PART 12
COMPLEX COMPOUNDS

I. REASONS OF COMPLEX COMPOUND FORMATION

I.1. CHARACTER OF BOND IN COMPLEX COMPOUNDS

Complexes are called compounds, in which an ion, (further called *central ion* or *central atom*) has bound to itself several neutral molecules or ions of opposite sign by means of donor-acceptor bonds.

The particles, bound to the central ion are so called *ligands* (or *addends* in some book).

Complex compounds are, for example, $[Ag(NH_3)_2]Cl$ in which ammonium molecules (ligands) bind to a silver ion (central ion) or $K_4[Fe(CN)_6]$, in which cyanide ions (ligands) bind to a Fe^{2+} ion (central ion).

The ligands bind to the central atom by means of a covalent bond (as donor-acceptor bond is a rather covalent bond). This means, that they bind tightly to the central atom and the complex practically doesn't dissociate in solution. The square brackets in the formulas of complex compounds include the central atom and the ligands.

All, what is inside these brackets, as $[Ag(NH_3)_2]$ is bound together tightly and is itself called the *internal sphere* of the complex. These ions, that one write outside the square brackets as Cl^- ions in the compound $[Ag(NH_3)_2]Cl$ form the *outer sphere* of the complex compound and are necessary just to compensate the charge of the internal sphere. In solutions the outer sphere ions completely dissociate away from the internal sphere (if one compares complex compound $[Ag(NH_3)_2]Cl$ to a usual compound like KCl, all the complex ion plays the role of K^+ ion and easily dissociates away from Cl^- ion.).

One has to note, that the complex compound all-in-all is electrically neutral. In the first example, Ag ion has a positive charge +1, and NH_3 molecules have no charge, therefore the charge of the complex ion $[Ag(NH_3)_2]^+$ is +1 as well. For this reason another particle must attach to

the complex ion, having a charge -**1** to compensate the charge of the complex ion. In our first example such a particle is a **Cl⁻** ion.

As well, in our second example, the complex ion consists of a central ion **Fe²⁺**, that has bound six **CN⁻** ions. In such a way, the complex ion has a total charge, that can calculate as

$$+2 + 6(-1) = -4$$

(it consists of one ion, having a charge +**2** and six ions, having a charge -**1**). To compensate this charge, four **K⁺** ions attach to the complex ion.

I. 2. WHAT PARTICLES CAN SERVE AS CENTRAL IONS AND WHAT - AS LIGANDS IN THE COMPLEX COMPOUNDS ?

As it mentioned previously, there is a donor-acceptor type bond between the central atom and the ligands in the complex compounds. For this reason the central ion has to have empty orbitals to serve as an acceptor and ligands have to have unshared electron pairs to serve as donors at the formation of the donor-acceptor bond. The discussion about most typical central ions and ligands will be below.

I.2.1. CENTRAL IONS.

All the metal ions are Typical particles, that have empty electron orbitals. When a metal ion form from a metal atom, it loses all the outer shell electrons and empty orbitals only remain in the outer shell.
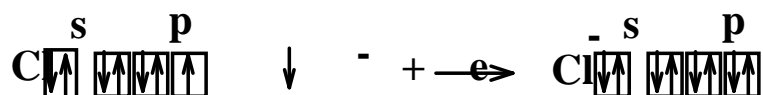
Thus, for instance, when a **Li⁺** ion is formed from a **Li** atom, the only electron from the **2s** orbital of **Li** is lost and the formed ion has an electron configuration **Li⁺** □ □□□, i.e. a **Li⁺** ion has four empty orbitals. Thus, **4** ligands can be attached to a **Li⁺** ion.

Openly, not all the metal ions are effective complex makers. By the most, strongly bound complexes form by these metals, which belong to the so-called *d-elements*. The latter have a partly filled d electron sub-level. Elements of **Pt, Pd, Fe, Ni, Co, Zn, Ag, Hg, Cu,** etc. are typical representatives of this group and are typical central ions in complex compounds. Nevertheless, all the other metal ions can form complexes as well, but the strength of bond in these complexes is much weaker and therefore the complexes formed by metals other than of d-elements can easily destroy. Each metal ion can form at least one type of complex - its hydration complex in its water solutions. Thus, for instance, the above

considerations about **Li** ion as a complex maker explains, why a **Li⁺** ion bound **4** molecules of hydration water).

I.2.2. LIGANDS.

As many negative ions (anions) have unshared electron pairs, because of they can act as ligands. For instance, a **Cl⁻** ion is formed from **Cl** atom, which has **7** electrons in its outer shell. The number of electrons on outer shell of **Cl** atom becomes **8,** if **Cl** atom one more electron gain and form **Cl⁻** ion. These **8** electrons form **4** pairs of unshared electrons:

$$\text{Cl} \begin{array}{cc} \mathbf{s} & \mathbf{p} \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow\,\uparrow\downarrow\,\uparrow} \end{array} \quad \downarrow^{-} \quad + \quad \xrightarrow{e} \quad \text{Cl}^{-} \begin{array}{cc} \mathbf{s} & \mathbf{p} \\ \boxed{\uparrow\downarrow} & \boxed{\uparrow\downarrow\,\uparrow\downarrow\,\uparrow\downarrow} \end{array}$$

Usually a chloride ion describes just as **Cl⁻**. If the unshared electron pairs play important role in the discussed properties of the ion, they show usually

in text as pairs of dots: $\mathbf{:\ddot{\underset{..}{Cl}}\vdots}$.

Typical ligands are all the halogenides **F⁻, Cl⁻, Br⁻, I⁻**. Most typical other negative ions, that can serve as ligands are the following: cyanide **CN⁻,** rodanide **SCN⁻,** thiosulfate **S₂O₃²⁻**, **OH⁻** and some other anions.

Besides the anions, some neutral molecules can act as ligands, too. Among the simplest compounds the most typical molecular ligands are **H₂O**, **NH₃** and **CO**, as the atoms of **N** and **O** in these molecules still have unshared electron pairs (see the electron configurations of these molecules in Part **11**).

Although the ligands can have several unshared electron pairs, in most cases only one of them can use for bond formation with the central atom. For instance, **Cl⁻** ion, mentioned above, has **4** pairs of unshared electrons positioned at four **sp³** hybrid orbitals of **Cl**. Just one of these orbitals can turn towards a central ion at a time. Thus, a **Cl⁻** ion is able to form **one** bond with the central atom (to use one of the free orbitals of the central atom) and therefore the notation uses a *monodentate ligand.* All the other ligands mentioned above are monodentate as well.

Polydentate ligands are able to use several free orbitals of the central atom. They will discuss in chapter V. Let we only mention here, that all of them are organic compounds, their unshared electron pairs lie at **different** atoms and there must be two or more **-CH₂-** groups between these atoms.

I. 3. HOW MANY LIGANDS CAN BE BOUND TO A GIVEN CENTRAL ATOM?

The number of ligands, that can bind to a given central atom is so-called the *coordination number* of the central atom.

