

Coordination compounds

Processes of formation and destruction of complexes are used:

- **in analytical chemistry;**
- **for allocation of chemical elements;**
- **in galvanotechnics;**
- **for corrosion control;**
- **in the production of nuclear fuel;**
- **In deactivation practice;**
- **for indication of toxic compounds;**
- **for production of substances with predetermined properties as catalysts.**

General information about coordination compounds

According to their contents, chemicals are divided into simple substances (H_2 , Cl_2 , O_2 etc) and compounds (H_2O , H_2SO_4 , Na_3PO_4).

In the late nineteenth century even more complex in structure and composition molecular compounds were produced, they are called complex or coordination compounds.

DEFINITIONS:

Coordination compounds - are chemical compounds, the lattices of which consist of integrated groups formed by ions or molecules able to exist independently.

Coordination compounds - molecular compounds, the formation of which from simple substances is not associated with the occurrence of new electron pairs.



Werner's coordination theory

Alfred Werner (12.XII.1866-15.XI.1919)

The Swiss chemist. The founder of chemistry of complex (coordination) compounds. Advanced and developed (1893) coordination theory of the structure of complex compounds, disproving the concept of the constancy of numbers valence. Predicted (1899) the existence of optically active isomers, not having asymmetric carbon atom. Nobel laureate.

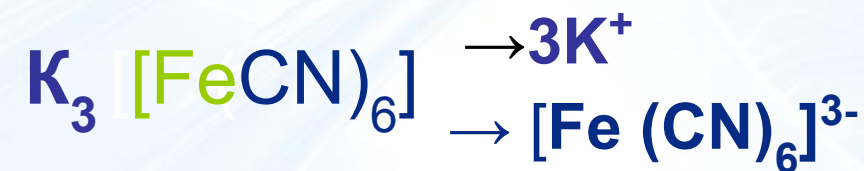
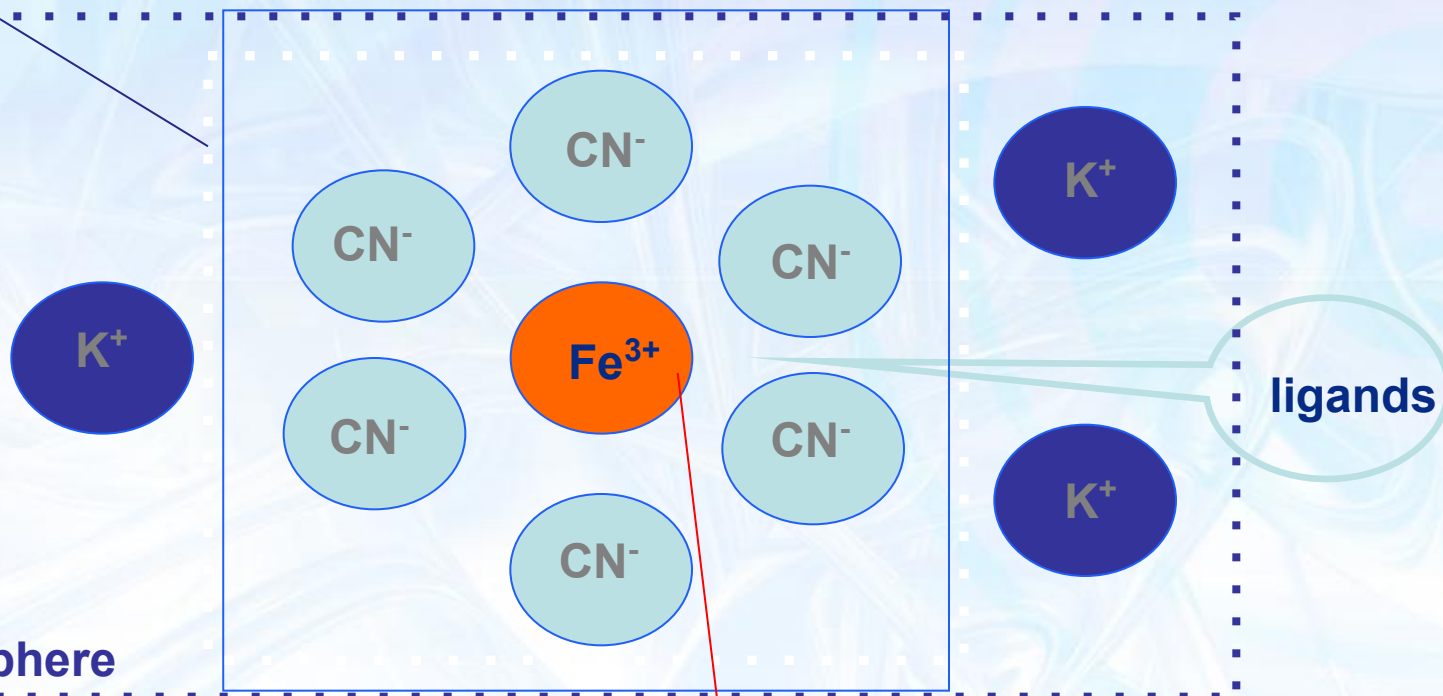
According to this theory, **in each complex compound there is a central ion (complexing)**, other ions, atoms or molecules - ligands (adends) are placed in a certain order around it.

The Central ion is associated with ligands by donor-acceptor mechanism, it forms an internal area of the complex.

The Central ion is acceptor and ligands are donors of electronic pairs. It is ionic bond between the inner and outer sphere.

The structure of coordination compounds

The internal sphere



Potassium hexacyanoferrate (III)

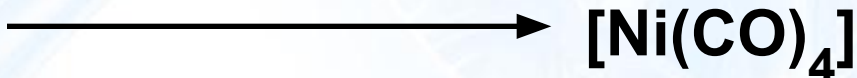
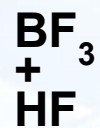
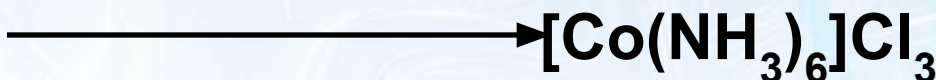
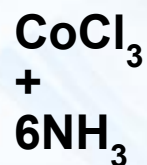
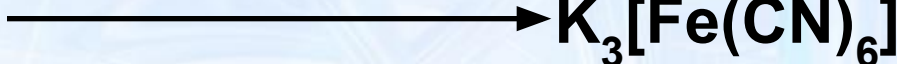
Complexing ion

Coordination theory of coordination compounds

(A. Werner, 1898)

Compounds of the first order
(valence-unsaturated)

Compounds of the highest order
(valence-saturated)



The number of places held by each ligand in inner complex sphere is a coordination capacity of the ligand.

