excellent
179 – 150	credit	good
149 – 120	credit	satisfactorily
119 – 0	not credited	unsatisfactorily

V.N. Karazin Kharkiv National University

Medical Chemistry

Module 1. Lecture 1

Chemistry of biogenic elements

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Department of Physical Chemistry

November,17 2021

Lecture topics

√ Fundamentals of chemistry.

√ Classification of chemical elements.

√ Classification of biogenic elements.

√ Periodic law and Periodic table.

√ Three important atomic properties: the atomic and ionic radii, the ionization energy, and the electron affinity.

√ Chemical bond.

√ Ionic bond.

√ Covalent bond.

√ Electronegativity of the elements and the type of the bond.

√ Coordination compounds.

√ Structure of coordination compounds.

√ Stability constants.

√ Coordination compounds in living systems.

√ Amino acids and their derivatives as ligands.

√ Nucleic acids and their derivatives as ligands.

√ Coordination compounds of Fe in living systems.

√ Coordination compounds of Fe and Mg in living systems.

Fundamentals of chemistry

Chemistry is the study of <u>matter</u>, its composition, structure and properties, and the chemical changes it undergoes.

Matter is anything that occupies space and has mass.

A substance is a form of matter that has a definite (constant) composition and distinct properties. Examples are water, ammonia, sugar, gold, oxygen, and etc.

Substances can be either **elements or compounds**. *An element* is a substance that cannot be separated into simpler substances by chemical means.

The symbols of some elements are derived from their Latin names – for example, Au from aurum (gold), Fe from ferrum (iron), and Na from natrium (sodium) – whereas most of them come from their English names.

On **the basis of atomic theory**, we can define ***an atom*** as the basic unit of an element that can enter into chemical combination.

Atoms actually possess ***internal structure***; that is, they are made up of <u>electrons, protons, and neutrons</u>.

Fundamentals of chemistry

The atomic number (Z) is the number of protons in the nucleus of each atom of an element. As atom is a neutral particle the number of protons is equal to the number of electrons, so the atomic number also shows the number of electrons in the atom.

The mass number (A) of an atom is the total number of neutrons and protons present in the nucleus of an atom of an element. *The number of neutrons* in an atom is equal to the difference between the mass number and the atomic number.

A molecule is an aggregate of at least two atoms in a definite arrangement held together by chemical forces (also called chemical bonds). A molecule may contain atoms of the same element or atoms of two or more elements joined in a fixed ratio.

An ion is an atom or a group of atoms that has a net positive or negative charge. The loss of one or more electrons from a neutral atom results in a **cation**, an ion with **a net positive charge**. The acceptance of electron(s) by an atom results in **an anion**, a particle with **a net negative charge**.
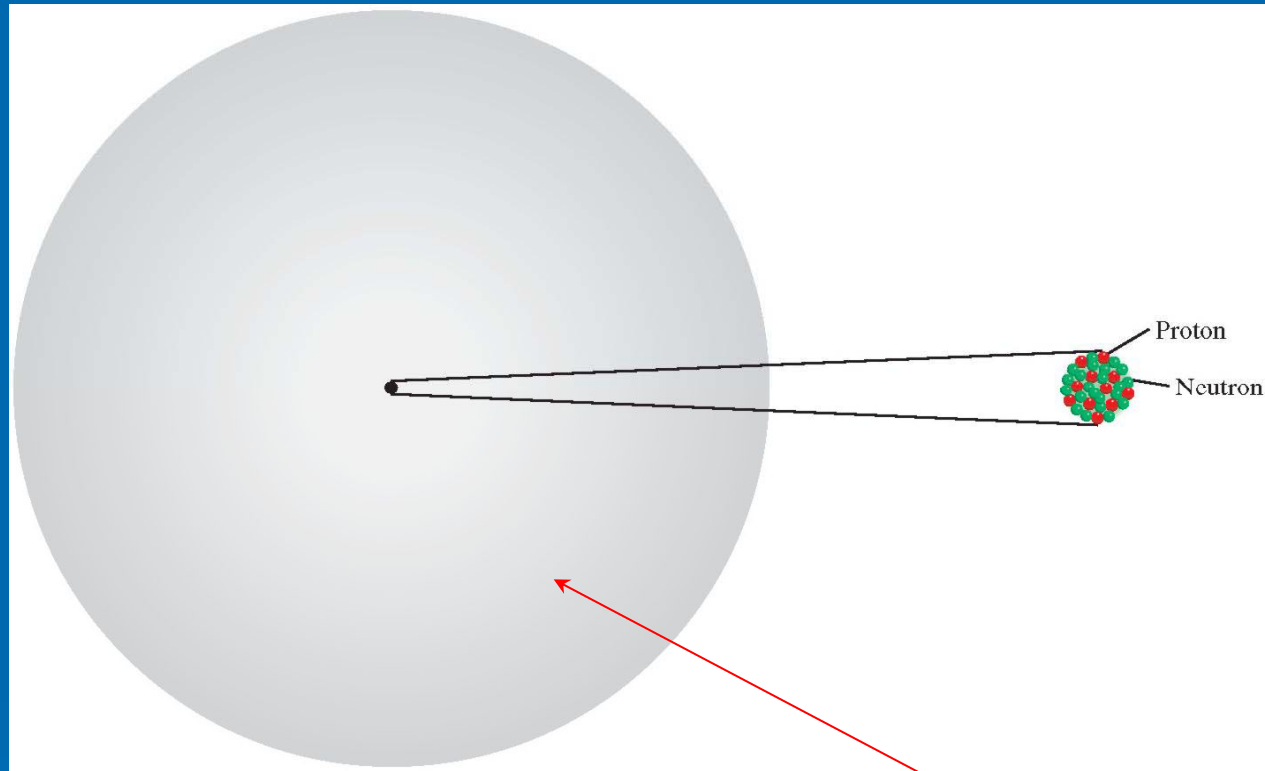
Fundamentals of chemistry

Figure 1. The atom.

The protons and neutrons of an atom are packed in an extremely small nucleus. Electrons are shown as 'clouds' around the nucleus.

Classification of chemical elements

√ natural and artificial;

√ metals and nonmetals;

√ according to the structure of outer energy level (incompletely filled subshells): s-, p-, d- and f-elements;

√ according to distribution on Earth's crust (widespread and rare). Of the 83 elements that are found in nature, 12 make up 99.7% of Earth's crust by mass. They are, in decreasing order of natural abundance, oxygen (O), silicon (Si), aluminum (Al), iron (Fe), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), titanium (Ti), hydrogen (H), phosphorus (P), and manganese (Mn);

√ radioactive elements (atomic nuclei are unstable), e.g. astatine (At), polonium (Po);

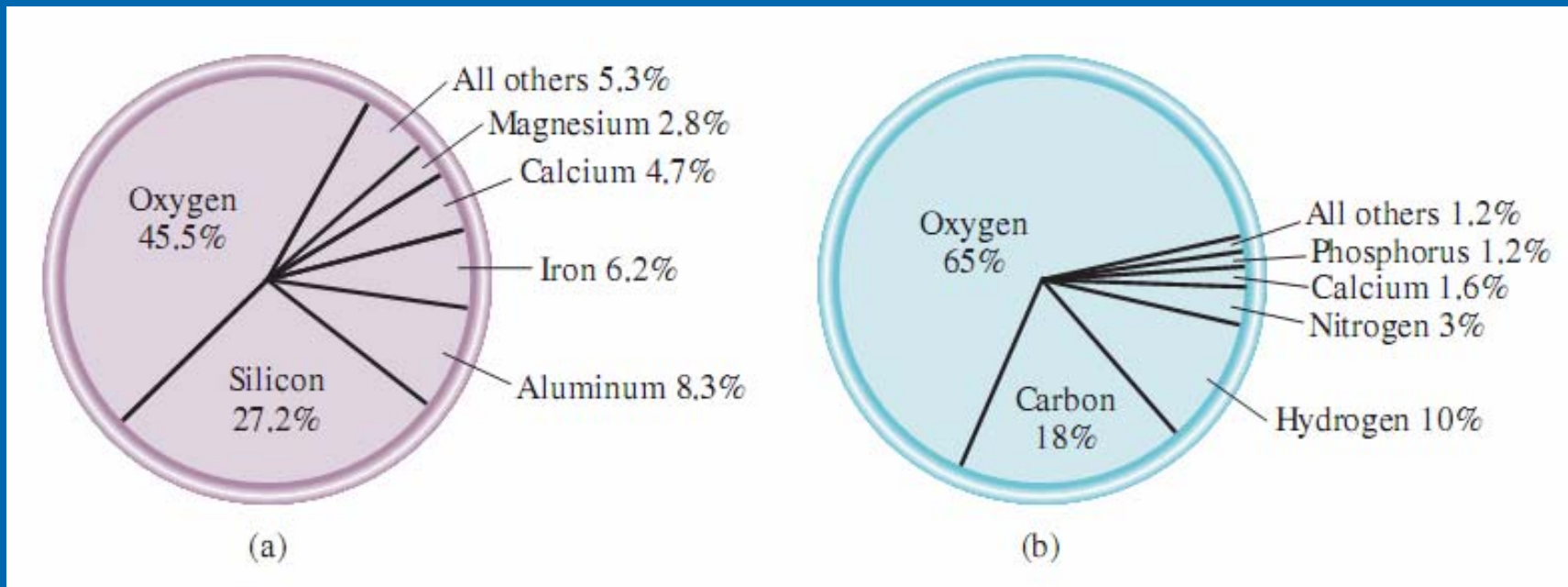√ according to importance for human and animal organisms (organogenic and biogenic).

