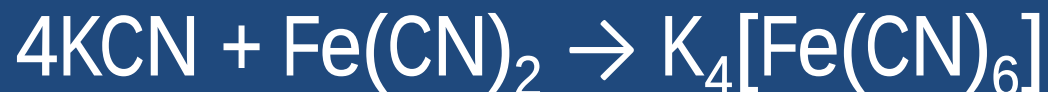
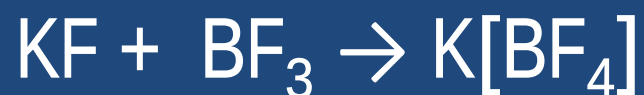
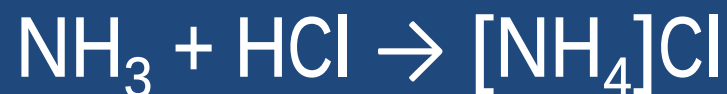


Complex (Coordination) Compounds

Common chemical compounds are built according to the rules of valence: NH_3 , H_2O , HCl and so on. These compounds are relatively simple.

They can react with each other producing more complex compounds.



Such compounds got the name of complex (coordination) compounds.

Complex compounds

are the compounds where in the nodes of their lattice there are complex ions or neutral complex particles, which can exist either in solutions or in fluxes.

The reactions in the result of which these complex compounds are formed are called the *complexation reactions*.

The first theory of the structure of complex compounds was devised by Alfred Verner in 1893.

The constituent parts of $K_4[Fe(CN)_6]$,
the structure of complex:

Inner sphere

Outer sphere



**Central
atom (CA)**

Ligands

**Coordination
number (CN)**

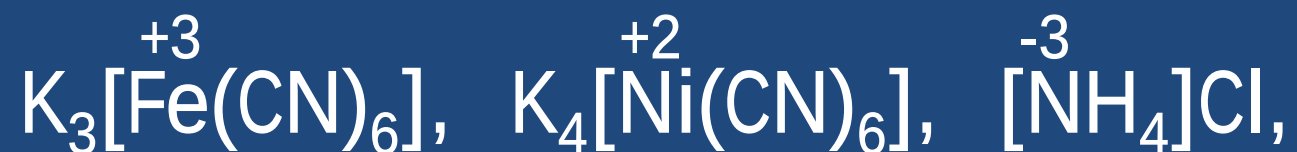
We should differentiate the inner coordination sphere and the outer sphere.

The inner coordination sphere is the aggregate of the central atom (complex former) and the ligands (molecules or ions). The charge of the inner sphere equals the algebraic sum of the charges of the central atom and the ligands. The inner sphere or a complex are enclosed in brackets.

The number of ligands participating directly in the bonding with the central atom is called the coordination number.

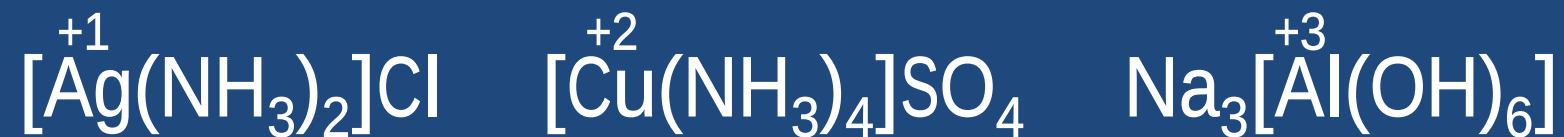
The outer sphere is the aggregate of all the ions situated outside the inner coordination sphere. The charge of the inner sphere is compensated by the ions of the outer sphere with the opposite sign.

Any element of the periodic table can function as a central atom in of the inner sphere. d- and f-elements show the highest complex forming ability, p-elements have somewhat lower ability and s-elements can function as a central atom very rarely. The central atom can have any oxidation number.



The value of the coordination number of the central atom depends on its nature, oxidation number, the nature of ligands and the conditions for the complexation reaction.