Each free orbital of a central atom is able to accept an electron pair of a ligand and each ligand (here and further until chapter V.**7**. monodentate ligands consider) is able to use just one electron pair, see discussion above. It means, that *the number of ligands, which can be bound to a given central atom is equal to the number of free orbitals of the central atom.*

Thus, in order to find the coordination number of a given central atom, one should know its electron configuration. In fact, it is not enough just to know the electron configuration of the central atom - the influence of the electric field of ligands on the electron configuration of the central atom has to be taken into account as well. This makes the task too complicated to be discussed in this short chemistry course.

For this reason, an empiric rule for determination of coordination numbers is very useful:

> *In most cases the coordination number of a central ion is equal to doubled charge of the central ion.*

Now let us see, how well this empiric rules suits the real coordination numbers of real central ions, see table **12**. **1**. As one can see from the few examples, in most cases the empiric rule gives a correct value of coordination number, but there are some exceptions, too, because the empiric rule is not based on any rules of quantum mechanics. In all the cases, when the the real coordination number of a central on differs from the one, determined using the empiric rule, one can use the electron configuration of the central ion and try to find an explanation for the value of the coordination number.

Table 12. 1. *Charges and coordination numbers of some central ions.*

charge of central ion	coord. number empiric rule	examples	other possible coord. numbers	examples
+1	2	Ag^+, Cu^+, Au^+	4	Li^+
+2	4	Cu^{2+}, Hg^{2+}, Pt^{2+}, $Ni^{2+,}$ $Zn,^{2+}$ Cd^{2+}, Co^{2+}	6	Fe^{2+}
+3	6	Fe^{3+}, Al^{3+}, Cr^{3+}, Co^{3+}	4	Au^{3+}

II. EXAMPLES OF COMPLEX FORMATION REACTIONS

EXAMPLE 1.

If a solution of NH_4OH is poured upon a precipitate of $AgCl$, the precipitate disappears, and a clear solution is obtained because a soluble complex compound is formed. First, let us decide, what is the central atom and what - the ligand in the formed complex. As **Ag** has a partly filled **d** electron sub-level, it can be the central atom (the complex maker). The ligands in this case can be NH_3 molecules, that are present in the solution, because ammonium hydroxide always is in an equilibrium with free molecules of ammonia and water:

$$NH_4OH \rightleftharpoons NH_3 + H_2O$$
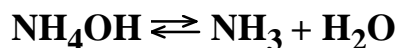
and NH_3 molecules are known as typical ligands.

The next question is - what number of ammonium molecules can be bound to an Ag^+ ion. As Ag^+ ion has a charge $+1$, according to the empiric rule, its coordination number is **2**. The formula of the complex ion complex ion will thus be $[Ag(NH_3)_2]$ (the charge of internal sphere is not shown yet)**.**

To understand, what other ions and in what number have to compensate the charge of the complex ion in the outer sphere, one must calculate the charge of the complex ion. As silver ion has a charge $+1$ and NH_3 molecules have no charge, the total charge of the complex ion is $+1$, the formula of the complex ion becoming $[Ag(NH_3)_2]^+$, therefore a charge -**1** is required for the ion in the outer sphere.

As there is only one type of negative ions in the solution - the Cl^- ions, the complete formula of the complex compound is $[Ag(NH_3)_2]Cl$. Now one can write the reaction equation for complex formation:

$$\underline{AgCl} + 2NH_4OH => [Ag(NH_3)_2]Cl + 2H_2O$$

EXAMPLE 2.

If a solution of **KSCN** (potassium rodanide) is added to a solution of $FeCl_3$, a bloody-red color appears - a complex compound is formed. In this

case the central ion can be the Fe^{3+} ion, as iron has a partly filled **d** electron sub-level. It's coordination number must be **6** (doubled **3**).

The ligands in this case can be SCN^- ions, thus, the formula complex ion without charge notation becomes $[Fe(SCN)_6]$. The total charge of this ion can be found as an algebraic sum of the charges of Fe^{3+} ion and six SCN^- ions, or $+3 + 6(-1) = -3$. If so, positive ions, having a total charge $+3$ are required in the outer sphere to compensate the negative charge of the complex ion. As the only type of positive ions in the solution are K^+ ions, the formula of the whole complex compound is $K_3[Fe(SCN)_6]$ and the reaction of complex formation looks like:

$$FeCl_3 + 6KSCN => K_3[Fe(SCN)_6] + 3KCl$$

Try to follow the same principles of complex formation reactions in the following examples:

EXAMPLE 3.

$$Hg(NO_3) + 4KI => K_2[HgI_4] + 2KNO_3$$

EXAMPLE 4.

$$AlCl_3 + 6NaOH(\text{excess}) => Na_3[Al(OH)_6] + 3NaCl$$
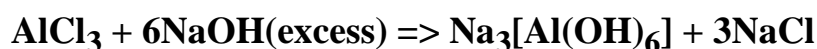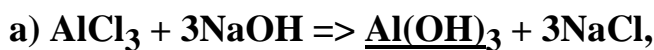
In this example, if **NaOH** is **not** taken in excess, just aluminium hydroxide is formed. One can imagine this reaction of complex formation as consisting two subsequent stages:

$$\text{a) } AlCl_3 + 3NaOH => \underline{Al(OH)_3} + 3NaCl,$$

$$\text{b) } \underline{Al(OH)_3} + 3NaOH => Na[Al(OH)_6]$$

EXAMPLE 5.

$$CoCl_3 + 4KCN + 2H_2O => K[Co(CN)_4(H_2O)_2] + 3KCl$$

To obtain this particular complex compound **KCN** has to be added precisely in a ratio **4** moles of **KCN** for each mole of $CoCl_3$. As Co^{3+} ion has a coordination number **6** and there is not enough **KCN** to supply **6** CN^- ions to each cobalt ion, the remaining two places in the coordination sphere of cobalt are occupied by water molecules, that also can serve as ligands and are, of course, present in solution. *To understand the situation completely, let*
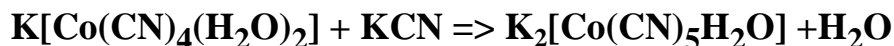
us mention, that water molecules as ligands are weaker than most of other particles mentioned above. For this reason, if both water molecules and some other possible ligands are present in the solution, water cannot compete with the other ligand, but just fills the remaining positions in the coordination sphere of the central ion.

If **KCN** is added in excess, all the **6** positions in the coordination sphere of **Co³⁺** are occupied by cyanide ions and a different complex compound is obtained:

$$CoCl_3 + 6KCN(excess) => K_3[Co(CN)_6] + 3KCl$$
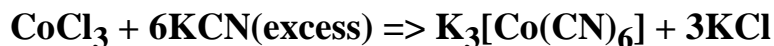
So, practically, according to the ratio between the numbers of moles of **KCN** and **CoCl₃** six different complex compounds, including **CN⁻** and **H₂O** as ligands, can be formed. Similar effect is observed also for many other complex makers - if there is too little ligand added, to fill all the positions in coordination sphere of complex maker, water molecules fill the remaining positions.

As water is a relatively weak ligand, water molecules are immediately pushed out of the coordination sphere if stronger ligand is added. For instance, if more **KCN** is added to a solution of **K[Co(CN)₄(H₂O)₂]**, the two water molecules can be gradually replaced by cyanide ions in the internal sphere of complex:

$$K[Co(CN)_4(H_2O)_2] + KCN => K_2[Co(CN)_5H_2O] + H_2O$$
<div align="center">and</div>

$$K_2[Co(CN)_5H_2O] + KCN => K_3[Co(CN)_6] + H_2O$$

III. STABILITY OF COMPLEXES

When talking about the stability of complex compounds, the bond between the central atom and ligands is considered. If this bond is destroyed in a process, the complex will decay, if this bond is not destroyed, the complex remains stable.