Figure 2. Natural abundance of the elements .
(a) *Natural abundance of the elements in percent by mass.*
(b) *Abundance of elements in the human body in percent by mass.*

For example, oxygen's abundance is 45.5 percent. This means that in a 100 g sample of Earth's crust there are, on the average, 45.5 g of the element oxygen.

Classification of biogenic elements

√ **Chemical elements essential to life forms** can be broken down into four major categories:

    1) bulk elements (H, C, N, O, P, S);
    2) macrominerals (Na, K, Mg, Ca, Cl);
    3) trace elements (Fe, Zn, Cu);
    4) ultratrace elements, comprised of nonmetals (F, I, Se, Si, As, B) and metals (Mn, Mo, Co, Cr, V, Ni, Cd, Sn, Pb, Li).

√ **Biological essentiality of these elements has been defined by certain criteria**:

    1) a physiological deficiency appears when the element is removed from the diet;
    2) the deficiency is relieved by the addition of that element to the diet;
    3) a specific biological function is associated with the element.

Bioelements can be divided for physiological processes as following:

√ **Elements for physiological processes in bioliquids** (C, H, O, N, P, Cl, K, Na, Ca, Mg).

√ **Elements for metabolism** (Fe, Zn, Cu, Mo, Co, I).

Of special interest are the trace elements, such as iron (Fe), copper (Cu), zinc (Zn), iodine (I), and cobalt (Co), which together make up about 0.1 percent of the body's mass. These elements are necessary for biological functions such as growth, transport of oxygen for metabolism, and defense against disease. There is a delicate balance in the amounts of these elements in our bodies. Too much or too little over an extended period of time can lead to serious illness, retardation, or even death.

√ **Elements decreasing generation and growth of microorganisms** (As, Sb, Ag).

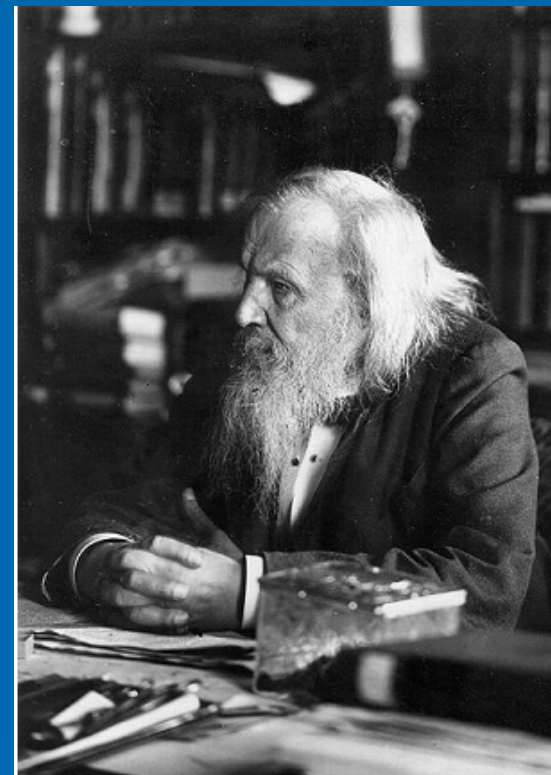√ **Elements for regulation of redox reactions** (Mn, Cu, Cr).

Periodic law and Periodic table

Recognition of periodic regularities in physical and chemical behavior and the need to organize the large volume of available information about the structure and properties of elements and their compounds **led to the development of the periodic law by Russian chemist D.I.Mendeleev.**

The modern periodic law: the physical and chemical properties of elements are **periodic functions of their atomic numbers**.

Visual expression of the periodic law is the *periodic table* – a chart in which elements having similar chemical and physical properties are grouped together.

Russian chemist
D.I.Mendeleev

The periodic table is a handy tool that correlates the properties of the elements in a systematic way and helps us to make predictions about chemical behavior.

IUPAC Periodic Table of the Elements

Key:

atomic number
Symbol
name
standard atomic weight

1																	18
1 **H** hydrogen 1.007 94(7)	2											13	14	15	16	17	2 **He** helium 4.002 602(2)
3 **Li** lithium 6.941(2)	4 **Be** beryllium 9.012 182(3)											5 **B** boron 10.811(7)	6 **C** carbon 12.0107(8)	7 **N** nitrogen 14.0067(2)	8 **O** oxygen 15.9994(3)	9 **F** fluorine 18.998 4032(5)	10 **Ne** neon 20.1797(6)
11 **Na** sodium 22.989 769 28(2)	12 **Mg** magnesium 24.3050(6)	3	4	5	6	7	8	9	10	11	12	13 **Al** aluminium 26.981 5386(8)	14 **Si** silicon 28.0855(3)	15 **P** phosphorus 30.973 762(2)	16 **S** sulfur 32.065(5)	17 **Cl** chlorine 35.453(2)	18 **Ar** argon 39.948(1)
19 **K** potassium 39.0983(1)	20 **Ca** calcium 40.078(4)	21 **Sc** scandium 44.955 912(6)	22 **Ti** titanium 47.867(1)	23 **V** vanadium 50.9415(1)	24 **Cr** chromium 51.9961(6)	25 **Mn** manganese 54.938 045(5)	26 **Fe** iron 55.845(2)	27 **Co** cobalt 58.933 195(5)	28 **Ni** nickel 58.6934(2)	29 **Cu** copper 63.546(3)	30 **Zn** zinc 65.409(4)	31 **Ga** gallium 69.723(1)	32 **Ge** germanium 72.64(1)	33 **As** arsenic 74.921 60(2)	34 **Se** selenium 78.96(3)	35 **Br** bromine 79.904(1)	36 **Kr** krypton 83.798(2)
37 **Rb** rubidium 85.4678(3)	38 **Sr** strontium 87.62(1)	39 **Y** yttrium 88.905 85(2)	40 **Zr** zirconium 91.224(2)	41 **Nb** niobium 92.906 38(2)	42 **Mo** molybdenum 95.94(2)	43 **Tc** technetium [98]	44 **Ru** ruthenium 101.07(2)	45 **Rh** rhodium 102.905 50(2)	46 **Pd** palladium 106.42(1)	47 **Ag** silver 107.8682(2)	48 **Cd** cadmium 112.411(8)	49 **In** indium 114.818(3)	50 **Sn** tin 118.710(7)	51 **Sb** antimony 121.760(1)	52 **Te** tellurium 127.60(3)	53 **I** iodine 126.904 47(3)	54 **Xe** xenon 131.293(6)
55 **Cs** caesium 132.905 4519(2)	56 **Ba** barium 137.327(7)	57-71 lanthanoids	72 **Hf** hafnium 178.49(2)	73 **Ta** tantalum 180.947 88(2)	74 **W** tungsten 183.84(1)	75 **Re** rhenium 186.207(1)	76 **Os** osmium 190.23(3)	77 **Ir** iridium 192.217(3)	78 **Pt** platinum 195.084(9)	79 **Au** gold 196.966 569(4)	80 **Hg** mercury 200.59(2)	81 **Tl** thallium 204.3833(2)	82 **Pb** lead 207.2(1)	83 **Bi** bismuth 208.980 40(1)	84 **Po** polonium [209]	85 **At** astatine [210]	86 **Rn** radon [222]
87 **Fr** francium [223]	88 **Ra** radium [226]	89-103 actinoids	104 **Rf** rutherfordium [261]	105 **Db** dubnium [262]	106 **Sg** seaborgium [266]	107 **Bh** bohrium [264]	108 **Hs** hassium [277]	109 **Mt** meitnerium [268]	110 **Ds** darmstadtium [271]	111 **Rg** roentgenium [272]							