In most cases the value of the coordination number is twice as high as the oxidation number of the central atom.



The greater is the charge of the central atom and the smaller is its radius, the more durable is the complex.

As ligands we can find ions and neutral molecules. Atoms of a ligand which help to make bonds with the central atom are called donor atoms. The most frequently used ligands with donor atoms of oxygen, nitrogen and sulphur.

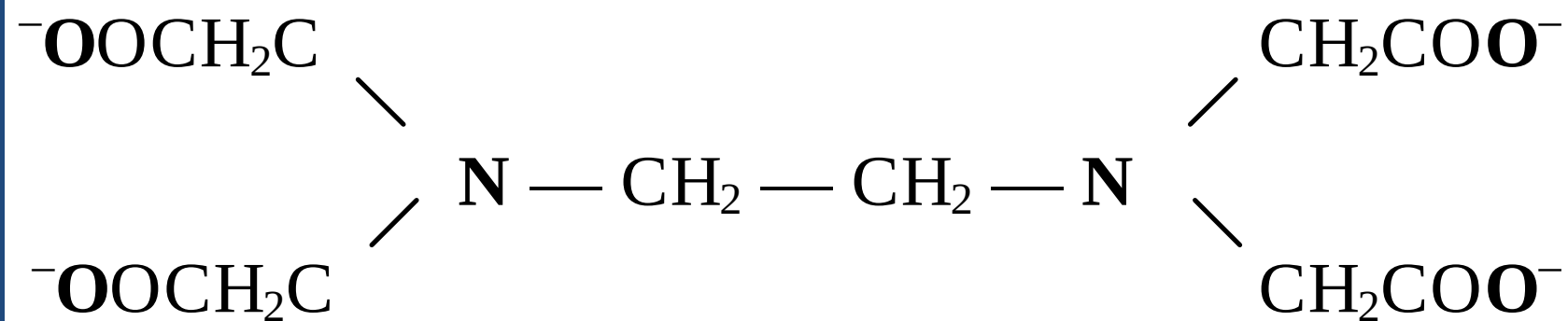
The number of donor atoms of a ligand forming the coordination bonds with the central atom is called the dentation of a ligand.

Monodentate ligands contain one donor atom: H_2O , NH_3 , OH^- , Cl^- .

Bidentate ligands contain two donor atoms and form two coordination bonds with the central atom: SO_4^{2-} , CrO_4^{2-} , molecules of ethylenediamine ($\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$), aminoacetic acid ($\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$).

There are also polydentate ligands containing more than two donor atoms.

For example, a hexadentate ligand which is the ethylenediaminetetraacetate ion of ethylenediaminetetraacetic acid (EDTA). It forms complexes with many metals owing to the oxygen atom of each of the four carboxylic groups and to both nitrogen atoms:



Proteins are the polydentate ligands.