Monodentants ligands – coordination capacity=1

Cl^- , Br^- , I^- , CN^- , NH_3

Bidentants ligands – coordination capacity=2

SO_4^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$. $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$

Polydentants ligands– ligands with the coordination capacity 3,4,6.

Complex compounds :

Coordination compounds
(complexing ion+ ligands)

Molecular complexes:
Quinone-hydroquinone;
Hydroquinone-methanol

Inclusion
compounds:
 $6\text{H}_2\text{O} \cdot \text{X}$, where
 $\text{X}=\text{Ar}, \text{Cl}_2, \text{CH}_4$ and
other

Coordination number of the central atom in the complex is the number of electron centers ligands (atoms or p-bonds), which interact directly with the complexing agent.

2. Classification and nomenclature of coordination compounds

The rules of the names of coordination compounds according IUPAC:

1. Cation is named at first, then anion. Name of the complex is written in one word.
2. In the name of the complex first list ligands (the first letters of the English alphabet), then the central atom.
3. Neutral ligands called without changes; in the names of negatively charged ligands add «o» to the end.
4. In case of several same ligands in the complex, before their name use the correct Greek numeral.
5. Name of complexing depends on the charge of the complex.
 - 5.1. For neutral and cationic – English name of the cation
 - 5.2. For the anionic complex - the Latin suffix «ate»

Nomenclature of coordinational compounds

$K[Co(CN)_4(CO)_2]$ - potassium dicarbonyltetracyanocobaltate(III)



+



ammoniumdiamminetetraathiocyanatochromate(III)

+



+



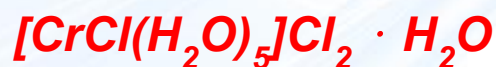
pentaamminechlorocobaltate(III) chloride



+



hexaaquachromium(III) chloride



pentaaquachlorochromium(III) chloride
monohydrate

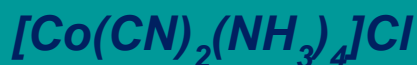


Tetraaquadichlorochromium(III) chloride
dihydrate

Classification of coordination compounds on different grounds

1. According to the sign of the electric charge of the complex

Cationic



Tetraamminedicyano-cobalt(III) chloride

Anionic



Potassium hexacyanoferrate(II)

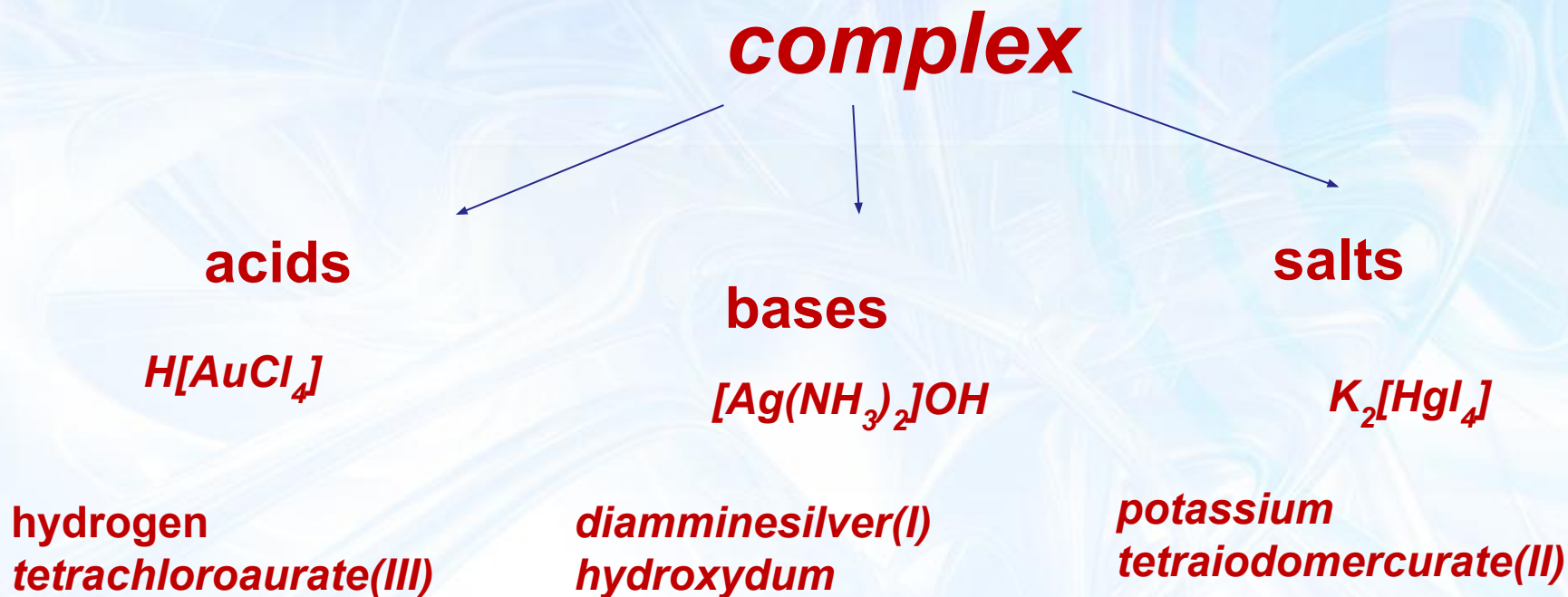
Neutral



Tetracarbonyl nickel(II)

Classification of coordination compounds on different grounds

2. According to their attachment to the definite class of compounds



Classification of coordination compounds on different grounds

3. By the nature of the ligands

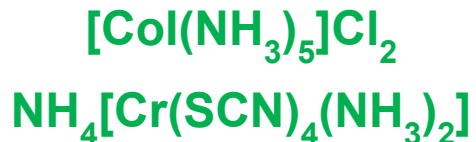
Aqua complexes



Acid complexes



Different ligands



Ammines



Cyanide



Hydroxocomplexes



Carbonyls



Carbonate



Classification of coordination compounds on different grounds

Polynuclear



μ - hydroxo- bis- [pentaamminechromiumchloride (III)]