57 **La** lanthanum 138.905 47(7)	58 **Ce** cerium 140.116(1)	59 **Pr** praseodymium 140.907 65(2)	60 **Nd** neodymium 144.242(3)	61 **Pm** promethium [145]	62 **Sm** samarium 150.36(2)	63 **Eu** europium 151.964(1)	64 **Gd** gadolinium 157.25(3)	65 **Tb** terbium 158.925 35(2)	66 **Dy** dysprosium 162.500(1)	67 **Ho** holmium 164.930 32(2)	68 **Er** erbium 167.259(3)	69 **Tm** thulium 168.934 21(2)	70 **Yb** ytterbium 173.04(3)	71 **Lu** lutetium 174.967(1)
89 **Ac** actinium [227]	90 **Th** thorium 232.038 06(2)	91 **Pa** protactinium 231.035 88(2)	92 **U** uranium 238.028 91(3)	93 **Np** neptunium [237]	94 **Pu** plutonium [244]	95 **Am** americium [243]	96 **Cm** curium [247]	97 **Bk** berkelium [247]	98 **Cf** californium [251]	99 **Es** einsteinium [252]	100 **Fm** fermium [257]	101 **Md** mendelevium [258]	102 **No** nobelium [259]	103 **Lr** lawrencium [262]

IUPAC – International Union of Pure and Applied Chemistry

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Periodic Table of elements: the 1-18 group designation has been recommended by the IUPAC

Periodic Table

√ *In modern periodic table* the elements are arranged by atomic number in horizontal rows called ***periods*** and in vertical columns known as ***groups or families***, according to similarities in their chemical properties.

√ All elements can be divided into three categories – metals, nonmetals, and metalloids.

√ Elements are often referred collectively by their group number (Group 1A, Group 2A, and so on). However, for convenience, some element groups have been given special names.

Group 1A elements (Li, Na, K, Rb, Cs, and Fr) are called **alkali metals.**

Group 2A elements (Be, Mg, Ca, Sr, Ba, and Ra) are called **alkaline earth metals.**

Elements in Group 7A (F, Cl, Br, I, and At) are known as **halogens.**

Elements in Group 8A (He, Ne, Ar, Kr, Xe, and Rn) are called **noble gases (or rare gases).**

Three important atomic properties

The fitness of an element for ***a biological role*** is a consequence of ***electronic structure***.

We now need to understand how electronic structure affects atomic and ionic radii, and the thermodynamic ability of an atom to release or acquire electrons to form ions or chemical bonds.

Three important atomic properties:

√ the atomic and ionic radii,
√ the ionization energy,
√ and the electron affinity.

These properties are of great significance in chemistry and biology, for they are controls on the number and types of chemical bonds the atom can form.

Indeed, we can use these properties to reveal an important reason for the unique role of carbon in biology.
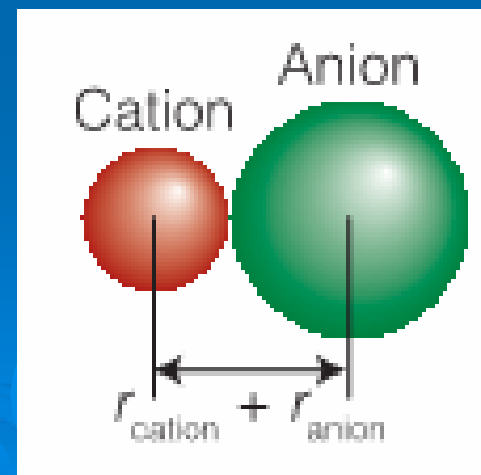
Atomic and ionic radii

The atomic radius of an element is half the distance between the centers of neighboring atoms in a solid (such as Cu) or, for nonmetals, in a homonuclear molecule (such as H_2 or S_8).

If there is one single attribute of an element that determines **its chemical properties** (either directly, or indirectly through the variation of other properties), then it is **atomic radius**.

In general, **atomic radii decrease from left to right across a period and increase down each group.**

The ionic radius of an element is its share of the distance between neighboring ions in an ionic solid. That is, the distance between the centers of a neighboring cation and anion is the sum of the two ionic radii.

Atomic and ionic radii

Table lists the radii of some ions that play important roles in biochemical processes.

Ion	Main biochemical function	r/pm
Mg^{2+}	Binds to ATP, constituent of chlorophyll, control of protein folding and muscle contraction	72
Ca^{2+}	Component of bone and teeth, control of protein folding, hormonal action, blood clotting, and cell division	100
Na^+		102
K^+	Control of osmotic pressure, charge balance, and membrane potentials	138
Cl^-		167

Ionization energy

The minimum energy necessary to remove an electron from a many-electron atom is its *first ionization energy*, I_1. *The second ionization* energy, I_2, is the minimum energy needed to remove a second electron (from the singly charged cation):

$$E(g) \rightarrow E^+(g) + e^-(g) \qquad I_1 = E(E^+) - E(E)$$

$$E^+(g) \rightarrow E^{2+}(g) + e^-(g) \qquad I_2 = E(E^{2+}) - E(E^+)$$

The ionization energy of an element plays a central role in determining the ability of its atoms to participate in bond formation.

After atomic radius, it is the most important property for determining an element's chemical characteristics.

Electron affinity

The electron affinity, E_{ea}, is the difference in energy between a neutral atom and its anion.

It is the energy released in the process

$$E(g) + e^-(g) \rightarrow E^-(g) \quad E_{ea} = E(E) - E(E^-)$$

The electron affinity is positive if the anion has a lower energy than the neutral atom.

Further analysis of ionization energies and electron affinities can begin to tell us *why carbon is an essential building block of complex biological structures*.

Among the elements in Period 2, C has *intermediate values of the ionization energy and electron affinity*, so it can share electrons (that is, form covalent bonds) with many other elements, such as H, N, O, S, and, more importantly, other C atoms.

As a consequence, such networks as long carbon–carbon chains (as in lipids) and chains of peptide links can form readily. Because the ionization energy and electron affinity of C are neither too high nor too low, the bonds in these covalent networks are neither too strong nor too weak.

As a result, biological molecules are sufficiently stable to form viable organisms but are still susceptible to dissociation (essential to catabolism) and rearrangement (essential to anabolism).

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Chemical bond

Atoms of most elements can interact with one another **to form compounds.**

The forces that hold these atoms together in compounds are called **chemical bonds.**
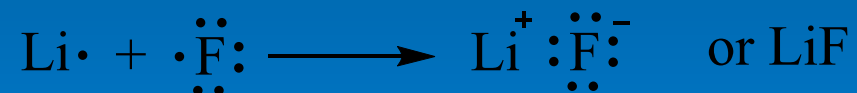
When atoms interact to form a chemical bond, only their outer electronic shells are in contact. For this reason, when we study chemical bonding, we are concerned with **the valence electrons of the atoms**.

! ! ! In general, the bonding of the atoms lowers the potential energy of the reacting particles. As the electron configuration and the strength of the nucleus-electron attraction determine the properties of an atom, the type and strength of chemical bonds determine the properties of a forming substance.

Ionic bond

An ***ionic bond*** is the electrostatic force that holds ions together in an ionic compound.

