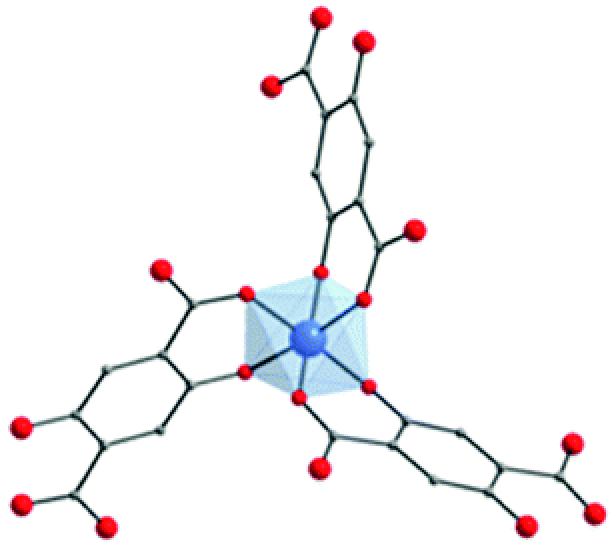


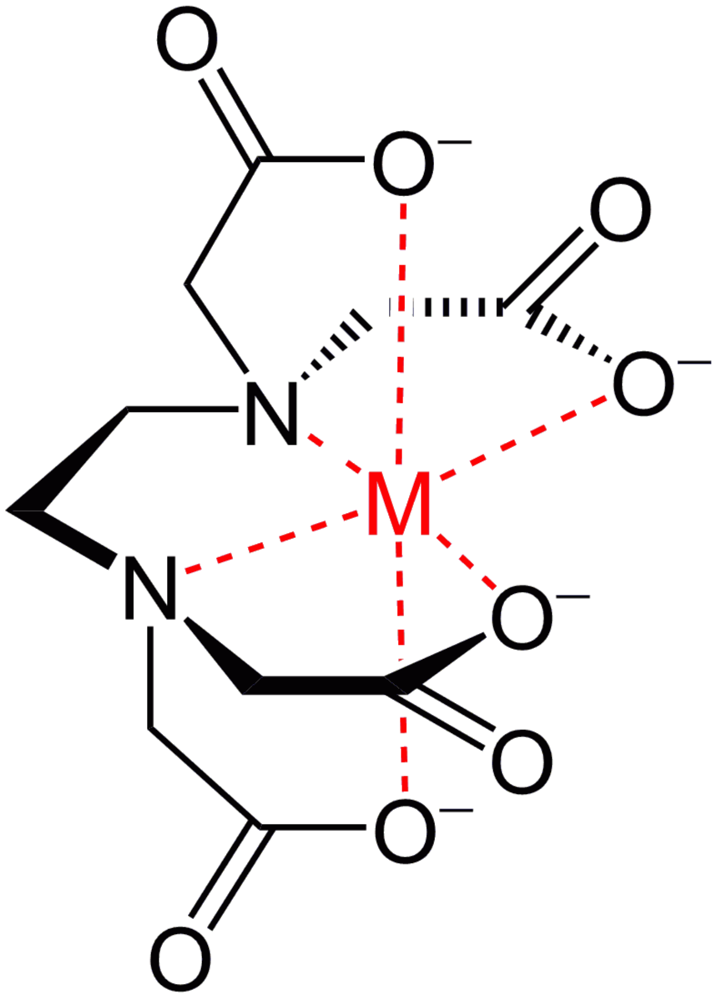
Coordination compounds

Lecture №5

Lecturer: aassistant of the Department of Biochemistry of “Professor V.F. Voino-Yasenetsky Krasnoyarsk State Medical University”
Darya Rudenko

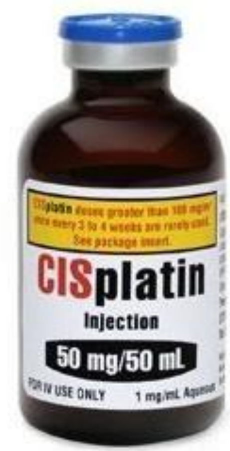
AIM

- To give an idea of the structure of coordination compounds, their role in the body, as well as their use as medicines



RELEVANCE

- **Coordination compounds** are extremely widespread in living and inanimate nature, used in industry, agriculture, science, and medicine.
- **Chlorophyll** is a complex compound of magnesium with porphyrins
- **Hemoglobin** contains an iron (II) complex with porphyrin rings. Numerous minerals are usually coordination compounds of metals.
- A significant number of drugs contain metal complexes as pharmacologically active substances, for example, **insulin** (zinc complex), **vitamin B12** (cobalt complex), **platinum** (platinum complex), etc.