Iso- and heteropoly acid



hydrogen μ -oxo-bis- [trioxochromate(VI)]



hydrogen μ -oxo-bis- [dioxosilicate(IV)]

phosphorus-molibdenum



phosphorus-wolframium



silicium-molibdenum



silicium-wolframium

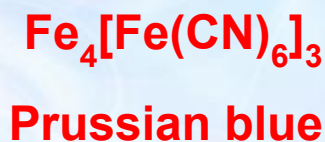


borum-wolframium

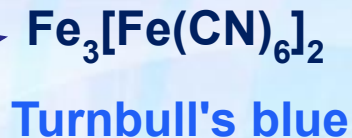


Classification of coordination compounds on different grounds

The presence or absence of cycles

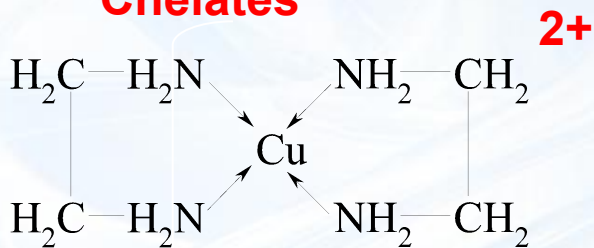


Simple



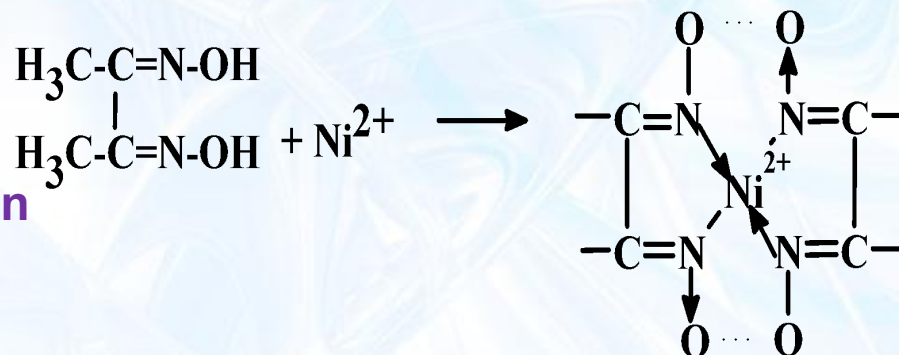
cyclic

Chelates



[[bis-ethylenediamine)copper(II)] cation

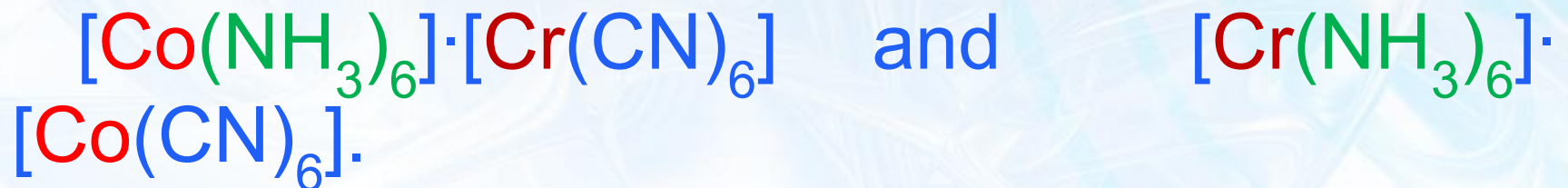
Chelate compounds



dimethylglyoximate nickel (II)

Isomerism of coordination compounds

Coordination isomerism is different allocation of ligand in internal coordination spheres. Interact differently with AgNO_3 two isomers -



The first compound gives sediment $\text{Ag}_3[\text{Cr}(\text{CN})_6]$, and the second - sediment $\text{Ag}_3[\text{Co}(\text{CN})_6]$.

Isomerism of coordination compounds

Geometric isomerism (CIS-TRANS isomerism) is different spatial location ligands around the central atom. So, $[\text{CoCl}_2(\text{NH}_3)_4]^+$ exists in two isomeric forms, which differ in the number of properties.



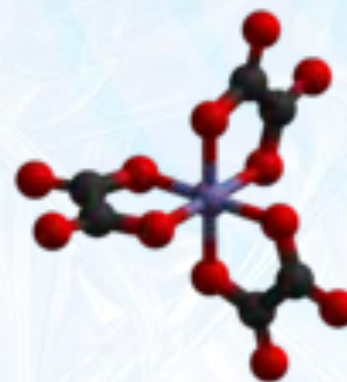
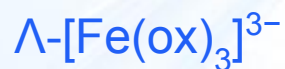
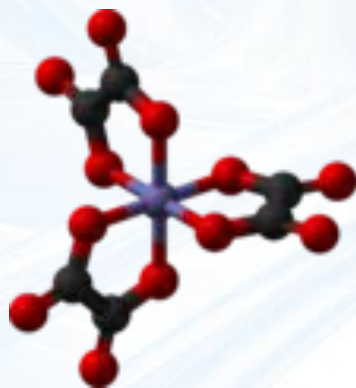
cis- $[\text{CoCl}_2(\text{NH}_3)_4]^+$



trans- $[\text{CoCl}_2(\text{NH}_3)_4]^+$

Isomerism of coordination compounds

Optical isomerism. Optical isomerism characterized by the ability to rotate the plane of polarization of plane-polarized light. Two isomers differ from each other by the direction of rotation of the polarization plane: one is called the right, and the other left isomer. Right- and left-isomers are mirror images of each other and cannot be combined in space



Isomerism of coordination compounds

Structural isomerism

Hydrated (solvation) isomerism is different allocation of molecules of the solvent between the internal and external spheres of complex compounds.

For example: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (purple),

$[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (light green),

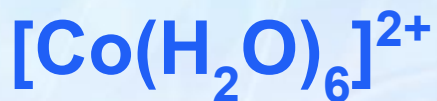
$[\text{Cr}(\text{H}_2\text{O})\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green).

Ionization isomerism is determined by the different distribution of charged ligands between internal and external spheres of the complex. Examples of compounds:

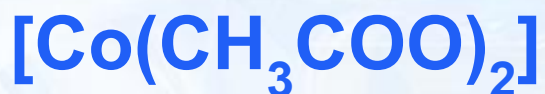
$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (red-purple),

$[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (red).