For example, the reaction between lithium and fluorine to form lithium fluoride. The electronic configuration of lithium is $1s^22s^1$, and that of fluorine is $1s^22s^22p^5$. When lithium and fluorine atoms come in contact with each other, the outer $2s^1$ valence electron of lithium is transferred to the fluorine atom. After this process the ions with stable electronic configurations are formed. The lithium cation (Li^+) has electronic configuration like helium atom, $1s^2$; the fluorine anion (F^-) – like neon, $1s^22s^22p^6$. The ionic bond in LiF is formed by the electrostatic attraction between the positively charged lithium ion and the negatively charged fluoride ion. The compound itself is electrically neutral.

$$Li\cdot \; + \; \cdot \ddot{\underset{\cdot\cdot}{F}}\colon \longrightarrow \; Li^+ \; \colon\ddot{\underset{\cdot\cdot}{F}}\colon^- \quad \text{or LiF}$$

$$Ca\colon \; + \; \cdot\ddot{\underset{\cdot\cdot}{O}}\cdot \longrightarrow \; Ca^+ \; \colon\ddot{\underset{\cdot\cdot}{O}}\colon^- \quad \text{or CaO}$$

Ionic bond

Ionic bonding occurs between elements when the energy required to remove the outer shell electrons (the ionization energy) of one of reacting elements is relatively low. ***Elements with such low ionization energies are metals. Non-metals*** generally contain more than three electrons in the outer shells of their atoms and ***have high tendency to accept electrons from another atoms***. ***Consequently substances formed by typical metals and nonmetals are ionic.***

In the formation of an ionic compound such as LiF or CaO, it is not only the electron transfer leads to formation of a stable substance. *Much more energy lowering value corresponds to the process of interaction of the gaseous ions giving a crystalline solid.*

The *lattice energy* is defined as *the energy needed to separate the ions in one mole of a solid substance to give a gaseous ions*. For example, this value for NaF equals 910 kJ/mol, for NaCl: 788 kJ/mol, for CsI: 613 kJ/mol.

The lattice energy indicates the strength of ionic interactions, which influences melting point, hardness, solubility, and other properties of ionic crystalls.
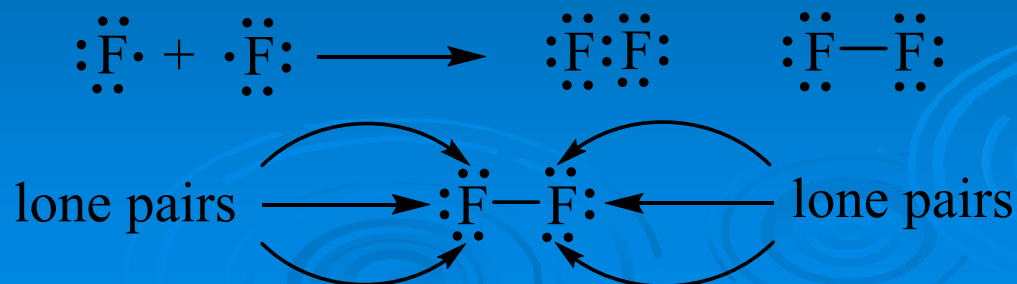
Covalent bond

When *two or more non-metals combine their atoms have to share electrons forming common electronic pair* and achieving the stable electronic configuration of a noble gas. This type of bonding is called *covalent bonding.*

So, in this type of chemical bond *two electrons are shared by two atoms.*

For the simplicity, the shared pair of electrons is often represented in the molecule by a single line. Thus, the covalent bond in the hydrogen molecule can be written as H–H, in hydrogen chloride molecule as H–Cl.

In a covalent bond, each electron in a shared pair is attracted to the nuclei of both atoms. This attraction holds the two atoms in the molecule together and is responsible for the formation of covalent bonds in other molecules. ❗ *Covalent bonding between many-electron atoms involves only the valence electrons.*

$$:\ddot{F}\cdot \; + \; \cdot\ddot{F}: \longrightarrow \;:\ddot{F}\!:\!\ddot{F}: \quad :\ddot{F}\!-\!\ddot{F}:$$

lone pairs $\longrightarrow :\ddot{F}\!-\!\ddot{F}: \longleftarrow$ lone pairs

Covalent bond

If two atoms are held together by one electron pair, the bond is called **a *single* bond**.

Sometimes, more than one pair of electrons is shared. For example, oxygen gas molecule, O_2. Here, each oxygen shares two pairs of electrons to achieve the electron configuration of neon. The structural formula of oxygen molecule is written as O = O.

If two atoms share two pairs of electrons, the covalent bond is called **a *double* bond**. Double bonds exist in molecules of carbon dioxide and ethylene. In a molecular structure, where three pairs of electrons are shared, the bond is called **a *triple* bond**, for example in nitrogen molecule, N_2.

$$H-\ddot{O}-H \qquad \ddot{O}=C=\ddot{O} \qquad \begin{matrix} H & & H \\ & C=C & \\ H & & H \end{matrix} \qquad :N\equiv N:$$
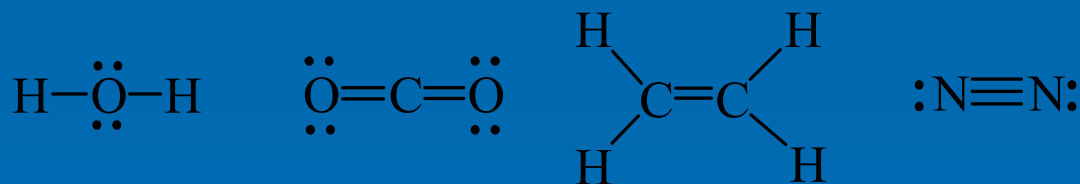
! For the predicting whether compounds are ionic or covalent we use general rule:
metal + non-metal $\rightarrow$ ionic bonding,
non-metal + non-metal $\rightarrow$ covalent bonding.

Electronegativity of the elements and the type of the bond

In a molecule like H$_2$, in which the atoms are identical, the electrons to be equally attracted by two hydrogen nucleus. However, if we have the <u>covalently bonded HF molecule</u>, the H and F atoms <u>do not share the bonding electrons equally</u>, because H and F atoms are characterized by different ability to attract electrons. **The bond in HF is called a *polar covalent bond***, because the electrons are shifted in the vicinity of the fluorine atom.

<u>A property of atoms that helps us distinguish a nonpolar covalent bond from a polar covalent bond is **electronegativity**</u>, **!** *the ability of an atom to attract toward itself the electrons in a chemical bond*.

An atom such as **fluorine**, which has a high electron affinity (tends to pick up electrons easily) and **a high ionization energy** (does not lose electrons easily), **has a high electronegativity**. On the other hand, **sodium** **has a low electron affinity**, **a low ionization energy, and a low electronegativity.**

Electronegativity

Electronegativity is a relative value, showing that an element's electronegativity can be measured only in relation to the electronegativity of other elements.

L. Pauling proposed a method for calculating relative electronegativities of most elements. These values are shown in Table. *There is no sharp distinction between a polar covalent bond and an ionic bond*, but **the following general rule** is helpful in distinguishing between them: **an ionic bond forms when the electronegativity difference between the two bonding atoms is 1.7 or more.**

Increasing electronegativity

Increasing electronegativity

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
H 2.1																	
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe 2.6
Cs 0.7	Ba 0.9	La-Lu 1.0-1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.2	
Fr 0.7	Ra 0.9																

Coordination compounds

A complex ion is an ion containing *a central metal cation* bonded to *one or more molecules or ions*. Complex ions are crucial to many chemical and biological processes.

Transition metals have a particular tendency to form complex ions because they have *incompletely filled d-subshells*.

This property enables them to act effectively in reactions with many molecules or ions that serve as electron donors.

For example, a solution of cobalt (II) chloride is pink because of the presence of the $Co(H_2O)_6^{2+}$ ions. When HCl is added, the solution turns blue as a result of the formation of **the complex ion $CoCl_4^{2-}$:**

$$Co^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq)$$

Coordination compounds

A coordination compound typically consists of a complex ion and counter ion. [Note that some coordination compounds such as $Fe(CO)_5$ do not contain complex ions.]

Our understanding of the nature of coordination compounds stems from the classic work of Alfred Werner*, who prepared and characterized many coordination compounds. In 1893, at the age of 26, Werner proposed what is now commonly referred to as Werner's coordination theory.

The valences of the elements in cobalt (III) chloride and in ammonia seem to be completely satisfied, and yet these two substances react to form a stable compound having the formula $CoCl_3 \cdot 6NH_3$. To explain this behavior, Werner postulated that most elements exhibit *two types of valence*: *primary valence and secondary valence*.