Two kinds of complex compound dissociation are known: *primary* and *secondary*. dissociation.

III.1. PRIMARY DISSOCIATION OF COMPLEX COMPOUNDS

An example of primary dissociation is the following reaction:

$$[Cu(NH_3)_4]SO_4 => [Cu(NH_3)_4]^{2+} + \boxed{SO_4^{2-}}$$
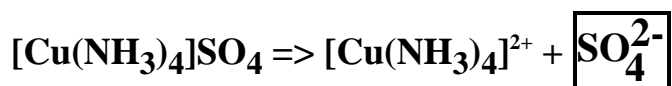
which is just a dissociation complex compound into outer sphere ions and complex ion. This dissociation doesn't touch the bond between the central atom and ligands, therefore it doesn't affect the stability of the complex ion. As any salt, the complex compounds in solutions dissociate completely into the ions of outer sphere and the complex ions.

Another example of primary dissociation is:

$$K_4[Fe(SCN)_6] => 3K^+ + [Fe(SCN)_6]^{3-}$$
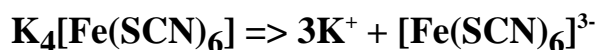
Thus, the degree of primary dissociation $\alpha = 1$ (complex compounds are strong electrolytes from the point of view of the primary dissociation). At the same time, the primary dissociation doesn't touch the stability of the complex ion. This means that it is, for instance, possible to change the outer sphere ions to another ones without destroying the complex ion, see the following example:

$$[Cu(NH_3)_4]SO_4 + Ba(OH)_2 => \underline{BaSO_4} + [Cu(NH_3)_4](OH)_2$$
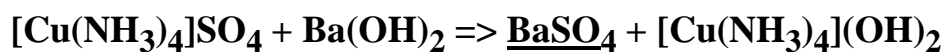
Here Ba^{2+} ions react with SO_4^{2-} ions and make a precipitate of $BaSO_4$,

therefore the outer sphere ions of the complex are changed to OH^- ions. At the same time, the internal sphere of the complex remains intact.

III.2. SECONDARY DISSOCIATION OF COMPLEX COMPOUNDS

Secondary dissociation of the complex compound is the dissociation of the complex ion into free ligands and free complex maker. Although the ligands are bound to the central ion by means of covalent bond (and therefore are tightly linked together), the complex ion always exists in a certain equilibrium with a small amount of free complex maker and free ligands.

For instance, the complex ion $[Cu(NH_3)_4]^{2+}$ is in an equilibrium with free Cu^{2+} ions and free NH_3 molecules:

$$[Cu(NH_3)_4] \rightleftarrows Cu^{2+} + 4NH_3 \qquad (12.\ 1)$$
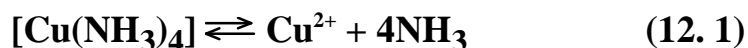
In fact, this is the equation of the summary equilibrium. The real dissociation of this complex ion occurs in four stages, loosing one NH_3 molecule at every stage.
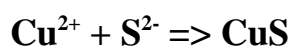
The equilibrium of the secondary dissociation is directly related to stability of the complex ion - while no other reagents are added to the

solution of complex compound, just an equilibrium exists and the dissociation of the complex ion occurs to a very small extent. The situation changes, as soon as a reagent is added, which is able to bind Cu^{2+} ions in a precipitate or to bind NH_3 molecules. In such a case one of the dissociation products is disappearing and the equilibrium of the secondary dissociation is shifted to the right - the complex ion dissocates more and more and is finally decomposed.

For instance, in the example with the amino complex of copper, the decay of the complex can occur if:

a) Na_2S solution is added.

In this case, Cu^{2+} ions disappear in a reaction of CuS precipitate formation :

$$Cu^{2+} + S^{2-} => \underline{CuS}$$

therefore the concentration of free Cu^{2+} ions is decreasing, the equilibrium of the secondary dissociation is shifted to the right and the complex is destroyed.

b) HCl solution is added.

At addition of HCl the free NH_3 molecules combine with H^+ ions from HCl to form NH_4^+ ions

$$NH_3 + H^+ => \boxed{NH_4^+}$$
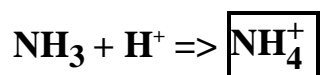
and therefore the concentration of the free NH_3 molecules grows smaller.

As for any equilibrium, a decrease of the concentration of a reaction product shifts the equilibrium towards the reaction products. In this case it causes a further dissociation of the complex and destruction of the complex ion as the result of it.

Stability of the complex is characterized by the so-called *instability constant* of the complex, that is at the same time the equilibrium constant of the secondary dissociation reaction (of the reaction (**12**. **1**) in our example) :

$$K_{instab.} = \frac{[Cu^{2+}] \times [NH_3]^4}{\left[Cu(NH_3)_4]^{2+}\right]}$$

From the discussion above one should understand, that

the smaller is the instability constant (the smaller concentrations of free complex maker and free ligands are present in the solution at the same complex concentration), the more stable is the complex.

Thus, to compare stability of complex ions, one has to compare their instability constants - the complex, having the smallest instability constant is the most stable one.

IV. DESTRUCTION OF COMPLEX COMPOUNDS

If it is necessary to destroy a complex compound, one can use two ways: bind the ligands or bind the central ion.

IV. 1. DESTRUCTION OF COMPLEX COMPOUNDS BY BINDING OF LIGANDS

There is no general rule, that could tell us, how to bind all the possible kinds of ligands - for some of them one can find reagents, which are able to bind the ligands and to destroy the complex compounds in such a way, for some ligands such reagents don't exist.

Let us only mention, that any complex, having ammonium molecules or **OH⁻** ions as ligands, can be destroyed by addition of an acid. The following examples illustrate complex destruction by means of ligand binding:

a) destruction of a complex **[Co(NH₃)₆)](NO₃)₃** by addition of **HCl**:

$$[Co(NH_3)_6](NO_3)_3 + 6HCl => 6NH_4Cl + Co(NO_3)_6$$

(the reason of complex destruction is, that **NH₃** molecules react with **H⁺** ions from **HCl** forming **NH₄⁺** ions);

b) destruction of the complex **Na₃[Cr(OH)₆]** by addition of **HNO₃**:

$$Na_3[Cr(OH)_6] + 6HNO_3 => 6H_2O + 3NaNO_3 + Cr(NO_3)_3$$
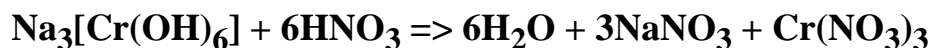
(the reason of complex destruction is the reaction of of **OH⁻** ions (ligands) with **H⁺** ions from **HNO₃** and formation of **H₂O**).

IV. 2. DESTRUCTION OF COMPLEX COMPOUND
## BY BINDING OF THE CENTRAL ION

The central ion can be bound if a reagent is added which reacts
with the central ion and forms a precipitate,

like it was discussed above about the complex ion $[Cu(NH_3)_4]^{2+}$.