Influence of the ligand field on coloring of the complexes



pink



hot pink



orange



Amplification of a field of ligands

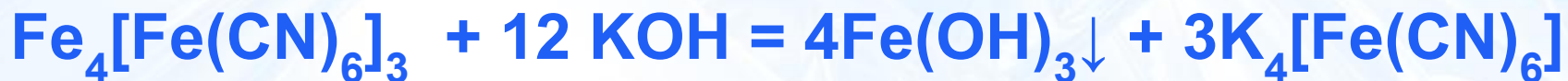
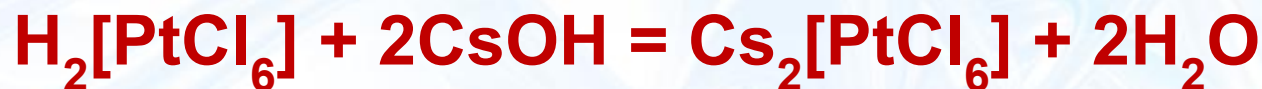
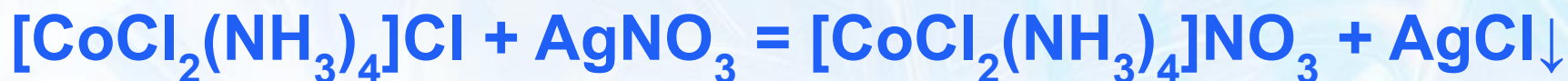
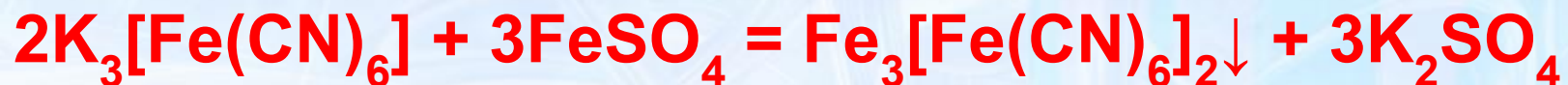


*2. The reactions of coordination compounds.
Stability of complex compounds and constant instability.*

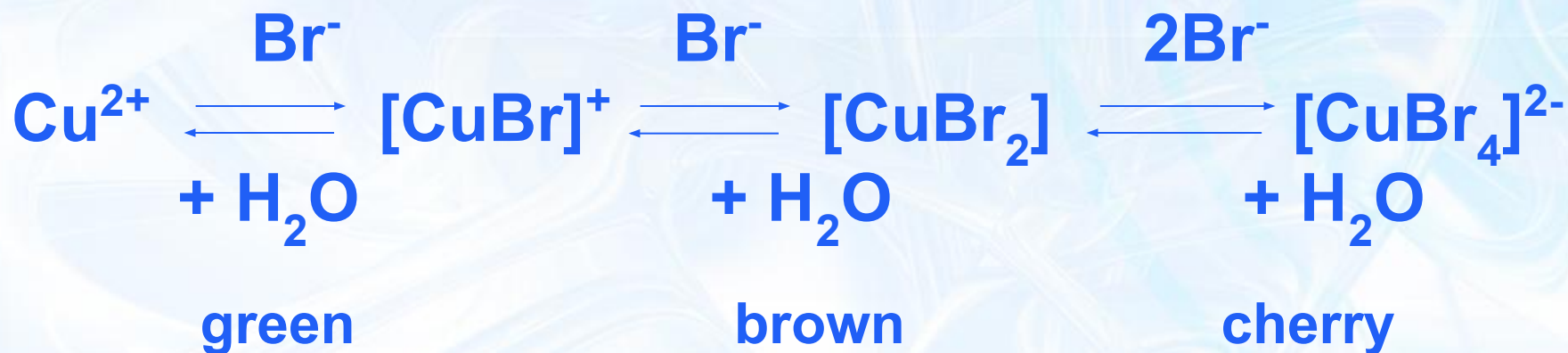
Dissociation of the CC on the external sphere (primary dissociation)



Reactions of complex on the outer sphere



Stepped formation and dissociation bromide complexes of copper(II)



Complexing constants

Joining the ligand L to the ion (atom) - M complexing to form a coordination compound ML



If the complex is formed, then the equilibrium constant is called the formation constant:

$$\beta = \frac{[ML]}{[M][L]}$$

For the reaction of complex formation ML_n :

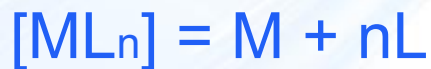


Total formation constant:

$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

$$K_{instab.} = \beta_n^{-1},$$

The inverse of formation constant is called the instability constant ($K_{instab.} = \beta^{-1}$) since it characterizes the ability of the complex to dissociate:



$$K_{instab.} = \frac{[M][L]^n}{[ML_n]}$$

Dissociation of the CC the inner sphere (secondary dissociation)



$$K_{instab.}^2 = \frac{[\text{Ag}(\text{NH}_3)]^+ [\text{NH}_3]}{[\text{Ag}(\text{NH}_3)_2]^+} = 1,2 * 10^{-4}$$



$$K_{instab.}^1 = \frac{[\text{Ag}^+][\text{NH}_3]}{[\text{Ag}(\text{NH}_3)]^+} = 4,8 * 10^{-4}$$

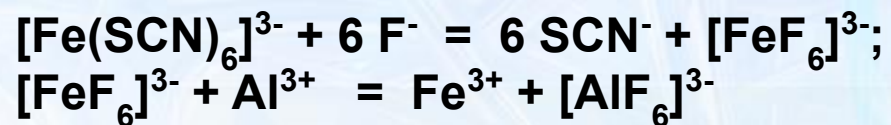


$$K = \frac{1}{K_{instab.}}$$

$$K_{instab.}^{gen.} = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2]^+} = 5,8 * 10^{-8}$$

At the same coordination number

Comparison of the strength of the complexes according general instability constants



Complex	General instability constant, $K_{\text{gen.}}^{\text{instab.}}$
$[\text{Fe}(\text{SCN})_6]^{3-}$	$5,9 \cdot 10^{-4}$
$[\text{FeF}_6]^{3-}$	$7,9 \cdot 10^{-17}$
$[\text{AlF}_6]^{3-}$	$2,1 \cdot 10^{-21}$

With different coordination number

2. Comparison of the stability of complexes according the concentration of the complexing

Example.