In modern terminology, *primary valence corresponds to the oxidation number* and *secondary valence to the coordination number of the element*. In $CoCl_3 \cdot 6NH_3$, according to Werner, cobalt has a primary valence of 3 and a secondary valence of 6.

* *Alfred Werner (1866–1919). Swiss chemist. Werner started as an organic chemist but became interested in coordination chemistry. For his theory of coordination compounds, Werner was awarded the Nobel Prize in Chemistry in 1913.*

Coordination compounds

Today we use the formula $[Co(NH_3)_6]Cl_3$ to indicate that the ammonia molecules and the cobalt atom form *a complex ion*; the chloride ions are not part of the complex but are held to it by ionic forces. Most, but not all, of the metals in coordination compounds are transition metals.

The molecules or ions that surround the metal in a complex ion are called ***ligands***. Every ligand has at least *one unshared pair* of valence electrons, as these examples show:
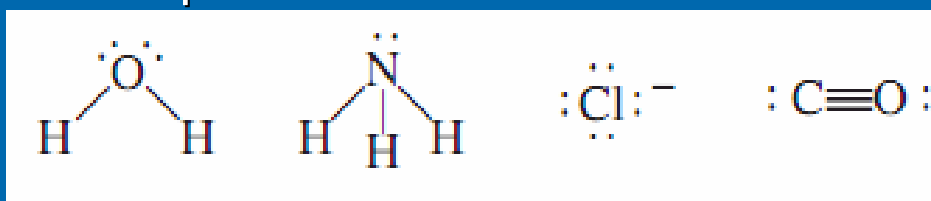
Thus, the metal-ligand bonds are usually *coordinate covalent bonds*. The atom in a ligand that is bound directly to the metal atom is known as the *donor atom*. *For example, nitrogen is the donor atom in the $[Cu(NH_3)_4]^{2+}$ complex ion.*

The coordination number in coordination compounds is defined as the number of donor atoms surrounding the central metal atom in a complex ion. *For example, the coordination number of Ag^+ in $[Ag(NH_3)_2]^+$ is 2, that of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[Fe(CN)_6]^{3-}$ is 6.*

The most common coordination numbers are 4 and 6, but coordination numbers such as 2 and 5 are also known.

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Coordination compounds

Depending on the number of donor atoms present, *ligands are classified as*
√ monodentate,
√ bidentate,
√ polydentate.

Bidentate and polydentate ligands are also called ***chelating agents*** because of their ability to hold the metal atom like a claw (from the Greek chele, meaning "claw").

One example is ethylenediamine-tetraacetate ion (EDTA), a polydentate ligand used to treat metal poisoning (Figure 3). Six donor atoms enable EDTA to form a very stable complex ion with lead. In this form, it is removed from the blood and tissues and excreted from the body. EDTA is also used to clean up spills of radioactive metals.
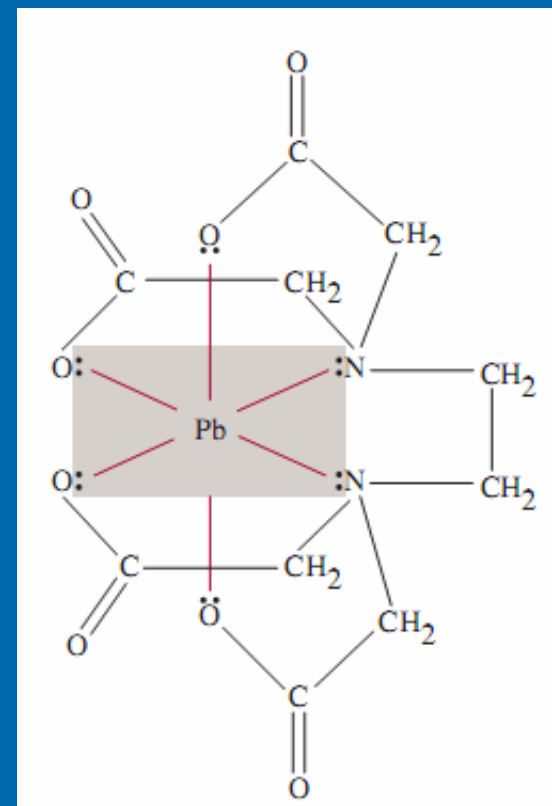
Figure 3. EDTA complex of lead. The complex bears a net charge of -2 because each O donor atom has one negative charge and the lead ion carries two positive charges. Only the lone pairs that participate in bonding are shown. Note the octahedral geometry around the Pb^{2+} ion.

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Coordination compounds

Another important property of coordination compounds is *the oxidation number of the central metal atom*. The net charge of a complex ion is the sum of the charges on the central metal atom and its surrounding ligands. In the $[PtCl_6]^{2-}$ ion, for example, each chloride ion has an oxidation number of -1, so the oxidation number of Pt must be +4. If the ligands do not bear net charges, the oxidation number of the metal is equal to the charge of the complex ion. Thus, in $[Cu(NH_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of Cu is +2.

Naming Coordination Compounds

The rules for naming coordination compounds are as follows:

1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compound, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ cations first, respectively.

2. Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.

3. The names of anionic ligands end with the letter *o*, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H_2O (aqua), CO (carbonyl), and NH_3 (ammine). Table lists some common ligands.

Ligand	Name of Ligand in Coordination Compound
Bromide, Br^-	Bromo
Chloride, Cl^-	Chloro
Cyanide, CN^-	Cyano
Hydroxide, OH^-	Hydroxo
Oxide, O^{2-}	Oxo
Carbonate, CO_3^{2-}	Carbonato
Nitrite, NO_2^-	Nitro
Oxalate, $C_2O_4^{2-}$	Oxalato
Ammonia, NH_3	Ammine
Carbon monoxide, CO	Carbonyl
Water, H_2O	Aqua
Ethylenediamine	Ethylenediamine
Ethylenediaminetetraacetate	Ethylenediaminetetraacetato

4. When several ligands of a particular kind are present, we use the Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* to name them. Thus, the ligands in the cation $[Co(NH_3)_4Cl_2]^+$ are "tetraamminedichloro." (Note that prefixes are ignored when alphabetizing ligands.) If the ligand itself contains a Greek prefix, we use the prefixes *bis* (2), *tris* (3), and *tetrakis* (4) to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di; therefore, if two such ligands are present the name is bis(ethylenediamine).

5. The oxidation number of the metal is written in Roman numerals following the name of the metal. For example, the Roman numeral III is used to indicate the +3 oxidation state of chromium in $[Cr(NH_3)_4Cl_2]^+$, which is called tetraamminedichlorochromium (III) ion.

6. If the complex is an anion, its name ends in -ate. For example, in $K_4[Fe(CN)_6]$ the anion $[Fe(CN)_6]^{4-}$ is called hexacyanoferrate (II) ion. Note that the Roman numeral II indicates the oxidation state of iron. Table gives the names of anions containing metal atoms.

The *inner sphere* of the complexes are shown in the brackets, the outside of brackets – *outer sphere*.

The names of anions containing metal atoms:

Metal	Name of Metal in Anionic Complex
Aluminum	Aluminate
Chromium	Chromate
Cobalt	Cobaltate
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Manganese	Manganate
Molybdenum	Molybdate
Nickel	Nickelate
Silver	Argentate
Tin	Stannate
Tungsten	Tungstate
Zinc	Zincate

Structure of Coordination Compounds

In studying the geometry of coordination compounds, we often find that there is more than one way to arrange ligands around the central atom. Compounds rearranged in this fashion have distinctly different physical and chemical properties.