At the same time addition of a reagent which is known to form an insoluble compound with the central ion doesn't always lead to destruction of the complex and precipitate formation. To answer the question whether or not will the complex be destroyed, if such a reagent is added, one has to compare two numerical values: the instability constant of the complex and the solubility product of the proposed precipitate.

Let us take the same $[Cu(NH_3)_4]Cl_2$ complex as an example. If a solution of Na_2S is added, Cu^{2+} ions are involved in two equilibriums at the same time:

1) they are involved in the equilibrium of the secondary dissociation of the complex ion:

$$[Cu(NH_3)_4]^{2+} \rightleftarrows Cu^{2+} + 4NH_3 \qquad (1)$$
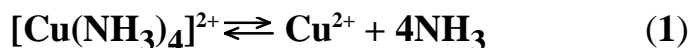
2) they are involved in the equilibrium of **CuS** precipitate formation-dissolution:

$$Cu^{2+} + S^{2-} \rightleftarrows \underline{CuS} \qquad (2)$$

Equilibrium (**1**) is characterized by the equilibrium constant, which is called the instability constant of the complex $K_{instab}[Cu(NH_3)_4]^{2+}$. The smaller is this constant, the more tightly Cu^{2+} ions are bound in the complex and the more stable is the complex.

Equilibrium (**2**) is characterized by the solubility product of **CuS** ($K_{sp,CuS}$). The smaller it is, the more tightly Cu^{2+} ions are bound in the precipitate **CuS**.

For this reason one has to compare these two constants to see, whether the complex can be destroyed or not. If $K_{inst.} >> K_{sp}$, the complex will be destroyed, if $K_{inst.} << K_{sp}$, the complex remains stable.

In this case $K_{instab} = 2 \times 10^{-13}$, $K_{sp,CuS} = 6 \times 10^{-31}$. This means, that the complex ion will be destroyed (as the solubility product is much smaller, than the instability constant and Cu^{2+} ions are therefore more tightly bound

in **CuS** precipitate, than in the complex ion. Destruction of the complex will occur according to reaction equation:

$$[Cu(NH_3)_4]Cl_2 + Na_2S => \underline{CuS} + 4NH_3 + 2NaCl$$
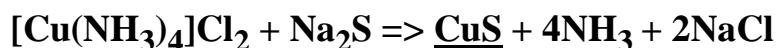
Other examples:

1) Let us decide, whether or not the complex $K_4[Fe(CN)_6]$ can be destroyed at addition of **Na$_2$S** solution.

The instability constant of this complex is $K_{inst} = 4 \times 10^{-36}$, the solubility product of the possible precipitate **FeS** being $K_{sp} = 5 \times 10^{-18}$. This means, that the complex will not be destroyed, as Fe^{2+} ion is better bound in the complex, than in the precipitate.

2) When a solution of **KI** is added to a solution of the complex compound $[Ag(NH_3)_2]Cl$, the possible precipitate is **AgI**, which is a weakly soluble salt. The instability constant of the complex is $K_{instab} = 9 \times 10^{-8}$ and the solubility product of **AgI** is $K_{sp} = 1.1 \times 10^{-16}$, therefore the complex ion will be destroyed, because Ag^+ ions are better bound in the precipitate:

$$[Ag(NH_3)_2]Cl + KI => \underline{AgI} + 2NH_3\uparrow + KCl.$$
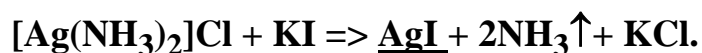
V. THE MAIN GROUPS OF COMPLEX COMPOUNDS

By the most, the complex compounds are classified according to the type of ligands.

V. 1. AQUA COMPLEXES.

Aqua complexes are these complex compounds, which have water molecules as ligands. All the metal ions in water solutions exist in a form of aqua complexes. When discussing the ordinary properties one can usually ignore formation of aqua complexes. Still, some properties of solutions cannot be understood without knowledge about the number of water molecules that are bound to a metal ion in its solution.

Ordinary metal ions, such as ions of alkaline metals K^+, Na^+, etc. or alkaline earth metals as Ca^{2+}, Mg^{2+}, Ba^{2+} etc. don't form strong aqua complexes.

Ions of metals, that have partly filled **d** electron sub-level, such as **Fe, Co, Ni, Pt** and others, already mentioned in the beginning of the Part **12**, form stronger aqua complexes, but,. nevertheless, aqua complexes are instable. As soon as another ligand is added to the solution, which forms a stronger complex, water is shifted out from the coordination sphere of the complex and replaced by the stronger ligand. A "stronger" ligand here means one that has a smaller K_{instab} with the same central ion than water molecules.

V. 2. AMINOCOMPLEXES.

Amino complexes are complex compounds, that have ammonium molecules as ligands. Examples of amino complexes are: $[Cu(NH_3)_4]SO_4$, $[Ag(NH_3)_2]Cl$, $[Pt(NH_3)_4](NO_3)_2$ etc. Amino complexes are not very strong complexes, too, but they are stronger, than the aqua complexes.

All the amino complexes can be destroyed by addition of any strong acid due to binding of ammonium molecules in ammonium ions (see above).

V. 3. ACIDOCOMPLEXES.

The complex compounds having acid remainder ions as ligands belong to the group of acido complexes

In other words, as soon as the ligand is a any negative ion except OH^-, for example Cl^-, Br^-, F^-, $\boxed{S_2O_3^{2-}}$, CN^-, SCN^-, etc. , the complex compound belongs to this group.

Examples of acido complexes can be compounds like $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $K_3[Ag(S_2O_3)_2]$, $Na_2[HgI_4]$, etc.

The ligands are rather tightly bound to the central ion in acidocomplexes, therefore acido-complexes are strong complexes - their instability constants are small. There is no general method for destruction of acidocomplexes - in each case one has to find a specific reagent, which is able to bind the central ion or the ligands.

V. 4. MIXED COMPLEXES.

In mixed complexes the complex compound contains several different ligands at the same time, for example compounds like $[Cu(NH_3)_2(H_2O)]Br$; $K_2[PtBr_2Cl_2]$; $[Zn(NH_3)_2Cl_2]$ can serve as examples of mixed complexes. Note, that there is no outer sphere in the last example - as Zn^{2+} ion has a charge +**2**, the charge of ammonium molecules is **0** and two Cl^- ions together have a charge -**2** already the complex ion is electrically neutral and no outer sphere is required.

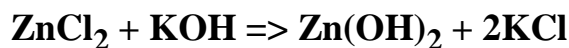## V. 5. HYDROXOCOMPLEXES.

Hydroxo complexes are complex compounds where OH^- ions serve as ligands.