Whether the reaction is feasible



Concentration $[\text{Ag}(\text{NH}_3)_2]^+$ and $[\text{Zn}(\text{NH}_3)_4]^{2+}$ equal to 0,1 mole/L.

$$K_{\text{gen.}}^{\text{instab.}} [\text{Ag}(\text{NH}_3)_2]^+ = 5,8 \cdot 10^{-8};$$

$$K_{\text{gen.}}^{\text{instab.}} [\text{Zn}(\text{NH}_3)_4]^{2+} = 8,3 \cdot 10^{-10}$$

With different coordination number

3. Comparison of the stability of the complexes of the stepped constants instability

Complex	Stepped instability constant
$[AlF_6]^{3-}$	$7,9 \cdot 10^{-8}$
$[AlF_5]^{2-}$	$1,3 \cdot 10^{-5}$

The reaction of complexes with the destruction of the complex

1. The formation of the stronger complex



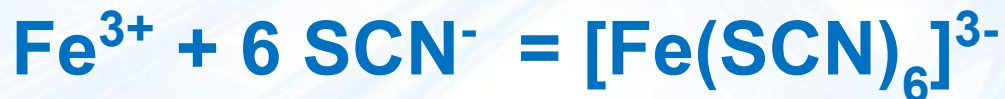
red color



lack of coloration

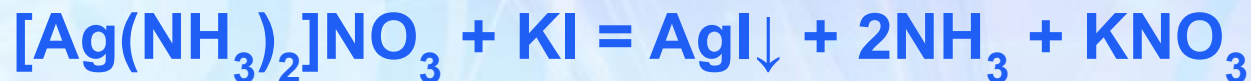


lack of coloration



red color

2. The formation of poorly soluble compound



3. Dilution



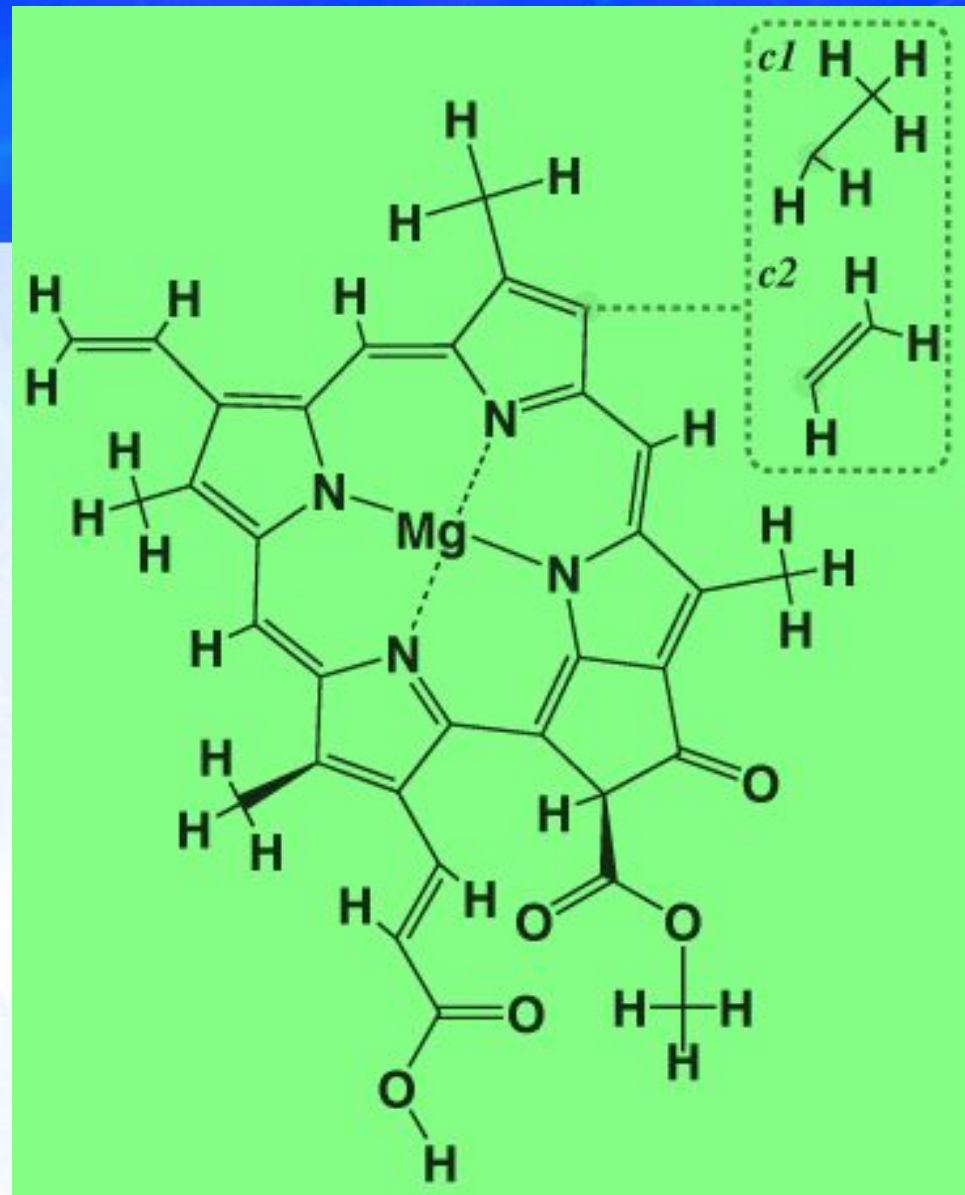
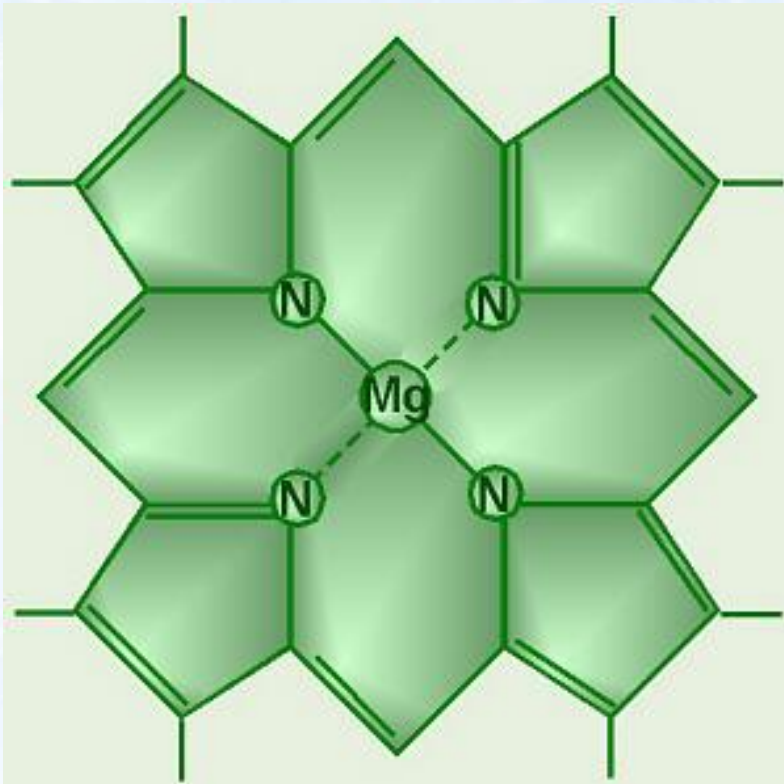
4. Heating