ALFRED WERNER (1866 – 1919)

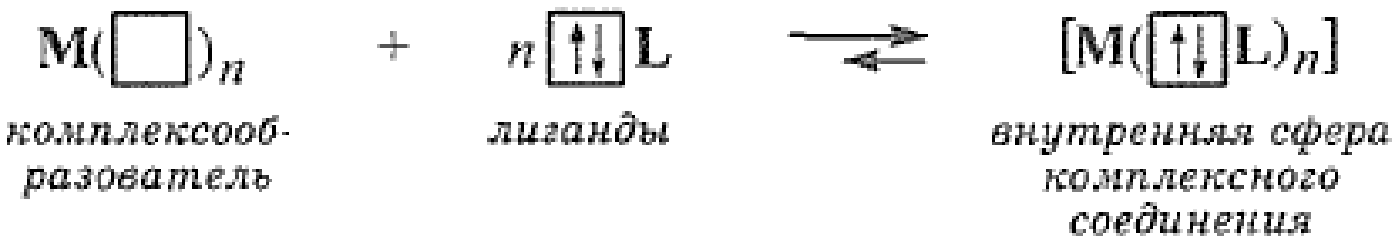
- Founder of the coordination theory of complex compounds.
- For his work in this area, he was awarded the Nobel Prize in Chemistry in 1913.

PLAN:

- **Basic definitions:** coordination compounds (CC), complexing agent, ligand, coordination number, denticity of ligands.
- **Complex charge** and oxidation state of the complexing agent.
- **Nomenclature** of complex compounds.
- **Electrons and geometric** configurations of some CC.
- **CC stability** constants.
- **Intracomplex compounds** are chelates.
- **The role of CC** in biology and medicine.

BASIC DEFINITIONS

- **Coordination compounds** are stable chemical compounds of complex composition, in which there is at least one connection arising from a donor - acceptor mechanism

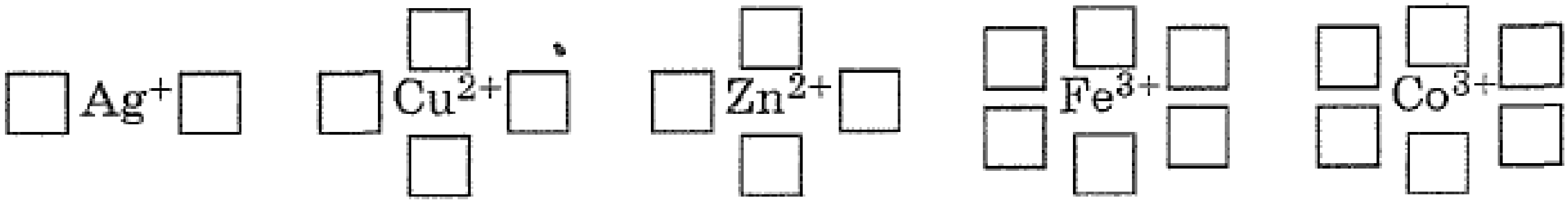


- **Complexing agent (central atom)** is an atom or ion that is an acceptor of electron pairs, providing free atomic orbitals and occupies a central position in a complex compound

The complexing agent and ligands constitute the inner sphere of the complex, more often charged with + or -. The outer sphere of the complex will be formed by counterions, which are ionically bonded to the inner sphere.

COMPLEXING AGENT

- The role of a complexing agent (CO) is played by elements whose atoms have vacant AOs **(d- and f-metals)**



- The coordination number (c.n.) is the number of free atomic orbitals provided by the complexing agent. Usually c.n. equal to twice the charge of the complexing ion. The most characteristic coordination numbers are 2,4,6.

Complexing agent	Coordination number
Ag^{+}	2
Cu^{2+}, Zn^{2+}	4
Fe^{3+}, Co^{3+}	6

COMPLEXATION ABILITY

according to the ability to complexation, metal cations can be arranged in the following order:

1) **transition metals**(M)
2) **alkaline earth metals** (Mg^{2+}, Ca^{2+})
3) **alkaline metals** (Na^{+} , K+)

- The complexation capacity of metals varies according to the Irving-Williams series:

$Ca^{2+} < Mg^{2+} < Mn^{2+} < Fe^{2+} < Cd^{2+} < Co^{2+} < Zn^{2+} < Ni^{2+} < Cu^{2+}$

- **Ligands are** molecules or ions that are donors of electron pairs and are directly bound to the complexing agent.

- The ligands are elements whose atoms have electron pairs or mobile π-electron pairs:

ligand anions

F^-, фторид; Cl^-, хлорид; Br^-, бромид; I^-, иодид; OH^-, гидроксид; NO_2^-, нитрит

CN^-, цианид; CNS^-, роданид; RS^-, тиолат; $RCOO^-$ карбоксилат

ligand molecules

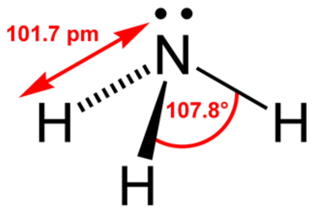
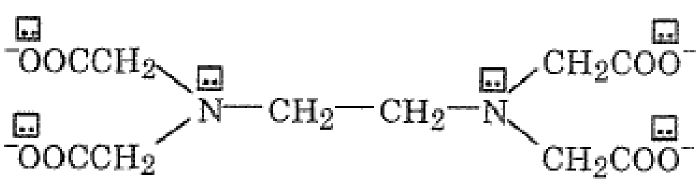
H_2O, вода; ROH, спирты; $R{-}O{-}R$, эфиры; CO, монооксид углерода

NH_3, аммиак; RNH_2, $RNHR$, амины; $RCH{=}CH_2$, $RC{\equiv}CH$ этиленовые и ацетиленовые углеводороды (за счет электронных пар π-связей)