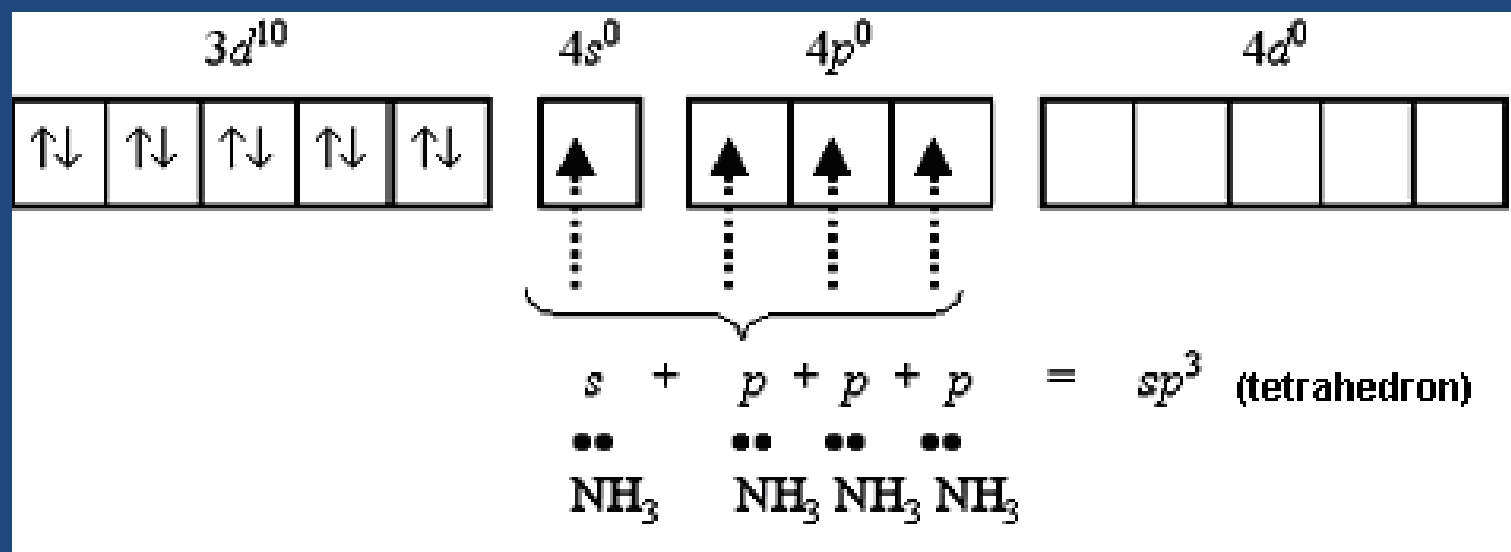
The nature of the chemical bond in complex compounds.

ü The bonds between the central atom and the ligands are the covalent.

Ligands are the donors of electron pairs and the central atom is the acceptor.