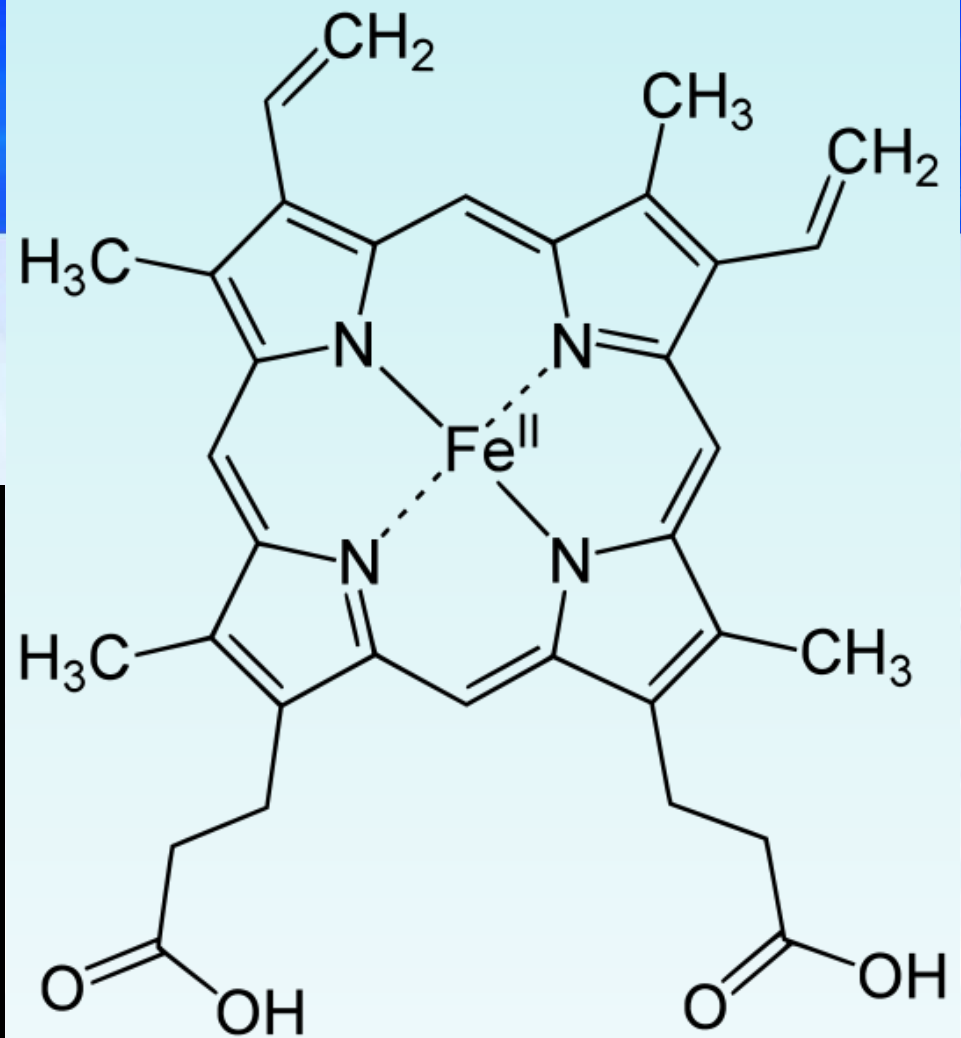
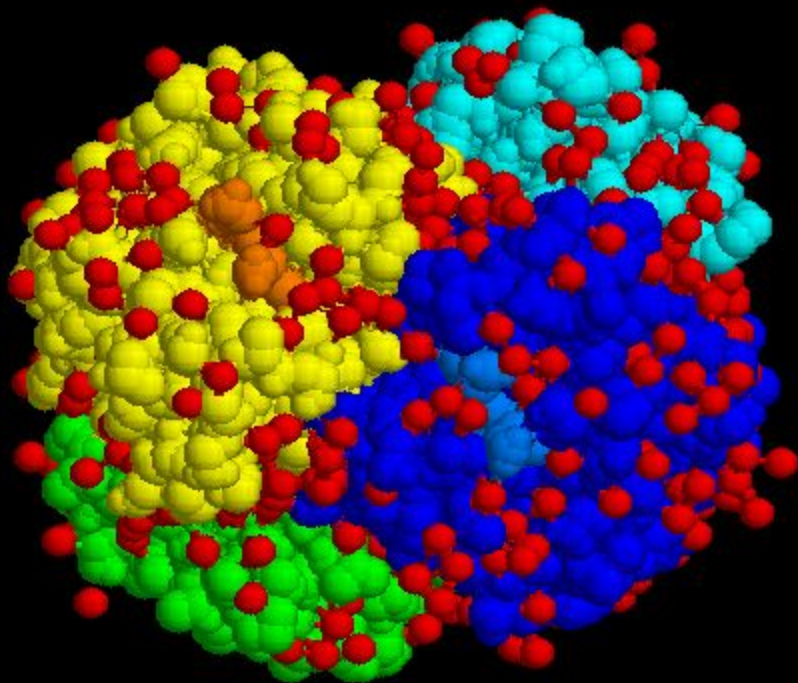
5. Red-ox reactions