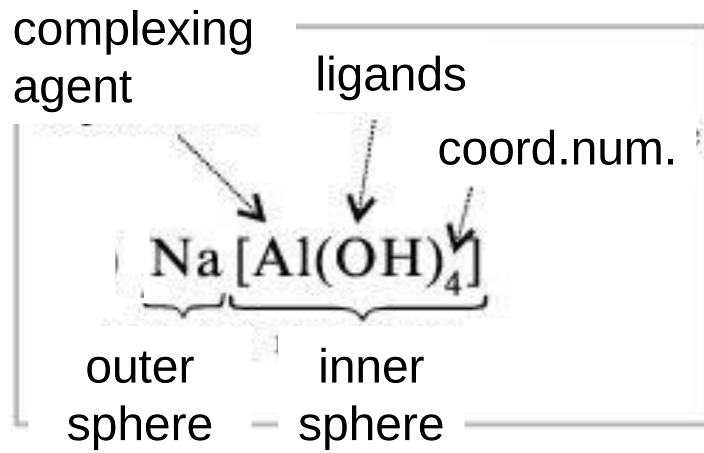
LIGAND CLASSIFICATION

(by the number of bonds formed)

Dentity is the number of bonds that a ligand forms with a complexing agent.

Ligands	The number of bonds formed	Examples
Monodentate	1 (donors of one electron pair)	
Bidentate	2 (donors of two electron pairs)	
Polydentate	>2	 Ethylenediaminetetraacetic acid

The inner sphere of a CC is a collection central atom and ligands linked by donor-acceptor bonds



- The inner sphere is highlighted with square brackets: $[NH_4]Cl$, $K_3[Fe(CN)_6]$.
- The charge of the inner sphere is equal to the sum charges of a complexing agent and ligands.

Inner sphere	Examples	Charges
Cation «+»	$[Cu(NH_3)_4]$	**z** = +2 + 4·0 = +2 $[Cu(NH_3)_4]^{2+}$
Anion«-»	$[Fe(CN)_6]$	**z** = +3 + 6·(-1) = -3 $[Fe(CN)_6]^{3-}$
Electrically neutral «0»	$[Fe(CO)_5]$	**z** = 0 + 5·(0) = 0 $[Fe(CO)_5]^0$

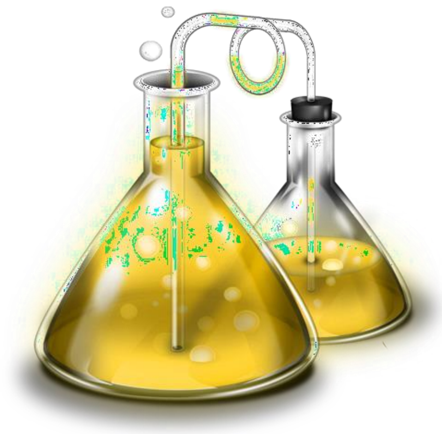
OUTER SPHERE OF CC

The charge of the inner sphere is compensated by the ions of the outer sphere

- **The outer sphere** of the complex compound is positively or negatively charged ions, neutralizing the charge of the complex ion and associated by ionic bond.

Cation CC	**Anion CC**	**Neutral CC**
inner sphere / outer sphere $[Cu(NH_3)_4]SO_4$ внутренняя сфера | Внешняя сфера	$Ca_3[Fe(CN)_6]$ Внешняя сфера | внутренняя сфера	$[Pt(NH_3)_2Cl_2]$ внутренняя сфера

PROPERTIES OF COMPLEX COMPOUNDS



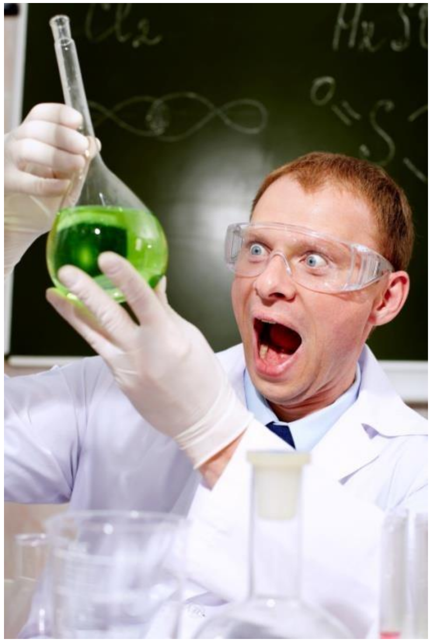
- **Dissociation in solutions**

1) The primary dissociation of a complex compound is the decomposition of a complex compound in solution into complex ion of the inner sphere and ions of the outer sphere (breaking of the ionic bond):

$$[Ag(NH_3)_2]Cl \rightarrow [Ag(NH_3)_2]^+ + Cl^-$$

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

2) Secondary dissociation of a complex compound - this is the disintegration of the inner sphere of the complex into its constituent components (breaking a covalent bond) is very difficult!