Examples of hydroxo complexes are: $Na_3[Cr(OH)_6]$; $K_3[Al(OH)_6]$, $Na_2[Zn(OH)_4]$ $K[Sb(OH)_4]$. These complex compounds are products of reactions between the salts or hydroxides of amphoteric metals and an excess of a strong base:

$$Al(OH)_3 + NaOH(excess) => Na_3[Al(OH)_6] \text{ or}$$

$$Cr(NO_3) + 6KOH(excess) => K_3[Cr(OH)_6] + 3KNO_3$$
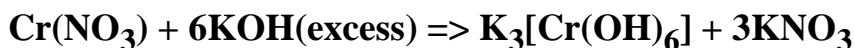
Remember, that if a salt of an amphoteric metal reacts with a strong base and the base is not taken in excess, just a precipitate of the hydroxide of the amphoteric metal will be obtained. In fact, if a strong base is being added to a solution of a salt of an amphoteric metal, first a precipitate of the appropriate hydroxide is formed, e. g.:

$$ZnCl_2 + KOH => Zn(OH)_2 + 2KCl$$

If the addition of the strong base is continued, the precipitate disappears due to complex formation:

$$Zn(OH)_2 + 2KOH => K_2[Zn(OH)_4]$$

As well as the amino complexes, the hydroxo complexes are not very strong. All of them can be destroyed by acid solutions, because H^+ ions of acids bind the ligands - OH^- ions, forming water, for example:

$$K_3[Cr(OH)_6] + 6HCl => 6H_2O + CrCl_3 + 3KCl$$
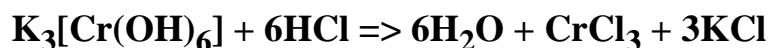
V. 6. COMPLEX ACIDS AND COMPLEX BASES.

In this case the classification of complex compound is not according to the ligands but according to the outer sphere ions:

Complex acids are complexes, having H^+ ions in the outer sphere.

Examples of complex acids are $H_2[PtCl_4]$; $H[AuCl_4]$; $H_4[Fe(CN)_6]$ etc. To have a positive H^+ ion as the ion of the outer sphere, the charge of the complex ion (of the internal sphere must be negative. This can be carried out, if the ligands are negative ions. For this reason the usual ligands in the complex acids are acid remainder ions.

Complex bases are complex compounds, having OH^- ions in the outer sphere.

Examples of complex bases are compounds like $[Cu(NH_3)_4](OH)_2$; $[Ni(NH_3)_4](OH)_2$.

To have a negative OH^- ion in the outer sphere, a positive charge of the complex ion (of the internal sphere) is required. The central ions are always positive, but the ligands have to be neutral molecules in this case - it is necessary to obtain a positive charge of the complex ion as a whole.

If negative ions serve as ligands, the charge of the complex ion becomes negative, as the coordination number of the central ion is always greater, than its charge.

For example if Cu^{2+} ion is the central ion and CN^- ions are ligands, then, as the coordination number of Cu^{2+} is **4**, four CN^- ions are bound and the complex ion $[Cu(CN)_4]$ has a charge -**2**, therefore OH^- ions cannot serve as the outer sphere ions, but some positive ions are required there.

For the reasons just discussed, ligands in the complex bases can be neutral molecules only. This is the reason why most of the complex bases contain NH_3 molecules as ligands.

An important property of both the complex acids and bases is, that all of them are strong electrolytes.

Such a behavior of complex acids and bases is caused by the fact, that the dissociation of the complex acids or bases into the complex ion and H^+ or OH^- ions is at the same time the primary dissociation of the complex compound, which, as it is explained in the chapter III, proceeds completely efficiency (for the primary dissociation $\alpha = 1$).

Thus, all the complex acids have to be treated as strong acids and all the complex bases - as strong bases.

V. 7. CYCLIC COMPLEXES OR CHELATES.

Chelates are a special group of complex compounds, that have a great biological importance. The main difference between the ordinary complex compounds and chelates is, that a special kind of ligands - the so-called polydentate ligands is present in chelates. The polydentate ligands are able to form cyclic complex compounds, where the central ion is found in the middle of a cyclic structure formed by several or sometimes even one large ligand molecule

A *polydentate ligand* usually is an organic molecule., in which several atoms having unshared electron pairs are spatially separated from each other. Such a ligand can turn several pairs of unshared electrons towards the central atom and is therefore able to occupy several positions in its coordination sphere. Usual ligands can use only one of their unshared pairs at a time, because of the reasons, discussed in chapter **1**. **2**. **2**.
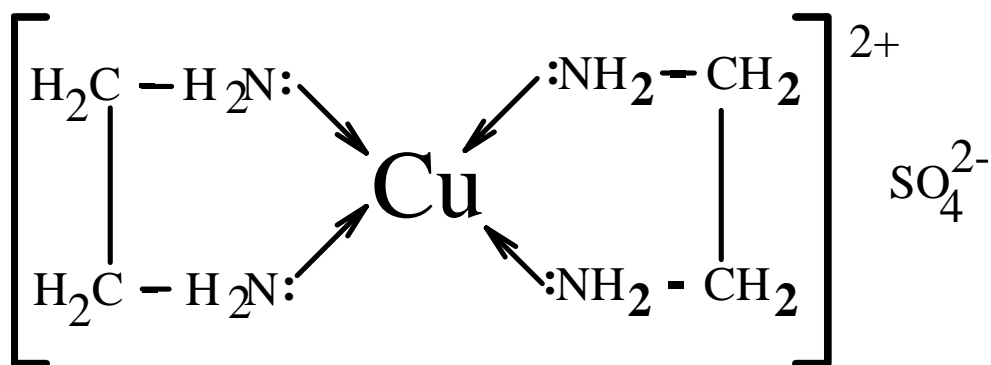
The simplest possible polydentate ligand is ethylene diamine (*en*):

$$H_2\overset{..}{N} - CH_2 - CH_2 - \overset{..}{N}H_2$$
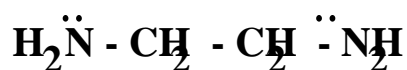
The **NH$_2$-** groups at the ends of molecule can be treated as molecules of ammonia where one of the hydrogen atoms is replaced by an organic radical. There are two unshared pairs of electrons at the two nitrogen atoms. The groups of atoms can rotate around the **C-H** and **C-N** bonds and therefore the molecule can finally be bent so, that both of the unshared pairs are oriented towards the central atom.

For instance, if a complex of ethylene diamine with **Cu^{2+}** ion is formed, the formula of the complex ion is **[Cu(en)$_2$]$^{2+}$** (en – ethylene diamine).The coordination number of copper ion is **4**, but as ethylene diamine has two unshared pairs of electrons, each molecule of it occupies two positions in the coordination sphere of copper ion. The structure of this complex compound in a planar projection looks as shown in fig.12.2.

As one can see, the two molecules of ethylene diamine surround the **Cu^{2+}** ion and the four unshared electron pairs, that belong to nitrogen atoms, are inserted into the four empty orbitals of copper ion. There are two cycles in the structure of this complex compound, each of them includes one ethylene diamine molecule and both of them share the copper ion.

$$\left[\begin{array}{c} H_2C - H_2N: \\ | \\ H_2C - H_2N: \end{array} \quad Cu \quad \begin{array}{c} :NH_2 - CH_2 \\ | \\ :NH_2 - CH_2 \end{array} \right]^{2+} \quad SO_4^{2-}$$

(The donor-accepter bonds are shown as arrows, usual covalent bonds - as lines).

Fig. 12. 2. *A planar projection of Cu^{2+} complex compound with ethylene diamine.*

The summary formula of this complex compound is **[Cu(en)$_2$]SO$_4$** (sulfate of ethylene diamine copper) as the charge **+2** of the complex ion (**+2** is obtained, taking into account, that their charge of copper ion is **+2** and the molecules of ethylene diamine have no charge) has to be compensated in the outer sphere.