Figure 4 shows four different geometric arrangements for metal atoms with monodentate ligands.
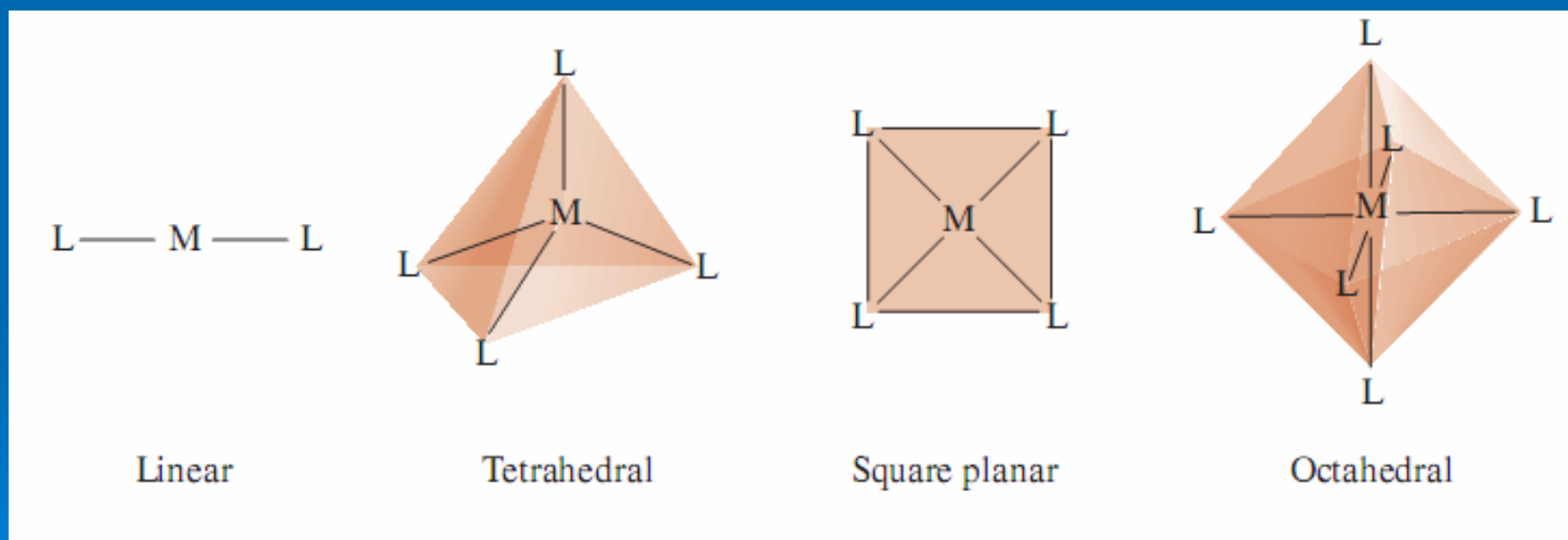
Figure 4.   Common geometries of complex ions.
In each case, M is a metal and L is a monodentate ligand.

In these diagrams, we see that <u>structure and coordination number</u> of the metal atom relate to each other as follows:

Coordination number	Structure
2	Linear
4	Tetrahedral or square planar
6	Octahedral

Stereoisomers are compounds that are made up of the same types and numbers of atoms bonded together in the same sequence but with different spatial arrangements.

There are two types of stereoisomers: geometric isomers and optical isomers. Coordination compounds may exhibit one or both types of isomerism.

Note, however, that many coordination compounds do not have stereoisomers.

Geometric Isomers

   Geometric isomers are stereoisomers that cannot be interconverted without breaking a chemical bond. Geometric isomers usually come in pairs. We use the terms '*cis*' and '*trans*' to distinguish one geometric isomer of a compound from the other.

   Cis means that two particular atoms (or groups of atoms) are adjacent to each other, and *trans* means that the atoms (or groups of atoms) are on opposite sides in the structural formula. The *cis* and *trans* isomers of coordination compounds generally have quite different colors, melting points, dipole moments, and chemical reactivities.
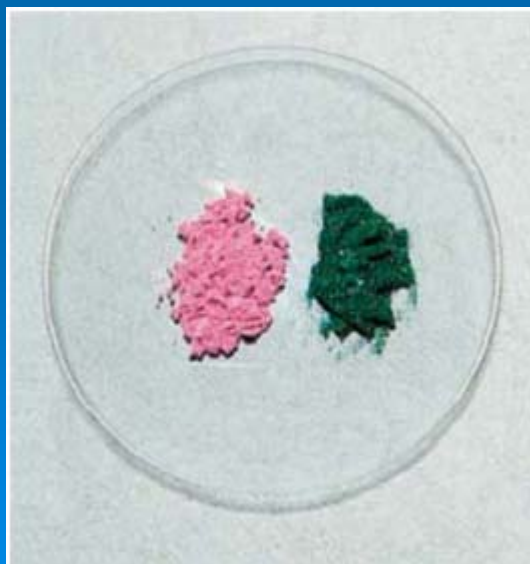
cis-tetraamminedichlorocobalt (III) chloride (left) and
trans-tetraamminedichlorocobalt (III) chloride (right)

Note that although the types of bonds are the same in both isomers (two Pt—N and two Pt—Cl bonds), the spatial arrangements are different.

Figure 5 shows the cis and trans isomers of diamminedichloroplatinum (II).
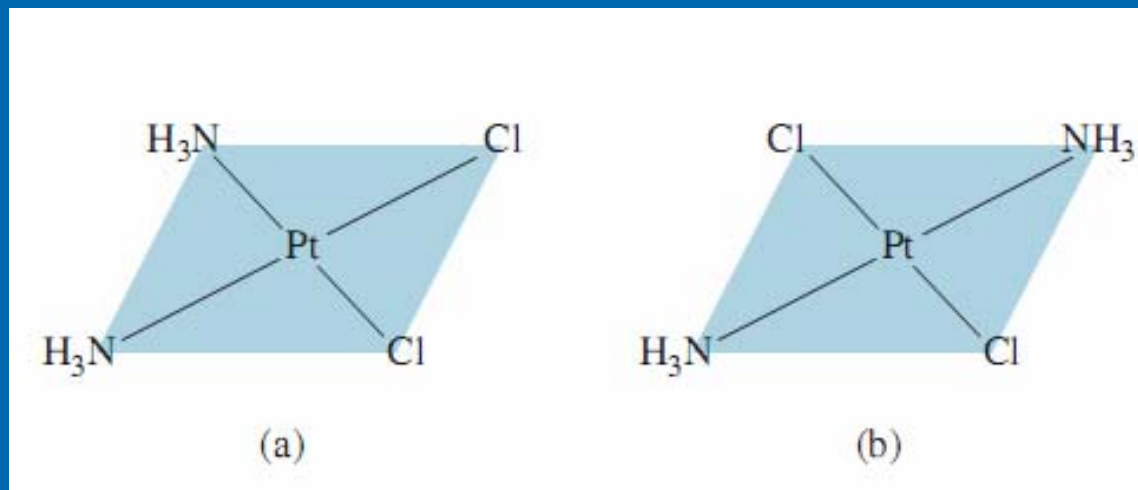
Figure 5. The (a) *cis* and (b) *trans* isomers of diamminedichloroplatinum (II).

Note that the two Cl atoms are adjacent to each other in the *cis* isomer and diagonally across from each other in the *trans* isomer.

Optical isomers

Optical isomers are nonsuperimposable mirror images. ("Superimposable" means that if one structure is laid over the other, the positions of all the atoms will match.)

Like geometric isomers, optical isomers come in pairs. However, the optical isomers of a compound have identical physical and chemical properties, such as melting point, boiling point, dipole moment, and chemical reactivity toward molecules that are not optical isomers themselves. Optical isomers differ from each other in their interactions with plane-polarized light.