$[Ag(NH_3)_2]^+ \leftrightarrows [Ag(NH_3)]^+ + NH_3$ 1st step

$[Ag(NH_3)]^+ \leftrightarrows Ag^+ + NH_3$ 2nd step

NOMENCLATURE COMPLEX CONNECTIONS

- When compiling the names of complex compounds, the anion is indicated first, and then the cation in the genitive case.
- Complex cation name:
- The numbers (2-di, 3-three, 4-tetra, 5-penta, 6-hexa) and the names of negatively charged ligands with the ending "o" (Cl^- - chloro, CN^- -
- cyano, etc.), then indicate the numbers and names of neutral ligands
- (water - aqua, ammonia - ammine).
- The complexing agent is called.
- A Roman numeral indicates the oxidation state of the complexing agent in brackets

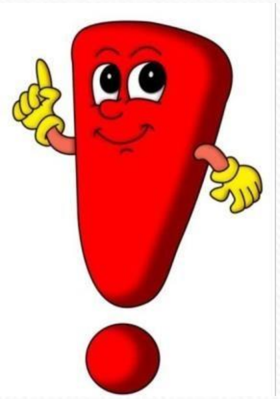
Formula	Name
$[Ag(NH_3)_2]Cl$	Diamminesilver chloride (I)
$[Zn(H_2O)_4]SO_4$	Tetraaquazinc sulfate(II)
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate (III)
$K_2[PtCl_4]$	Potassium tetrachloroplatinate (II)

STABILITY OF CC

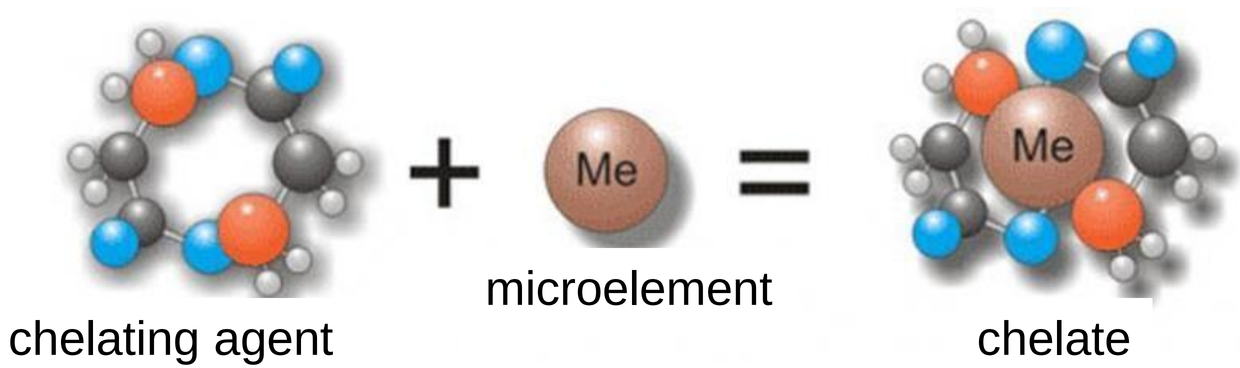
- To quantitatively characterize the stability of the inner sphere of the complex compound, the equilibrium constant is used the constant of instability of the CC (K inst/ K нест):

$$[Ag(NH_3)_2]^+ \rightleftarrows Ag^+ + 2NH_3 \qquad K_{нест} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

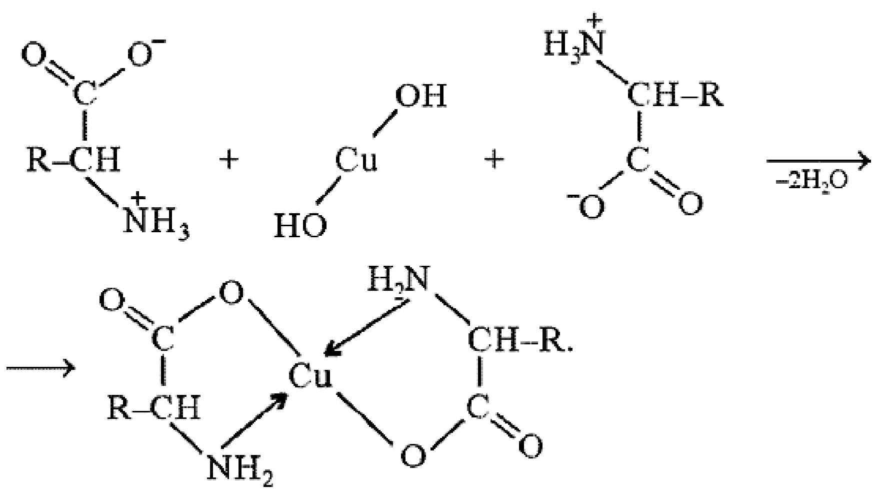
- The lower K inst, the more stable the inner sphere of the complex, the less it dissociates in an aqueous solution.
- To bind ions from a solution, it is extremely effective to use the complexation reaction.

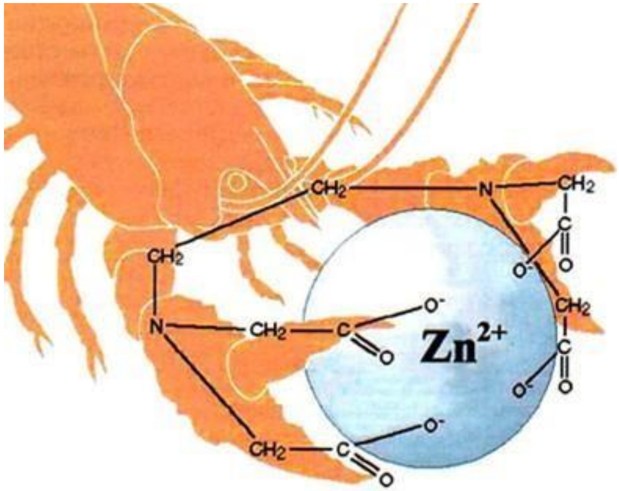


- **Chelates (from Lat. Chela - claw)** are stable metal complexes with polydentate ligands, in which the central atom is a component of the cyclic structure.