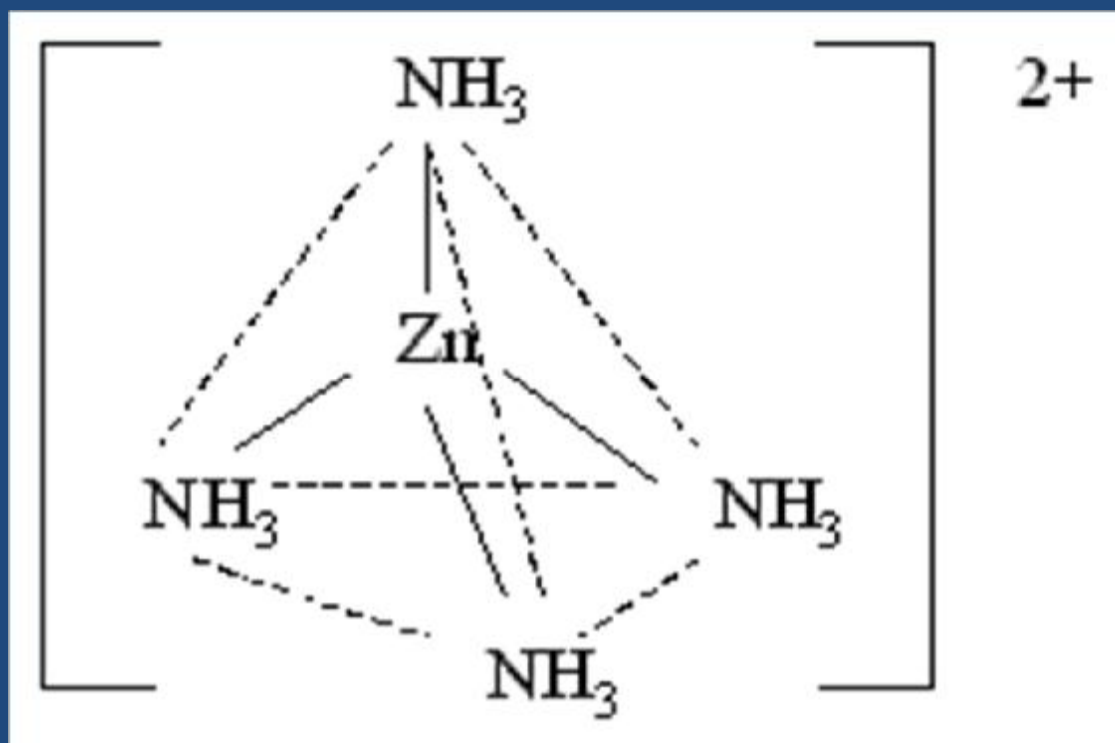


Cation $[\text{Zn}(\text{NH}_3)_4]^{2+}$ includes the central atom of zinc (II). The electron shell of zinc ion has the formula $[\text{Ar}] 3d^{10} 4s^0 4p^0$ and can be represented as follows:



Vacant 4s- and 4p-orbitals of zinc atom form four sp^3 -hybrid orbitals, directed at the corners of a tetrahedron. Each molecule of ammonia has an unshared pair of electrons of nitrogen atom.

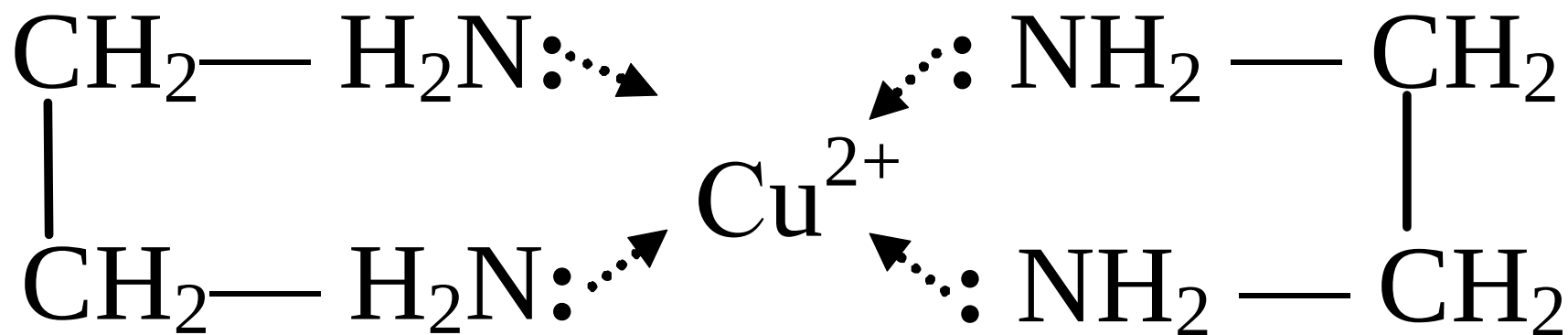
The orbitals of nitrogen atom containing the unshared pairs of electrons are overlapped by sp^3 -hybrid orbitals of zinc atom forming a complex cation of tetraaminezinc (II) - $[Zn(NH_3)_4]^{2+}$:



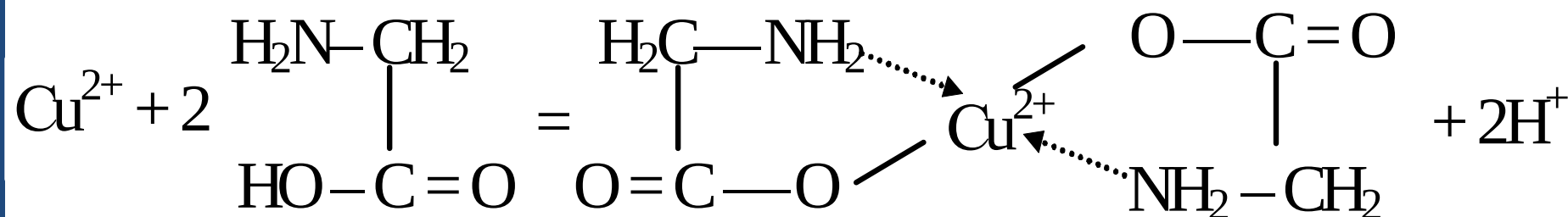
ü The inner coordination sphere is connected with the outer sphere by an ionic bond.