Figure 6 shows the cis and trans isomers of dichlorobis(ethylenediamine)cobalt (III) ion and their images. Careful examination reveals that the trans isomer and its mirror image are superimposable, but the cis isomer and its mirror image are not. *Therefore, the cis isomer and its mirror image are optical isomers.*
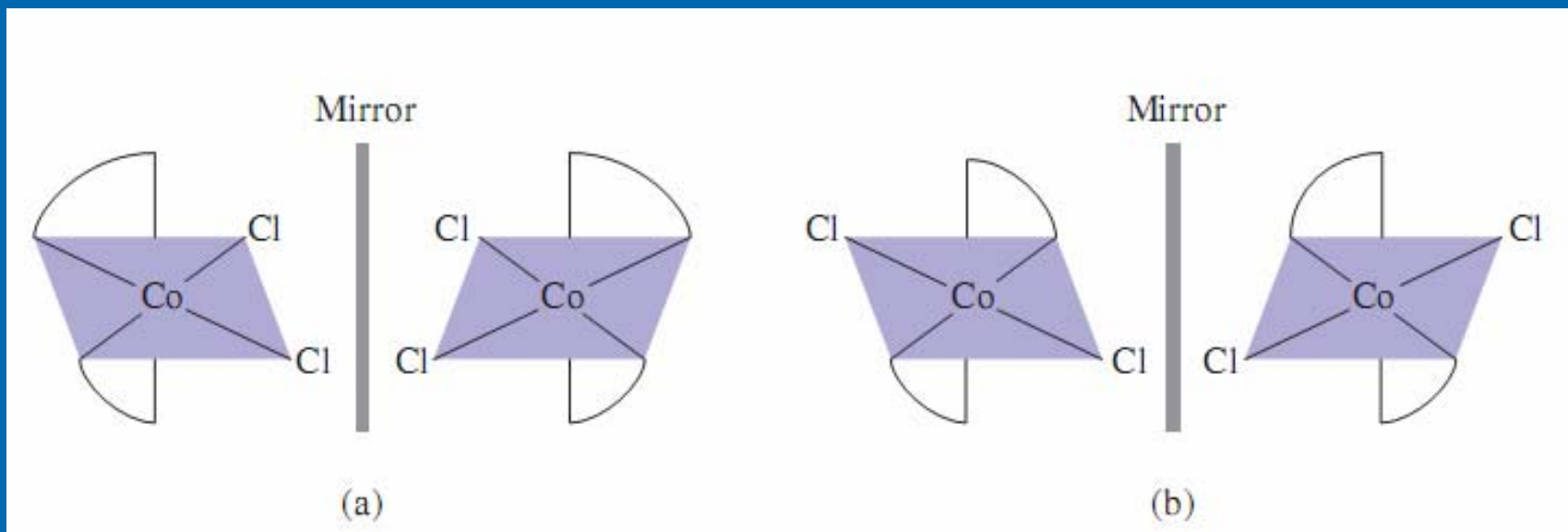
Figure 6. The (a) cis and (b) trans isomers of dichlorobis(ethylenediamine)cobalt (III) ion and their mirror images.

If you could rotate the mirror image in (b) 90° clockwise about the vertical position and place the ion over the trans isomer, you would find that the two are superimposable.

No matter how you rotated the cis isomer and its mirror image in (a), however, you could not superimpose one on the other.

Stability constants

Thermodynamic stability of complex ion can be characterized by _stability_ or _formation constant_ which is a thermodynamic property and may be determined in terms of equilibrium species concentrations. In general the complexation process may be described by stepwise formation process as shown (charges omitted for the simplicity):

$$M + L \rightarrow ML,$$
$$ML + L \rightarrow ML_2,$$
$$ML_2 + L \rightarrow ML_3.$$
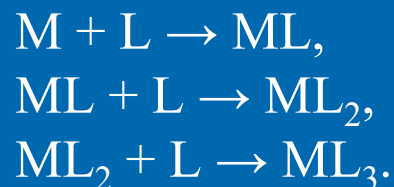
For these steps stability constants is determined by the expressions:

$$K_1 = \frac{[ML]}{[M][L]} \qquad K_2 = \frac{[ML_2]}{[ML][L]} \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

For the overall process of ML3 formation
$$M + 3L \rightarrow ML_3,$$

$$\beta_3 = \frac{[ML_3]}{[M][L]^3}$$

the _overall stability constant_ is used

$$\beta_3 = K_1 \cdot K_2 \cdot K_3$$

Coordination compounds
in living systems

Coordination compounds play important roles in the living on the Earth. They are essential in the storage and transport of oxygen, as electron transfer agents and as parts of enzymes, etc. As a ligands in these compounds may be present different organic molecules: carbohydrates and polysaccharides, aminoacids and proteins, nucleotides and nucleic acids.

Amino acids contain a central carbon, called theacarbon, to which a hydrogen atom and three substituent groups are attached: the amine group ($–NH_2$), a carboxylic acid group ($–COOH$), a side chain ($–R$) group is unique for each amino acid. The general formula of amino acids is

$$H_2N-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-COOH$$
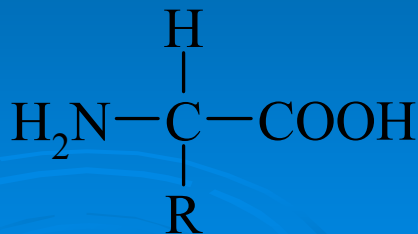
Amino acids and their derivatives as ligands

Polypeptides are formed through the polymerization of any combination of the 20 naturally occurring amino acids. Relatively short polypeptide chains have important hormonal functions in biological species.

Proteins are classified as polypeptide chains exceeding 50 amino acids in length, whereas *enzyme* molecules usually contain more than 100 amino acid residues.
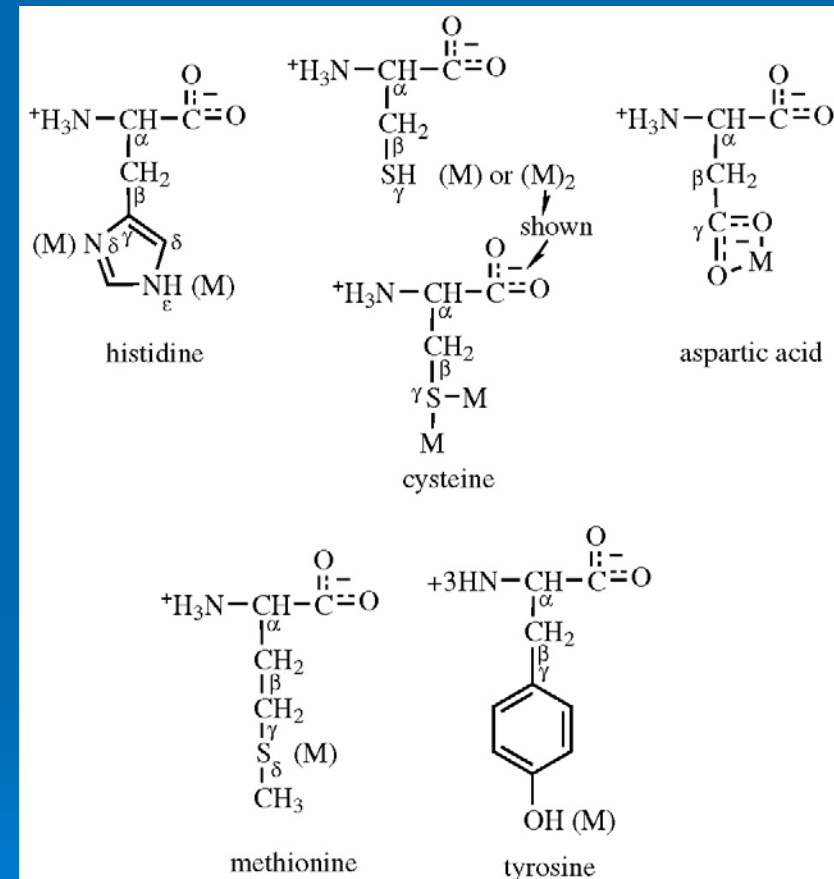
Metal ion bonding modes to amino acid residues in proteins

Nucleic acids and their derivatives as ligands

Nucleic acids may be divided on two groups: ribonucleic acids (RNA) and deoxyribonucleic acid (DNA).

Nucleic acids are polymeric molecules formed by nucleotides.

The nucleotide molecule includes nitrogenous base, sugar, and phosphate unit.

Nitrogenous base plus sugar moiety are called nucleosides.
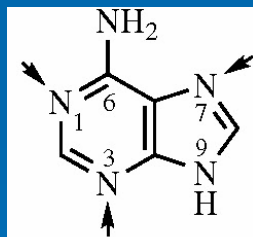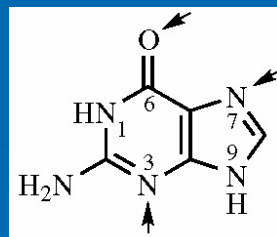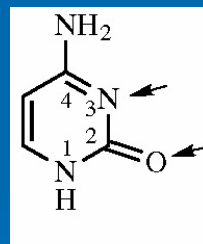
Adenine, A   Guanine, G   Cytosine, C   Uracil, U   Thymine, T
5-Methyl uracil
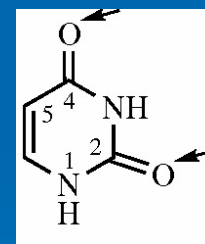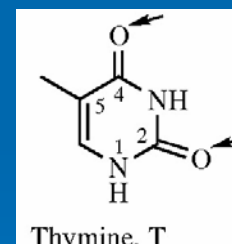
Nitrogenous bases of nucleic acids, common metal binding sites on nucleobases are indicated by arrows.