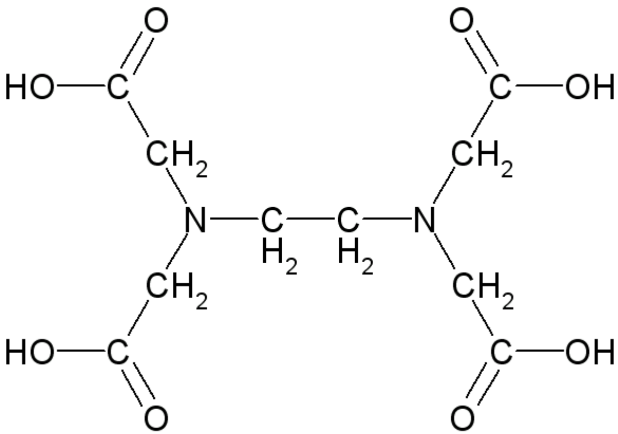
- **Amino acid chelating complex:**



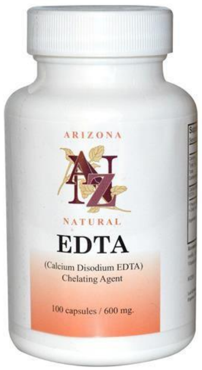


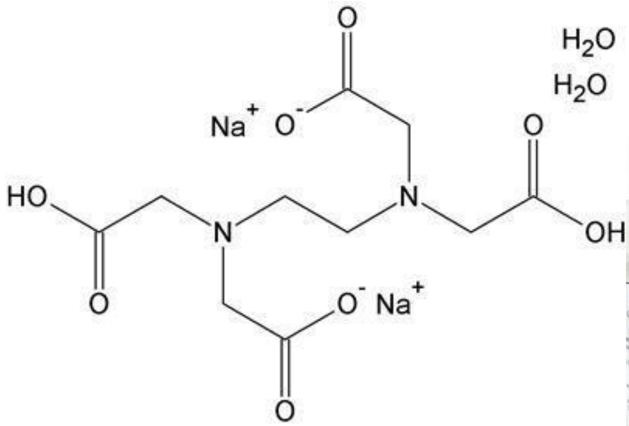
ETHYLENEDIAMINETETRAACETIC ACID (EDTA) AND TRILON B.

- Ethylenediaminetetraacetic acid (EDTA) and its disodium salt Trilon B are some of the most effective chelating ligands.



EDTA





$Na_2EDTA{\cdot}2H_2O$

•**EDTA** forms stable complexes with almost all metal cations, except for alkaline ones.

•Used in analytical practice to determine the content of metal ions.

•**EDTA** **in medicine:**

•a detoxifier to remove radioactive and toxic heavy metals from the body.

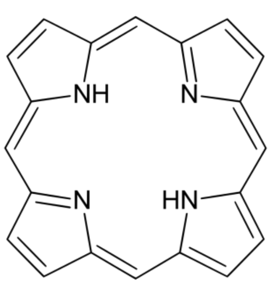
•for blood preservation

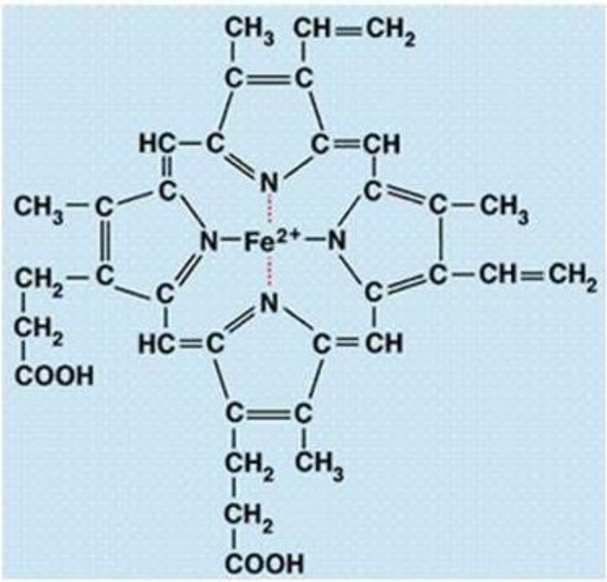
•antidote for hydrocyanic acid poisoning.