- Chlorophyll

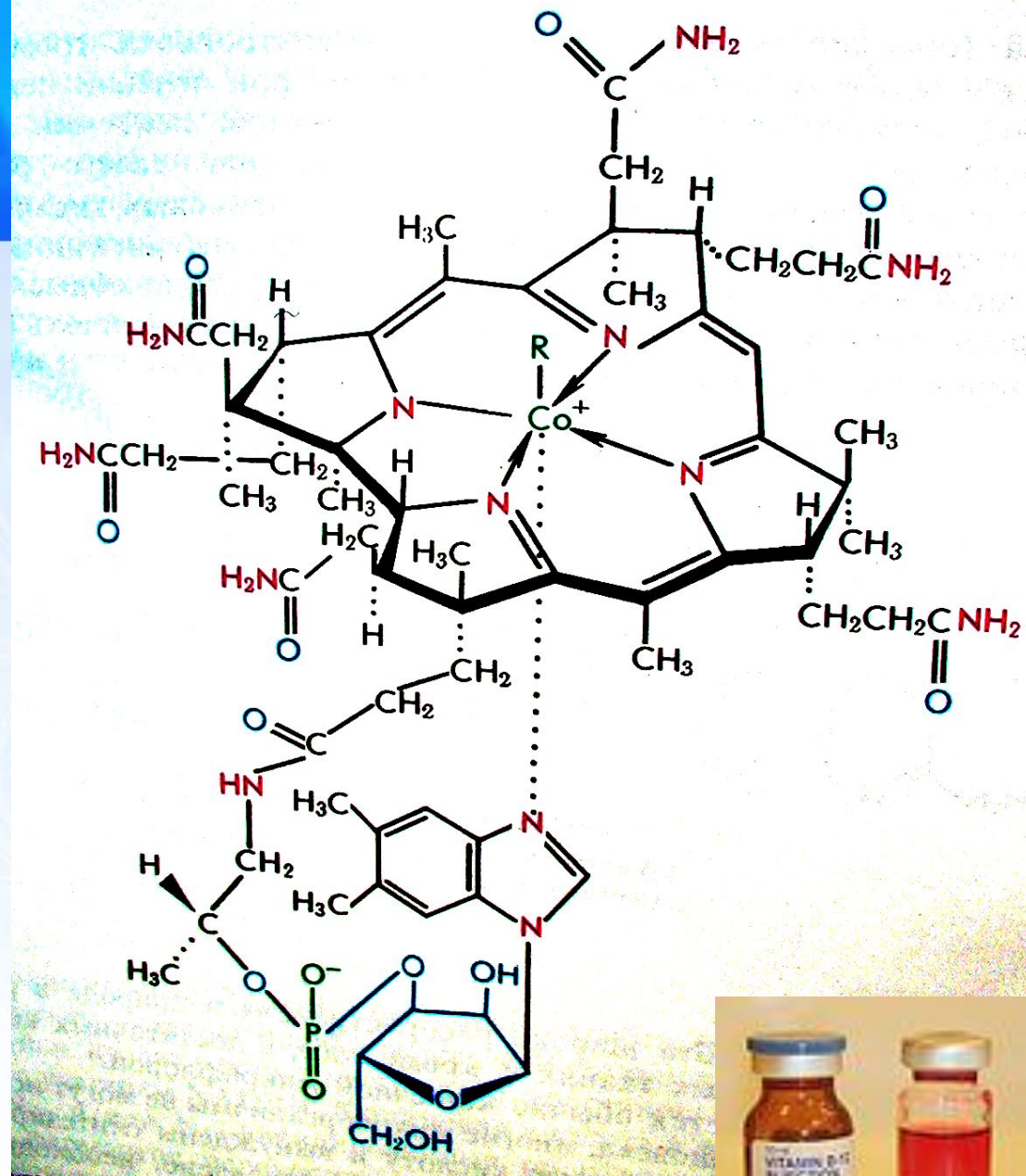


- Hemoglobin



B₁₂

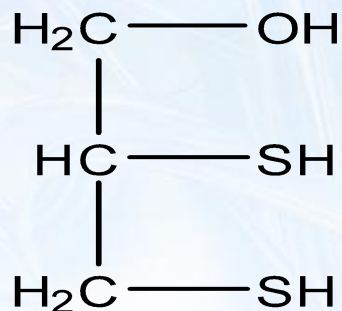
Vitamin B₁₂ cobalamin



THE APPLICATION OF COMPLEXES IN MEDICINE

Substances, eliminating effects of poisons on the biological structure and inactivate poisons by chemical reactions are called antidotes.

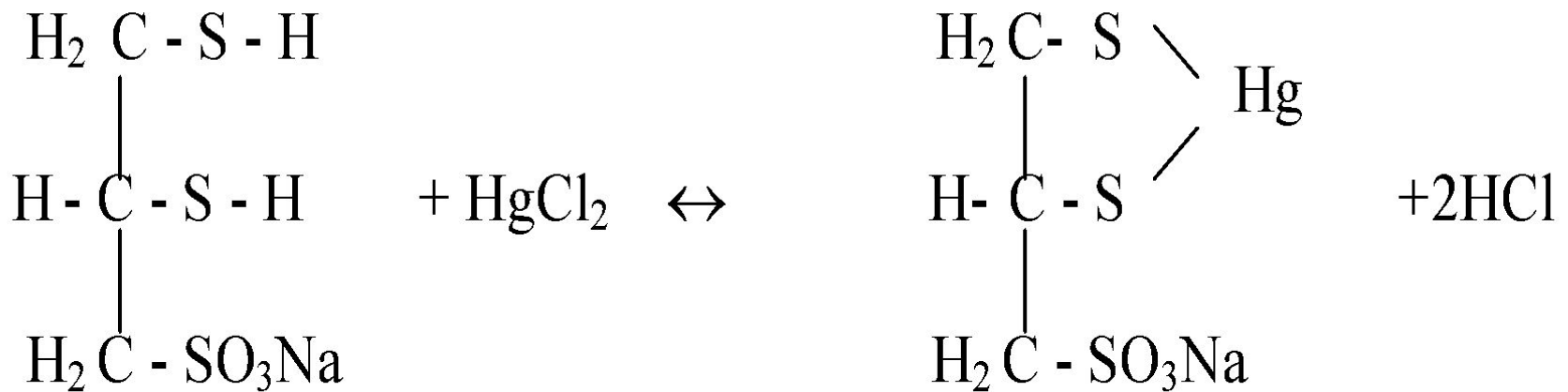
One of the first antidotes that is used in chelation therapy is British anti-lewisite (Dimercaprol)



This drug effectively removes arsenic, mercury, chromium and bismuth from the body . The use of drugs of this series is based on the formation of more stable complexes with metal ions than the complexes of these ions with sulfur-containing groups of proteins, amino acids and carbohydrates.