Cyclic complexes or chelates.

Complexes with polydentate ligands contain cycles which include the central atom. Such complexes are called chelates. The example of such complex can be ethylenediammine copper (II) complex:



The group of chelates also includes the inner complex compounds which have the central atom linked with ligands by a covalent bond formed according to donor-acceptor and exchange mechanisms.



The inner complex compounds are hemoglobin, chlorophyll, vitamin B₁₂, many enzymes and other biologically active compounds.

Classification and nomenclature of complex compounds.

I. According to the charge of the inner sphere the complexes can be:

Cationic: $[\text{Ag}(\text{NH}_3)_2]^+\text{Cl}$ diamminesilver (I) chloride;
 $[\text{Cu}(\text{NH}_3)_4]^{2+}\text{SO}_4$ tetraamminecopper (II) sulphate.

Anionic: $\text{K}_4[\text{Fe}(\text{CN})_6]^{4-}$ potassium hexacyanoferrate (II); $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{-1}$ potassium amminetrichlorplatinate (II).

Neutral: $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0$ trichlorotriamminecobalt;
 $[\text{Fe}^0(\text{CO})_5]^0$ pentacarbonil iron.

II. This classification of complex compounds is based on the nature of ligands.

Acidocomplexes. As ligands are the acid residua Cl^- (chloro); CN^- (cyano); CNS^- (rhodanic); NO_2^- (nitro); SO_4^{2-} (sulphate) and so on.

Aminocomplexes. As ligands are the ammonia molecules: $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$; $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$; $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$.

Aquacomplexes. As ligands are the molecules of water: $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$; $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

Hydroxocomplexes. As ligands are hydroxide ions OH^- : $\text{Na}_3 [\text{Al}(\text{OH})_6]$; $\text{Na}_2 [\text{Zn}(\text{OH})_4]$.

Carbonyl complexes. In carbonyl complexes CO-ligands are covalent-bonded with the help of carbon atom with the metal having zero oxidation number: $[\text{Ni}(\text{CO})_4]$; $[\text{Fe}(\text{CO})_5]$.

Dissociation of complex compounds in solutions.

The inner and the outer spheres of a complex compound differ greatly according to the stability.

Particles, situated in the outer sphere, are bound with a complex ion by electrostatic forces and can easily dissociate in water solution. Ligands, situated in the inner sphere, are more firmly bonded with the central atom and dissociate to a smaller extent. That's why the dissociation of complex compounds has two stages.

At the first stage the dissociation occurs as the dissociation of strong electrolytes:



At the second stage the dissociation occurs as the one of weak electrolytes, it's reversible and partial:



The ion dissociation $[\text{Ag}(\text{NH}_3)_2]^+$ like the dissociation of any weak electrolyte is expressed by the constant of chemical equilibrium:

$$K_{\text{ch.eq.}} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[[\text{Ag}(\text{NH}_3)_2]^+]} = K_i$$