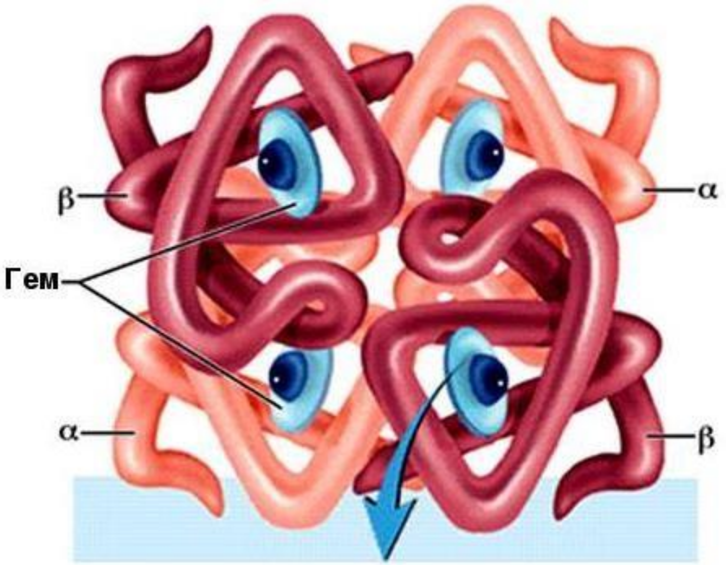
NATURAL COMPLEXES WITH MACROCYCLIC LIGANDS

- **Hemoglobin** is a complex iron-containing protein of animals with blood circulation, capable of reversibly binding with oxygen, ensuring its transfer to tissues. In vertebrates, it is contained in erythrocytes.

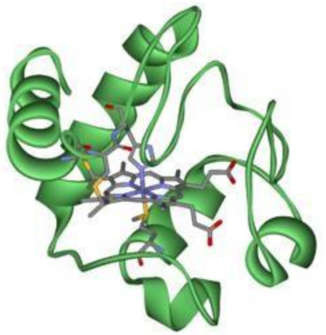
Hemoglobin is a complex compound of iron (II) with porphyrins



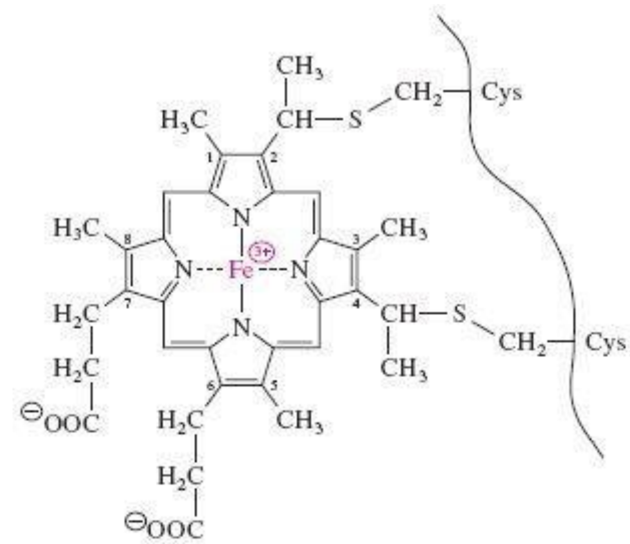




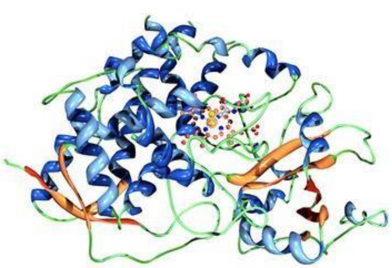
NATURAL COMPLEXES WITH MACROCYCLIC LIGANDS



- **Cytochromes (hemoproteins)** are small globular proteins that contain a covalently bound heme located in an internal "pocket" of amino acid residues.
- **Cytochromes are present in all cells of organisms.**
- Cytochromes catalyze ORR.

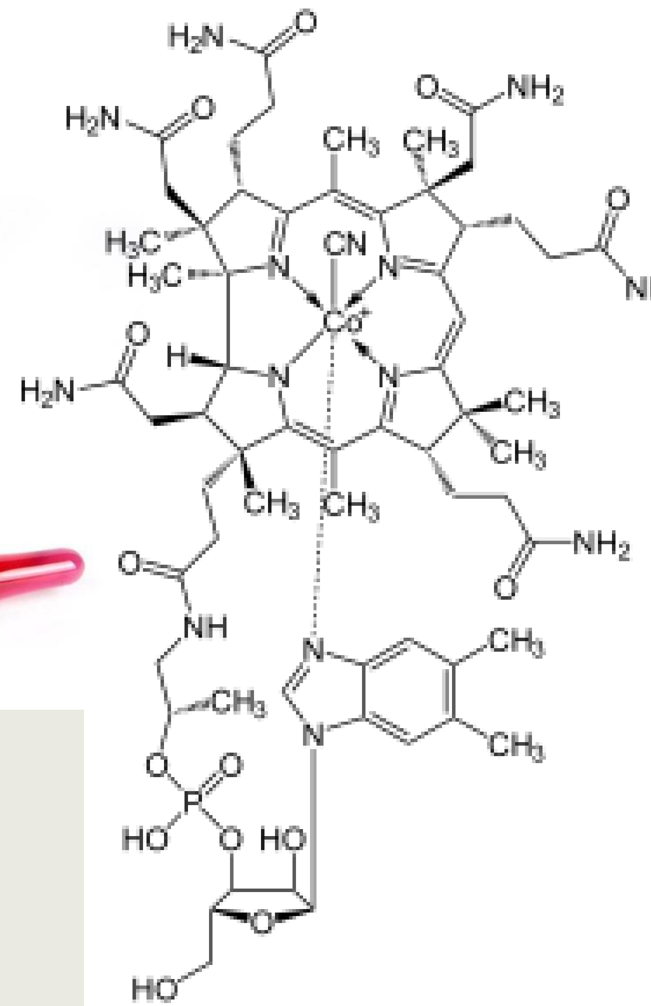


Cytochrome *c* heme group



NATURAL COMPLEXES WITH MACROCYCLIC LIGANDS

- **Vitamin B12** has the most complex structure in comparison with other vitamins, the basis of which is the corrin ring.