Nucleic acids and their derivatives as ligands
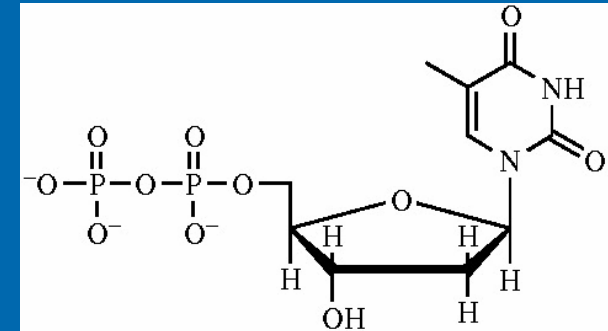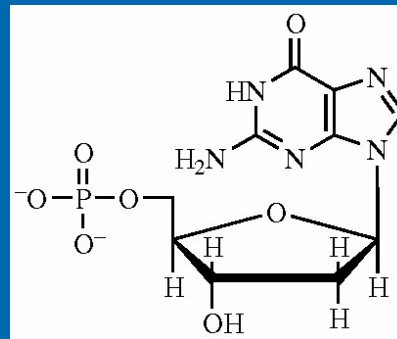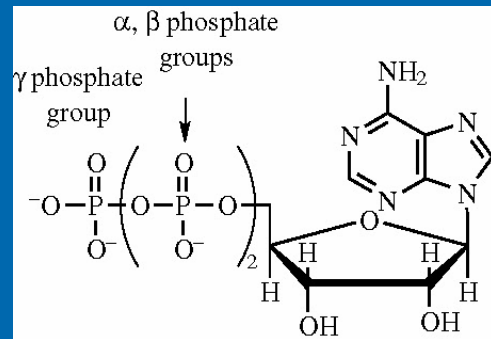
Nucleotides: adenosine triphosphate (ATP), deoxyguanosine monophosphate (dGMP) and deoxythymidine diphosphate (dTDP)
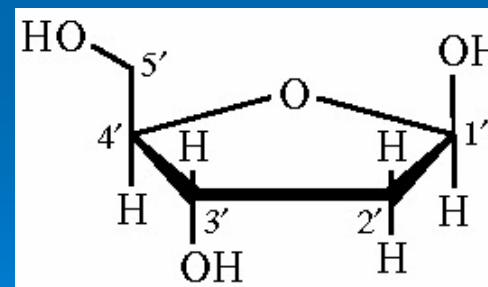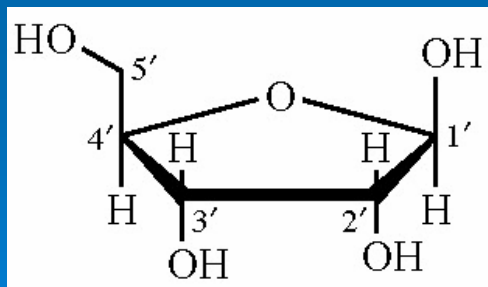

Ribose and deoxyribose

# Coordination compounds of Fe in living systems

The *porphine molecule* forms an important part of the hemoglobin structure. Upon coordination to a metal, the H^+ ions that are bonded to two of the four nitrogen atoms in porphine are displaced. Complexes derived from porphine are called *porphyrins*, and the iron-porphyrin combination is called the *heme* group. The iron in the heme group has an oxidation number of +2; it is coordinated to the four nitrogen atoms in the porphine group and also to a nitrogen donor atom in a ligand that is attached to the protein. The sixth ligand is a water molecule, which binds to the Fe^{2+} ion on the other side of the ring to complete the octahedral complex.


Porphine Fe^{2+}-porphyrin

(a)   (b)   (c)
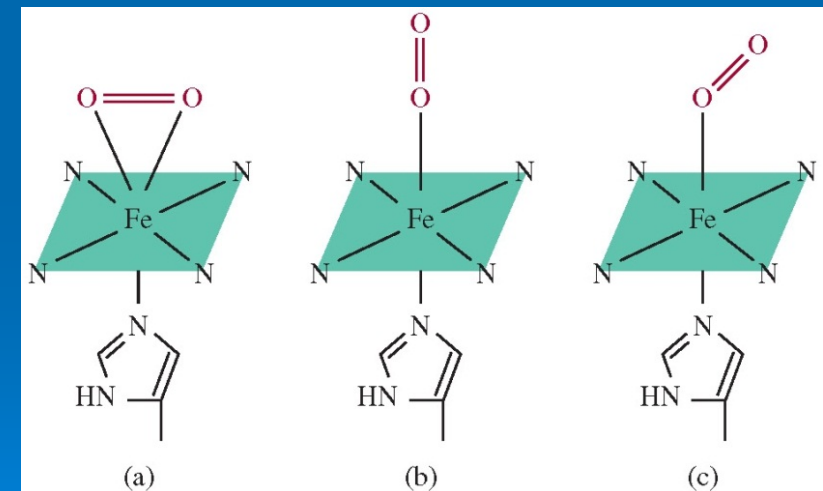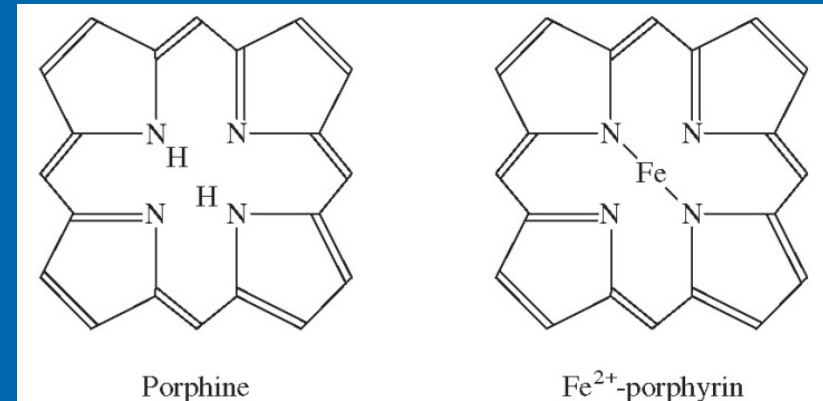
Possible ways for molecular oxygen to bind to the heme group in hemoglobin

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Coordination compounds of Fe and Mg in living systems

The heme group in hemoglobin. The Fe^{2+} ion is coordinated with four N atoms of the porfirine cycle and nitrogen atom of the heme group. The ligand below the porphyrine is the histidine group, which is attached to the protein. The sixth ligand is a water molecule.
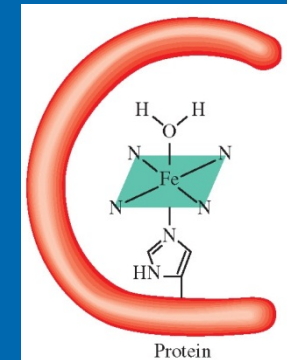
The heme group in cytochrome c. The ligands above and below the porphyrin are the methionine group and histidine group of the protein, respectively.
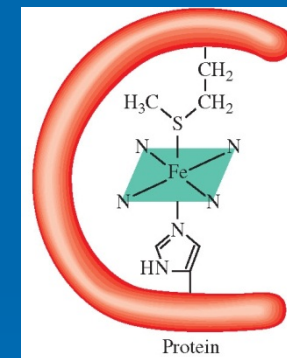
The *chlorophyll molecule*, which is necessary for plant photosynthesis, also contains the porphyrin ring, but in this case the metal ion is Mg^{2+} rather than Fe^{2+}.

The porphyrin structure in chlorophyll. The dotted lines indicate the coordinate covalent bonds. The electron-delocalized portion of the molecule is shown in color.

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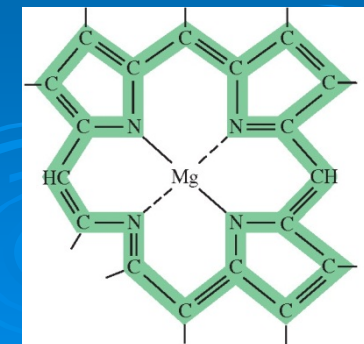
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