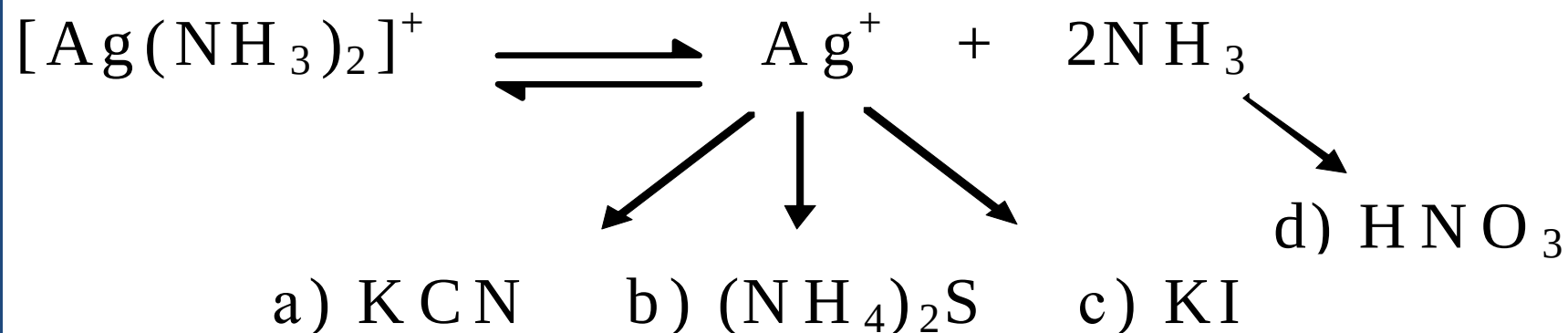
The constant of chemical equilibrium $K_{\text{ch.eq.}}$ in case of the dissociation of a complex ion is called the constant of instability K_i . It characterizes the stability of the inner sphere of complex compounds.

ü The less is K_i , the more stable is the complex.

$$\text{Constant of stability } K_s = \frac{1}{K_i}$$

Destruction of complex compounds.

To destroy a complex you should shift the equilibrium of dissociation of the inner sphere to the right. This can be achieved by the formation of a more stable complex, an almost insoluble precipitate, a weak electrolyte or a gaseous product. For example, the equilibrium of ion dissociation $[\text{Ag}(\text{NH}_3)_2]^+$ can be shifted to the right by binding of Ag^+ or NH_3 :





$$K_i. [\text{Ag}(\text{CN})_2]^- = 1 \cdot 10^{-21} < K_i. [\text{Ag}(\text{NH}_3)_2]^+ = 6,8 \cdot 10^{-8}$$



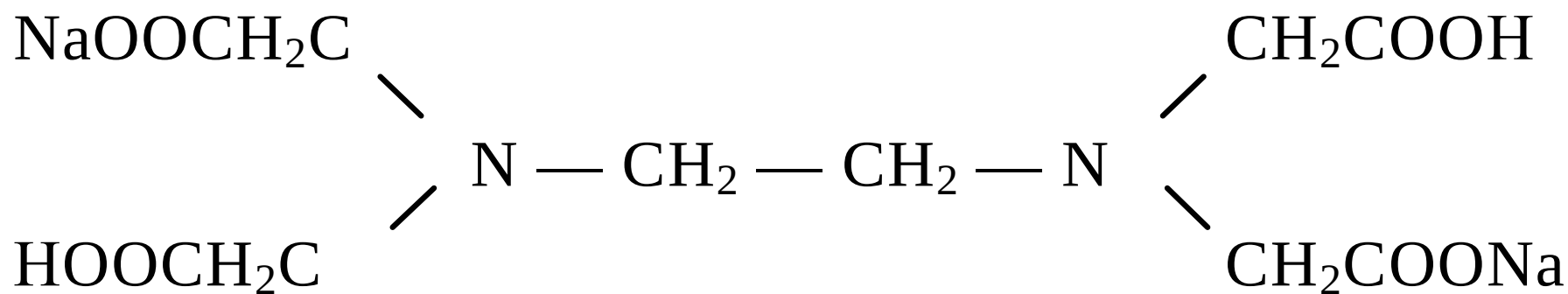
Usage of complex compounds.

In a human body there is a constant process of destruction and formation of biocomplexes from the cations of biometals (iron, copper, zinc, cobalt) and bioligands (porphyrins, aminoacids, proteins, polypeptides, nucleic acids, ATP).

The study of the processes taking place in the organism to form complex compounds can be of great importance for prevention and treatment of a number of diseases.

In medicine there is a special trend connected with the usage of complexons which is called chelation therapy.

The disodium salt of ethylenediaminetetraacetic acid (EDTA or complexon III, trade name trilon B) has got a wide distribution.



With the help of this salt it's possible to increase the excretion of ions of toxic metals from the organism.