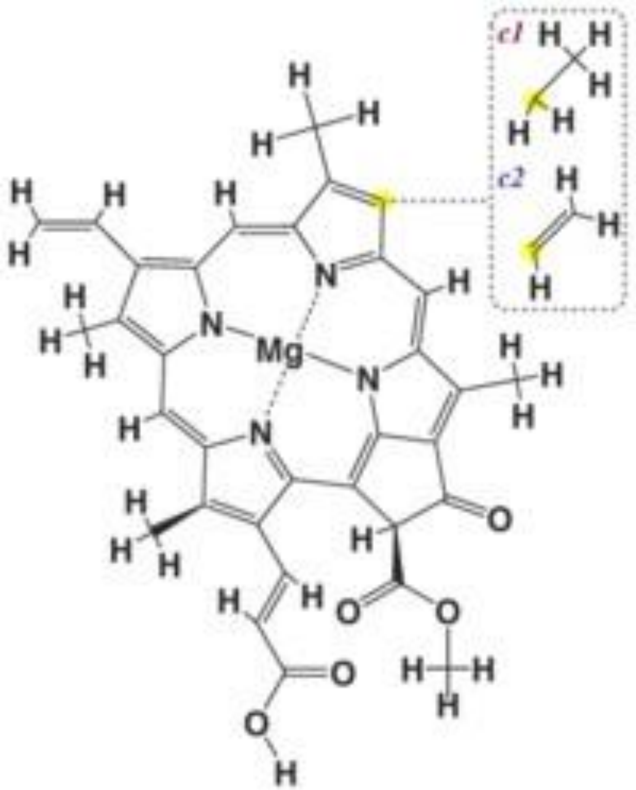


•Vitamin B12 deficiency is the cause of some types of anemia.
•Neither animals nor plants are able to synthesize vitamin B12.
•Synthesized by microorganisms: bacteria,
•actinomycetes.
•Of the animal tissues, the liver and kidneys are the richest in vitamin B12, where it accumulates.

Vitamin B12 is a cobalt complex

NATURAL COMPLEXES WITH MACROCYCLIC LIGANDS

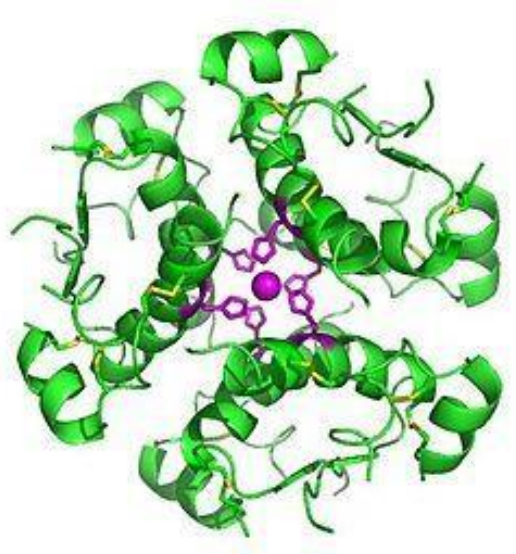
- **Chlorophyll** is a green pigment that causes plant chloroplasts to turn green. With his participation, the process of photosynthesis is carried out.



Chlorophyll is a complex compound of magnesium with porphyrins

A significant number of drugs contain metal complexes as pharmacologically active substances

- **Insulin is a peptide hormone.** It has a multifaceted effect on metabolism in almost all tissues.
- The main action of insulin is to lower the concentration of glucose in the blood.



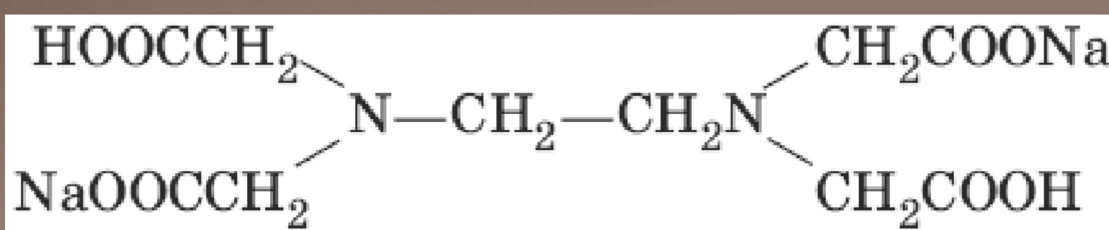
Insulin in drug form is a zinc complex

COMPLEXOMETRY

COMPLEXOMETRY

This is a quantitative analysis method based on the complexation reaction to obtain strong chelate compounds of metals with chelator

Chelators are polydentate ligands capable of forming stable chelated complex compounds.