In fact, the two cycles in the structure of complex are situated in two perpendicular planes, therefore the real structure of the complex compound is spatial instead of planar.

One can imagine also other possible chelate type complexes, in which organic molecules, containing more than one amino group, serve as ligands (try to write, for instance, a structure of propylene diamine **H$_2$N-CH$_2$-CH$_2$-CH$_2$-NH$_2$** complex with **Zn^{2+}** having chloride ions in the outer sphere).

V. 8. INTERNAL COMPLEXES

A still more interesting subgroup of chelates from biological point of view are the so called internal complexes, that are chelates without any outer sphere.

> *The ligands are bonded to the central ion by means of both donor-accepter and usual chemical bonds in the internal complexes .*

The simplest possible ligand, that can be bound to the central ion in such a way, is amino acetic acid:

$$H_2\ddot{N} - CH_2 - COOH$$
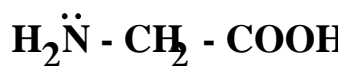
The nitrogen atom of the amino group has an unshared electron pair and therefore is able to make donor-accepter bonds with central ion, the hydrogen ion of the carboxyl (**-COOH**) group can be replaced by a metal ion as any hydrogen ion in a molecule of an acid.

At the complex formation between the amino acetic acid and the copper ion the following reaction occurs:

$$\textbf{Ni}^{2+} + \textbf{2H}_2\textbf{N-CH}_2\textbf{-COOH} => \textbf{[Ni(H}_2\textbf{N-CH}_2\textbf{-COO)}_2\textbf{]} + \textbf{2H}^+$$
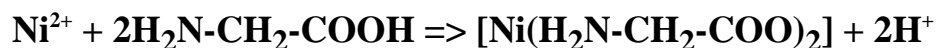
The obtained complex compound has no outer sphere, because **Ni**$^{2+}$ ion has a charge +**2** and the two amino acetate ions have charges **2**(-**1**) = -**2**. A planar projection of this complex compound is shown in fig. **12. 2.**, but the structure of the same compound in two perpendicular planes can be imagined as shown in fig. **12. 3**.
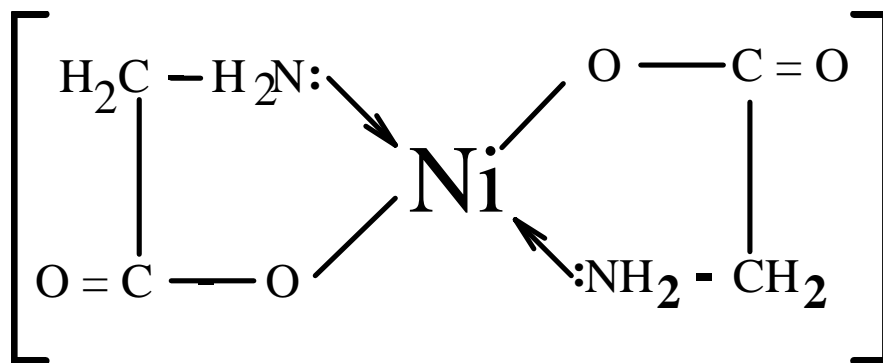

***Fig. 12. 2**. A planar projection of Ni²⁺ complex with amino acetic acid.*
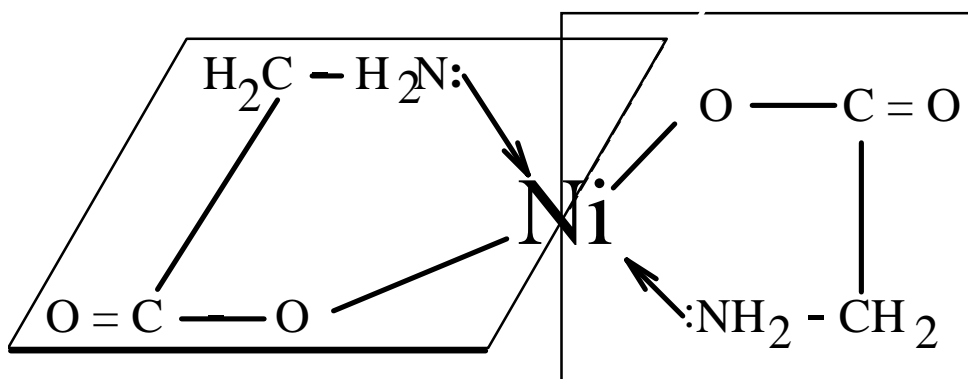*(usual chemical bonds are shown as lines, donor-accepter bonds - as arrows).*
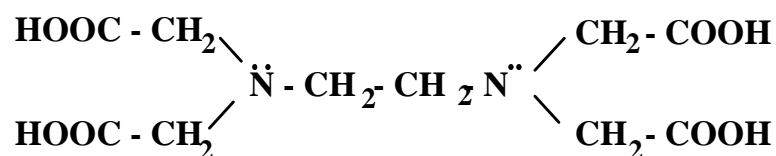

*Fig. **12. 3**. Structure of of nickel(II) amino acetate complex*
in two perpendicular planes.

It is already mentioned above that there is no outer sphere in the internal complexes, because the positive charge of the central ion is already compensated by negative charges of the ligand already inside the internal sphere. Both the lack of outer sphere and the fact, that the central ion is enclosed in a cyclic structure, formed by ligands in two planes, leads to a very great stability of internal complexes.

The two discussed ligands ethylene diamine and amino acetic the acid are *bidentate* ligands that are able to occupy two positions in the coordination sphere of the central atom – ethylene diamine, because it has two unshared electron pairs and can therefore form two donor-accepter bonds, amino acetic acid - because it is able to form one ordinary bond (using the hydrogen ion of the carboxyl group) and one donor-accepter bond (using the unshared electron pair of the amino group).

The next ligand, that is going to be discussed, is a bit more complicated. It is called ethylene diamine tetra acetic acid (**EDTA**) and it has a great importance in chemistry. Formula of **EDTA** can seem rather complicated:

$$HOOC-CH_2 \diagdown \qquad \diagup CH_2-COOH$$
$$\qquad \ddot{N}-CH_2-CH_2 \ N\text{\tiny ..}$$
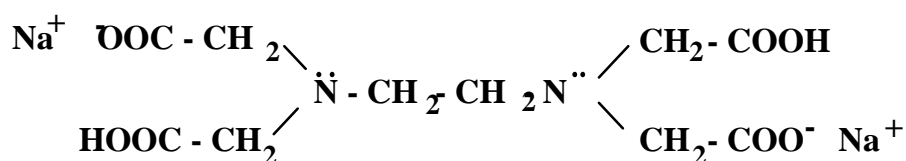$$HOOC-CH_2 \diagup \qquad \diagdown CH_2-COOH$$

but it can be easily understood, if one considers it as a molecule of ethylene diamine, in which the hydrogen atoms of amino groups are replaced by acetic acid radicals (**-CH$_2$-COOH**).

EDTA is a *hex dentate* ligand - it can form **4** ordinary bonds using the four -**COOH** groups and **2** donor-accepter bonds using the unshared electron pairs of the two nitrogen atoms, all-in all being able to occupy **6** positions in the coordination sphere of with a central ion.