-antidotes: (Dimercaprol)

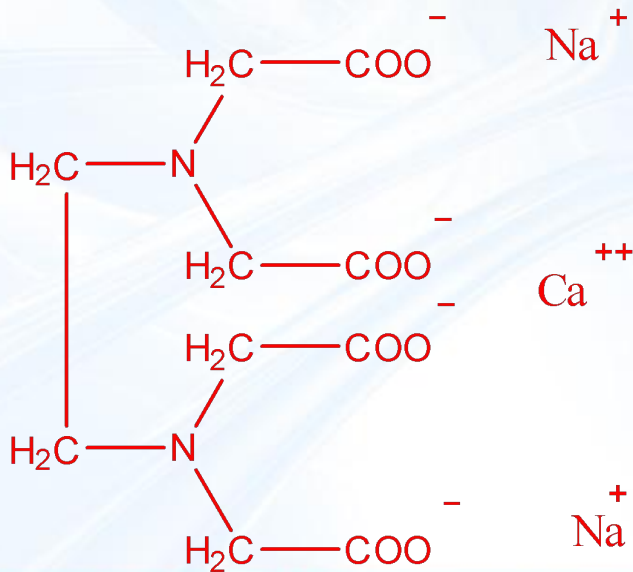
Mercaptide bond



EDTA, Na₂EDTA, Na₂CaEDTA

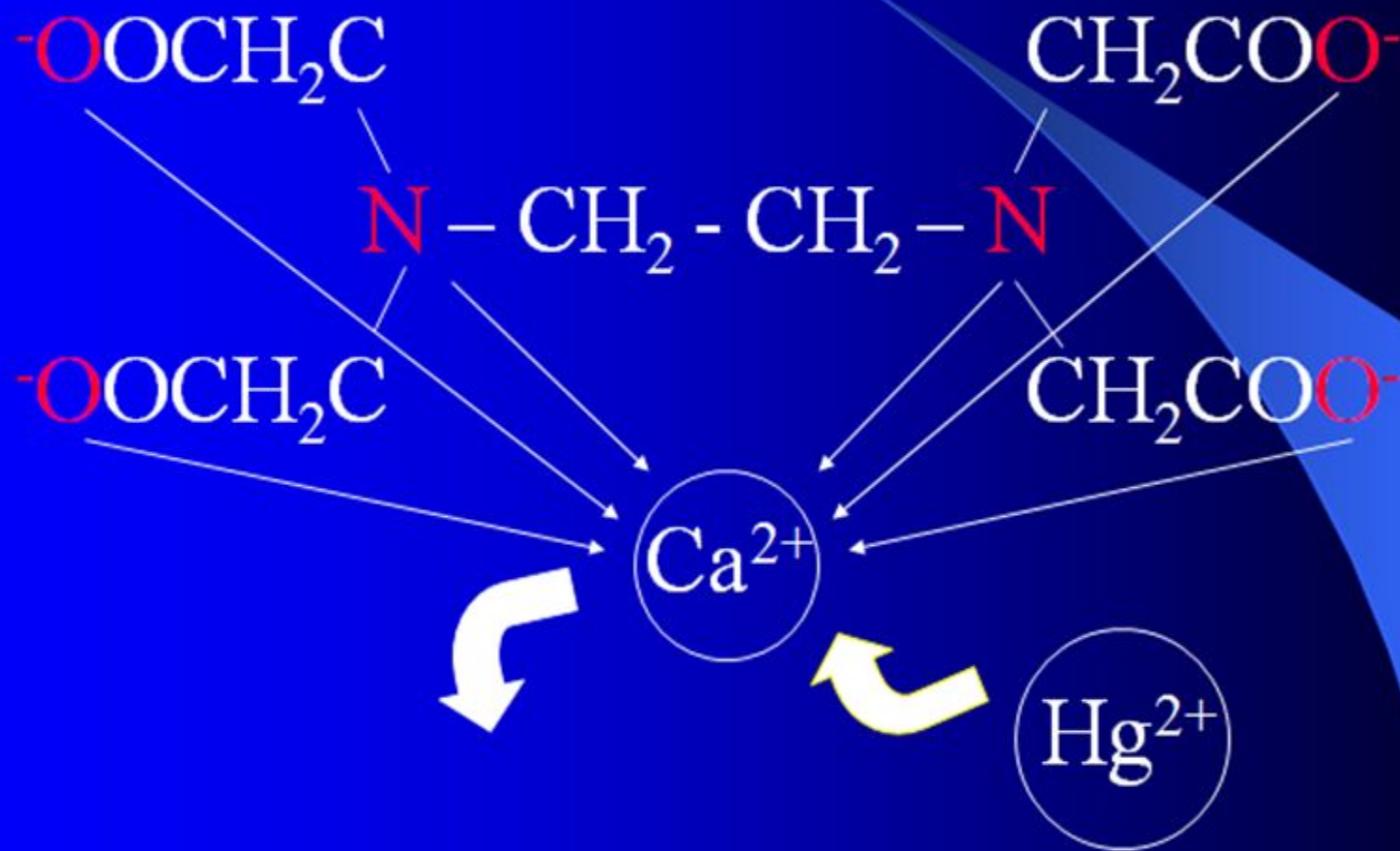
THE APPLICATION OF COMPLEXES IN MEDICINE

For the lead removing using preparations based on EDTA. The administration of large doses of drugs is dangerous as they bind calcium ions, which leads to violation of many functions. Therefore tetatsin used, CaNa_2EDTA , which is used for removing lead, cadmium, mercury, yttrium, cerium and other rare earth metals and cobalt.

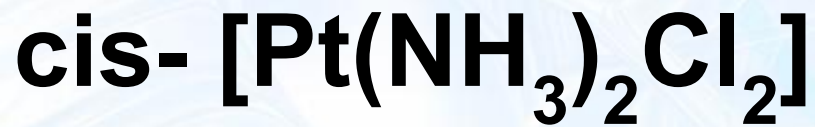


Tetatsin are introduced into the organism in the form of 5-10% solution on the basis of physiological solution. For binding poison that is in the stomach, tetatsin lavage is used. The drug is effective and fast acting in inhaled administration method. It is rapidly absorbed and circulates in the blood for a long time. Furthermore, tetatsin is used for protection of gas gangrene. It inhibits the action of zinc and cobalt ions, which are activators of the enzyme lecithinase, which is a gas gangrene toxin.

- Complexons: (Tetatsin)



-anticancer drug:
dihlorodiamminplatinum cis-isomer
(cis-platin)



The image features a blue-themed background with abstract, swirling patterns and light effects. A prominent dark blue horizontal band spans the middle of the frame. The text "The End" is centered within this band in a white, bold, sans-serif font. The top and bottom edges of the image show lighter blue and purple-toned abstract textures.

The End