Trilon B is a chelator in analytical practice

Complexometry is widely used in sanitary and clinical analysis for the quantitative determination of metal ions.

DETERMINATION OF WATER HARDNESS

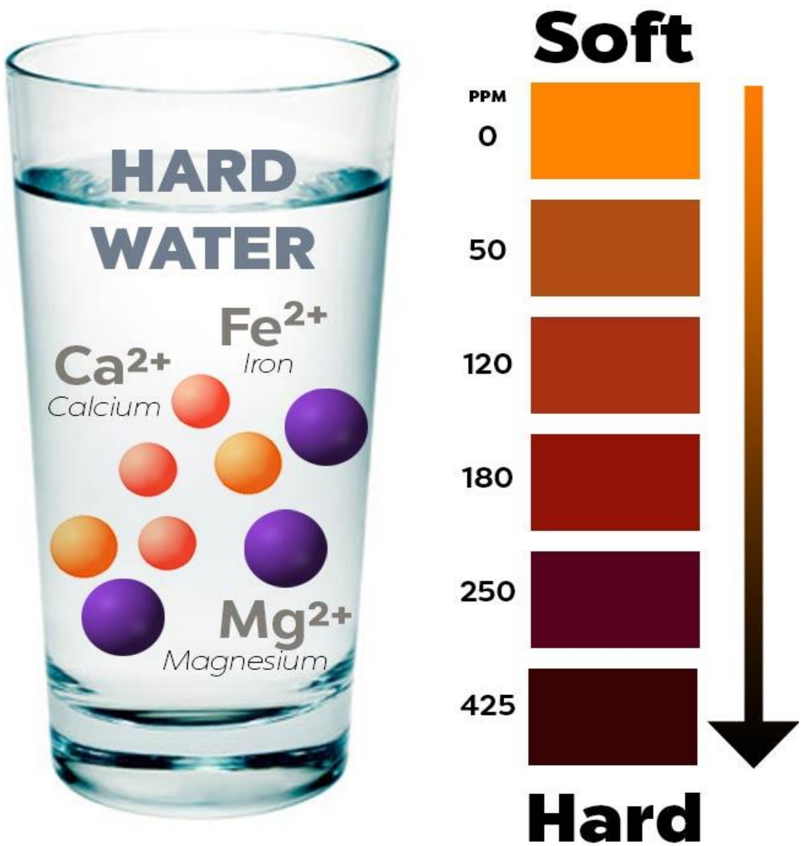
- **Water hardness** is a set of chemical and physical properties of water associated with the content of dissolved salts of alkaline earth metals in it, mainly calcium and magnesium **(the so-called "hardness salts").**

Water hardness

TEMPORARY (carbonate) hardness due to the presence $Ca(HCO_3)_2$, $Mg(HCO_3)_2$

CONSTANT (non-carbonate) hardness due to the presence $CaSO_4$, $CaCl_2$, $MgSO_4$, $MgCl_2$

Total water hardness



1 dH corresponds to the concentration of the alkaline earth element, numerically equal to 1/2 of its millimole per liter **(1** dH **= 1 milligram equivalent in liter).**

Water Hardness Scale		
mg/L & ppm as CaCO3	dH	Classification
0 - 75	0 - 4	Soft
75 -150	4 - 8.5	Slightly Hard
150 - 300	8.5 - 17	Hard
300+	17+	Very Hard

Complexometric determination of water hardness

1. Measure 100 ml of the investigated H2O into a conical flask.
2. Add 5 ml of the ammonia-buffer mixture to the water, then 7-8 drops of an alcohol solution of the indicator of eriochrome black T.
3. Mix thoroughly, the solution turns wine-red.
4. Titrate the mixture with 0.05 e solution of Trilon B until blue.
5. Determine the volume of Trilon B consumed for titration.
6. Repeat titration 3 times.
7. Calculate the total water hardness (dH).

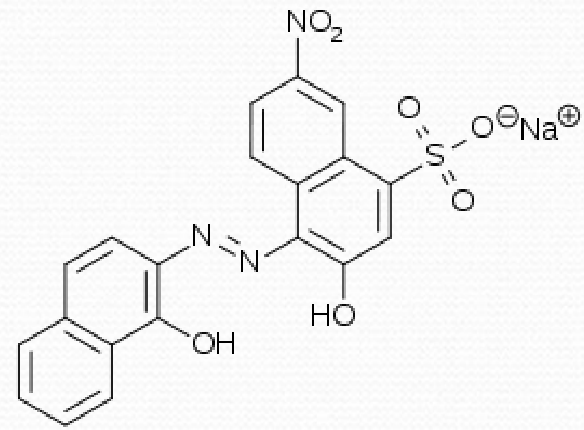
$$\mathbf{dH} = \frac{Cэ(Trilon\ B)\cdot V(Trilon\ B)\cdot 1000}{V(H_2O)}$$

COLOR CHANGE OF H_2O SAMPLE DURING TITRATION:

hardness cations are present

approximation to an equivalence point

equivalence point (metal cations are complexed)



- **Eriochrome black T** is used as a complexometric indicator for the determination of Mg, Mn, Pb, Zn, Cd ions
- At pH 9.5-10.0 it has a **blue color**, and its complexes with calcium, magnesium and zinc ions under the same conditions are **red-violet**