As an acid **EDTA** is **4**-valent , therefore its formula can be written in a shorter way as **H$_4$Y**, assigning a symbol **Y^{4-}** to the acid remainder ion.

The coordination number of many metal ions is **4**, therefore they need a *tetra dentate* ligand to form a complete internal complex. **EDTA** itself is not suitable for these purposes, but one can easily obtain a tetra dentate ligand from **EDTA**, replacing two of the four carboxyl hydrogen ions of **EDTA** by sodium ions and forming a bisubstituted sodium salt **Na$_2$H$_2$Y** :

$$Na^+ \ \ ^-OOC-CH_2 \diagdown \qquad \diagup CH_2-COOH$$
$$\qquad \ddot{N}-CH_2-CH_2\ N\text{\tiny ..}$$
$$HOOC-CH_2 \diagup \qquad \diagdown CH_2-COO^- \ Na^+$$

The bisubstituted **Na** salt of **EDTA** is called Complexeone III or Trylone B.

When trylone B (Na_2H_2Y) forms internal complexes with bivalent metal ions, a planar projection of complex looks like shown in the fig. **12. 7**.

If Trylone B reacts with a trivalent metal ion, like Co^{3+}, the complex is also be formed in the molar ratio moles **1:1**. It means, that only **4** out of **6** free orbitals of the central Co^{3+} ion are used for complex formation. The reason for this phenomenon is the complicated spatial structure of the complex. It could seem, that in this case one central ion has to bind **3/2** Trylone molecules, but, in fact, the half-molecule of the second Trylone cannot be spatially situated around the central ion, as the first one has already completely surrounded it.

For this reason

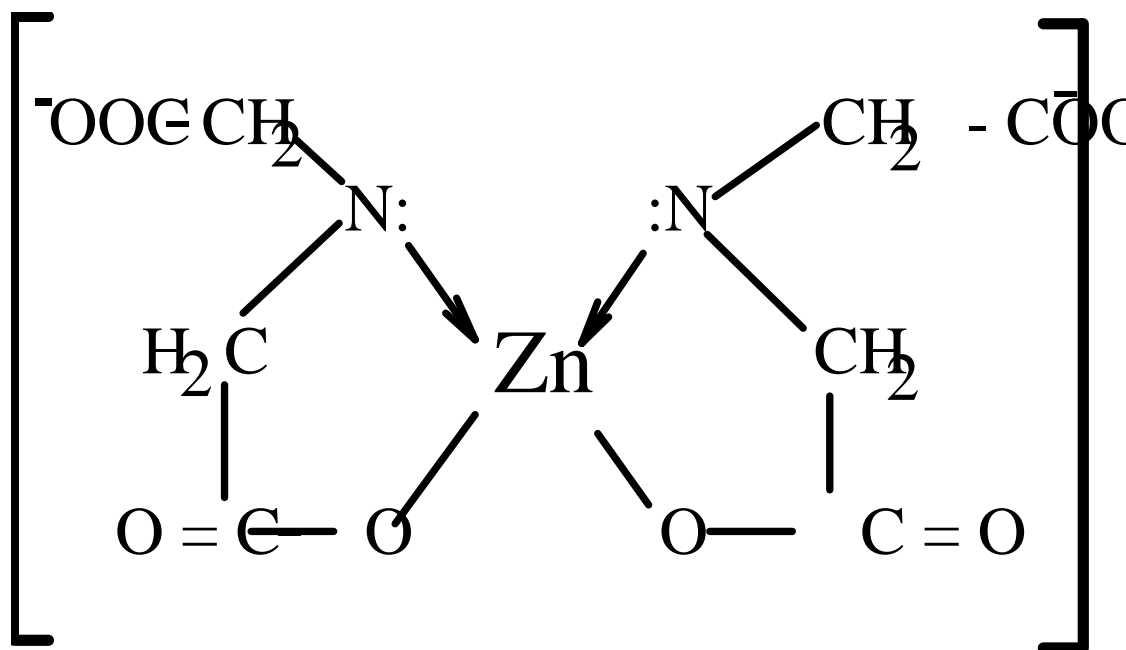*a metal ion of any valence (charge) binds one molecule of Trylone B.*

Fig. 12. 4. *A planar projection of zinc(II) complex with Trylone B*

PRACTICAL APPLICATIONS OF TRYLONE B

Trylone B has several important practical applications:

1. It is widely used for *water softening*. Water, containing bivalent metal ions is called *hard water* and it cannot be used for photographic processes, for cooling in car engines, for radiators of central heating in buildings etc,.

as it is making salt precipitates at high temperatures. If Trylone B is added, the metal ions are bound in complexes and therefore don't form any precipitates and don't disturb the photographic processes etc.

2. In stomatologic investigations and prophylactic care. Trylone B is often used for *etching of tooth enamel* when modeling of caries processes *in vitro* ("in vitro" here means experiments with extracted tooth outside the organism). As well, it can be used for etching of enamel of live tooth before prophylactic treatment with remineralizing agents.

3. Trylone B is used in analytical chemistry for titration of metal ions. This method is called *complexonometric titration* (see next chapter).

VI. COMPLEXONOMETRIC TITRATION

Complexonometric titration is used for determination of metal ion concentrations.

Let us discuss complexonometric titration of calcium. For determination of Ca^{2+} concentration it is a very important method, as there is no other suitable way for its determination except the *atomic absorption spectrometry* which is a rather expensive method and not available in every laboratory.

As Ca^{2+} ion is able to form a complex with trylone B in a molar ratio **1:1** (see before), the task seems rather easy. Ca^{2+} form a complex with Trylone, therefore one has just to titrate the Ca^{2+} containing solution by Trylone B. The only problem here is - how to detect the titration endpoint. One can use the so-called *metal indicators* for these purposes. Metal indicators are organic ligands, that form rather unstable **colored** complexes with metal ions. For instance, a metal indicator, called *eryochrome black* (let us assign to it a symbol **Er** in the further text) is suitable for Ca^{2+} titration.

Er itself has a blue color. At **pH = 10 Er** forms a red complex with Ca^{2+}:

$$\underset{blue}{Er} + Ca^{2+} \rightleftarrows \underset{red}{[CaEr]^{2+}}$$
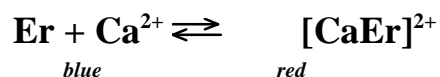
Thus, the Ca^{2+} containing solution turns red when **Er** is added. Just a little amount of **Er** has to be added so that just a little part of Ca^{2+} ions are involved in the complex with **Er** to turn the color of solution red. The greatest part of Ca^{2+} ions remain free. When one starts titration of the solution by Trylone B, its anions H_2Y^{2-} react with the free Ca^{2+} ions forming a colorless complex:

$$Ca^{2+} + H_2Y^{2-} => [CaY]^{2-} + 2H^+$$
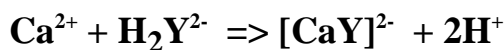
While just the free Ca^{2+} ions react with Trylone, the red complex of Ca^{2+} with **Er** still exists. When all the free Ca^{2+} ions are used up, Trylone starts reacting with these Ca^{2+} ions, that are included in the **[CaEr]** complex (as **[CaEr]** complex is weak and Ca^{2+} complex with Trylone is strong, Trylone takes Ca^{2+} ions from **[CaEr]** complex). As the result, the red color of **[CaEr]** complex disappears and the blue color of free Er is restored. Thus the color of solution changes from red to blue at titration endpoint.

VII. BIOLOGICAL ROLE OF COMPLEX COMPOUNDS

All of the metal ions in living organisms are involved complexes with proteins and enzymes, therefore the role of complex compounds in the life processes is great.

Proteins and enzymes are polydentate ligands because many spatially separated **-NH$_2$**, **=NH** or **≡N** groups are present in their molecules. As polydentate ligands, proteins and enzymes form chelate-type complexes with metal ions.

One can outline several most important functions of complex compounds in the living organisms:

1) Stabilization of enzyme structures. Metal ions, for instance, **Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}** and many others are involved in complexes with enzymes in living organisms. These enzymes that include metal ions are called *metallo enzymes*. The function of metal ions in these complexes is to keep the enzymes in their appropriate spatial configurations. As it was discussed above (see Part **9**), an enzyme has to be complementary to its substrate, i.e. the enzyme must have an appropriate spatial configuration to be able to recognize its substrate. If no metal ions are present the enzyme can appear in many different spatial configurations most of which are inactive.

2) Addition of thermal stability to enzymes. Presence of metal ions in the structures of enzymes provides extra thermal stability to the enzymes, especially if the metal content in the enzyme is high.

3) Transfer of nerve impulses. Complex compounds of **K^+** and **Na^+** are responsible for transfer of nerve impulses.

4) Realization of oxidation-reduction processes. Oxidation-reduction processes that occur in the organisms are catalyzed by enzyme complexes

with these metals, which can have several different oxidation numbers as **Fe** (+**2** or +**3**), **Cu** (+**1** or +**2**), **Mn** (+**2**,+**3**,+**4** etc.). The metal ion plays the role of electron transporter from the reduced form of substrate to the oxidized one in these enzymes.

Now let us mention the biological role of some most important metal ions.

K$^+$, Na$^+$	- involved in formation of nerve impulses,
Ca^{2+}, Mg^{2+}, Mn^{2+}	- stabilization of enzyme configurations,
Cu^{2+}	- involved in the enzymes, which carry out the unreeling of protein double

helixes,

Co^{3+}, Zn^{2+}	- in enzymes, catalyzing ester hydrolysis, (enzymes called *peptidases,*

hydrolases)

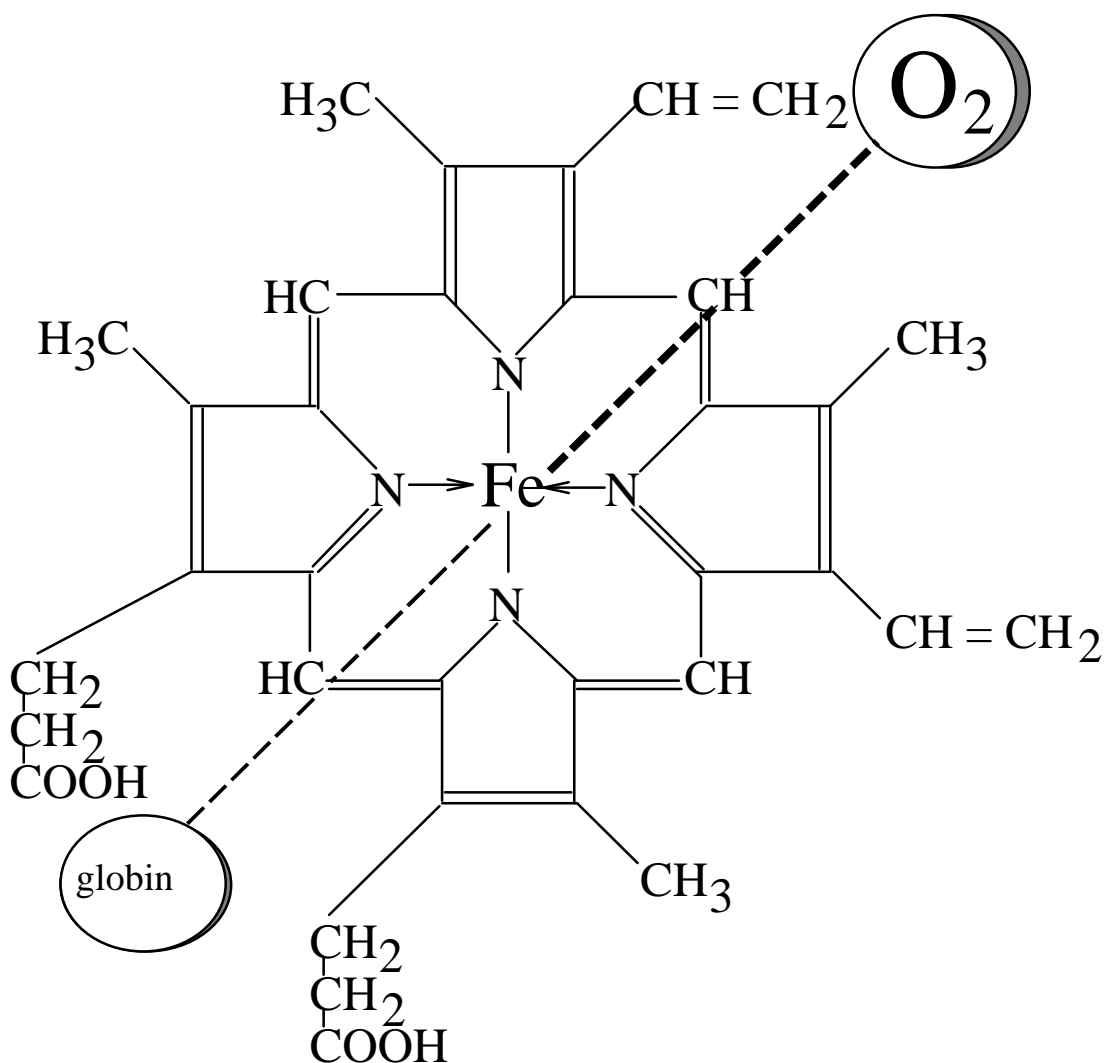|	
Mg^{2+}	- activates enzymes, that carry out phosphate reactions.
Cu^{2+}, Co^{2+}, Fe^{2+}	- involved in these enzymes, which carry out the oxidation processes.

Fig. 12. 8. *The structure of hemoglobin.*

A special role of Fe^{2+} complex with so-called proto porphyrin ring is observed in breathing processes - the hemoglobin is a Fe^{2+} complex, see structure in fig. **12. 5**.

Four out of **6** positions in the coordination sphere of Fe^{2+} ion are used by *proto porphyrin ring* in the structure of hemoglobin, one by globin (a protein) and one by a molecule of O_2. This compound is the one, that binds oxygen from the air in lungs and transports it to tissues.

Several structures similar to the one of hemoglobin are also known in the nature. There is a similar structure in B_{12} where Fe^{2+} ion is replaced by a Co^{2+} ion. As well, a substitution of Fe^{2+} ion by a Cu^{2+} ion leads to formation of *hemo cyanin* which serves for oxygen binding in some lower organisms. A structure similar to hemoglobin with Mg^{2+} instead of Fe^{2+} is known as *chlorophyll* and is very important in vegetable kingdom.