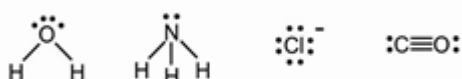


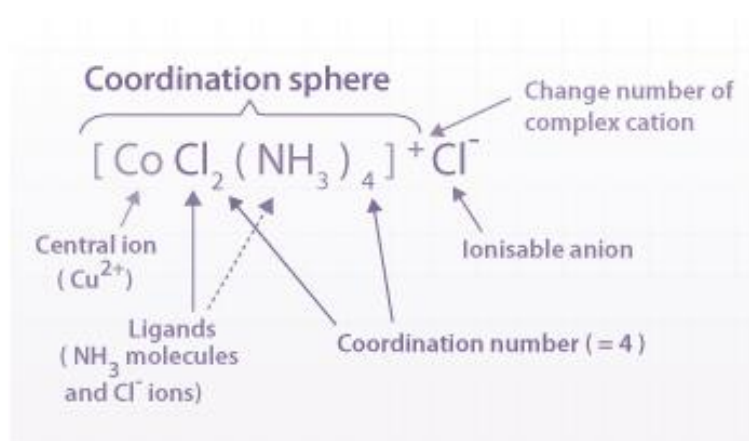
## COORDINATION COMPOUNDS

### Structure of the coordination compounds

Coordination compounds are products of an inert metal atom or metal cation (Lewis acid) with anions or neutral molecules that are electron donors (Lewis bases). A ligand has at least one unshared pair of valence electrons, e.g.:



As a result of such a reaction, coordination (donor-acceptor) bonds are formed.



Coordination number of a central atom in a molecule or crystal is the number of atoms, molecules or ions bonded to it. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.

### Formation constant for complex

The reactions of formation of complexes in solutions are subject to the mass-action law. If the central ion Me forms a complex with the L-ligand in the reaction:



the equilibrium of the complex formation reaction, called the stability constant or formation constant ( $K_f$ ,  $\beta$ ), is given by:

$$\beta = \frac{[MeL]}{[Me][L]}$$

The constant of the reaction running in the surreal direction, i.e. the dissociation reaction of the complex, called the complex instability constant, expresses the formula:

$$K = \frac{[Me][L]}{[MeL]}$$

Complex formation constant and complex instability constant are related to the dependence:

$$\beta = \frac{1}{K}$$

Stability constants of the complexes, expressed by the powers of the number 10, are more convenient to give in the form of their logarithms ( $\log \beta$ ). Exemplary values of  $K_f$  are given in Table 1.

Table 1. Formation constants for some complex ions

Complex Ion	$K_f$	Complex Ion	$K_f$
$AgCl_2^-$	$1.8 \times 10^5$	$CuCl_2^-$	$1 \times 10^5$
$Ag(CN)_2^-$	$2 \times 10^{20}$	$Cu(NH_3)_4^{2+}$	$2 \times 10^{12}$
$Ag(NH_3)_2^+$	$1.7 \times 10^7$	$FeSCN^{2+}$	$9.2 \times 10^2$
$Ag(S_2O_3)_2^{3-}$	$1 \times 10^{13}$	$Fe(CN)_6^{3-}$	$4 \times 10^{36}$
$Al(OH)_4^-$	$1 \times 10^{33}$	$Fe(CN)_6^{4-}$	$4 \times 10^{45}$
$Cd(CN)_4^{2-}$	$2 \times 10^{18}$	$Hg(CN)_4^{2-}$	$2 \times 10^{41}$
$Cd(NH_3)_4^{2+}$	$2.8 \times 10^7$	$Ni(NH_3)_6^{2+}$	$9 \times 10^8$
$Cd(OH)_4^{2-}$	$1.2 \times 10^9$	$PtCl_4^{2-}$	$1 \times 10^{16}$
$Co(NH_3)_6^{2+}$	$1 \times 10^5$	<i>trans</i> - $Pt(NH_3)_2Cl_2$	$3 \times 10^{28}$
$Co(NH_3)_6^{3+}$	$1 \times 10^{23}$	<i>cis</i> - $Pt(NH_3)_2Cl_2$	$3 \times 10^{29}$
$Co(NH_3)_5Cl^{2+}$	$2 \times 10^{28}$	$Zn(CN)_4^{2-}$	$6 \times 10^{16}$
$Co(NH_3)_5NO_2^{2+}$	$1 \times 10^{24}$	$Zn(NH_3)_4^{2+}$	$3.6 \times 10^8$
		$Zn(OH)_4^{2-}$	$3 \times 10^{14}$

Knowledge of the stability of complexes allows prediction of ligand exchange reactions. Considering, for example, cadmium iodide complexes ( $\log \beta = 6,1$ ) and mercury ( $\log \beta = 30,3$ ), it can be predicted that the mercury ion will collect iodide ions from the iodine cadmium complex practically completely, because the difference in  $\beta$  of both complexes is very high.

## Nomenclature of complexes

The coordination compounds are named in the following way.

1. When naming coordination compounds, always name the cation before the anion. This rule holds regardless of whether the complex ion is the cation or the anion.

2. In naming the complex ion:

A) Name the ligands first, in alphabetical order, and then name the metal atom or ion.

B) The names of some common ligands are listed in Table 2.

- *Anionic ligands end in "-o."* For anions that end in "-ide" (e.g. chloride,

hydroxide), "-ate" (e.g. sulfate, nitrate), and "-ite" (e.g. nitrite), change the

endings as follows:

-ide → -o; (e.g., chloride → chloro and hydroxide → hydroxo)

-ate → -ato; (e.g., sulfate → sulfato and nitrate → nitrato)

-ite → -ito; (e.g., nitrite → nitrito)

For neutral ligands, the common name of the molecule is used (e.g.  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$  (ethylenediamine)).

Important exceptions: water is called 'aqua', ammonia is called 'ammine', carbon monoxide is called 'carbonyl', and the  $\text{N}_2$  and  $\text{O}_2$  molecules are called 'dinitrogen' and 'dioxygen'.

Table 2. Names of Some Common Ligands

	Ligands	Names		Ligands	Names
Anionic Ligands	$\text{Br}^-$	bromo	Neutral Ligands	$\text{NH}_3$	ammine
	$\text{F}^-$	fluoro		$\text{H}_2\text{O}$	aqua
	$\text{O}^{2-}$	oxo		$\text{NO}$	Nitrosyl
	$\text{OH}^-$	hydroxo		$\text{CO}$	Carbonyl
	$\text{CN}^-$	cyano		$\text{O}_2$	dioxygen
	$\text{C}_2\text{O}_4^{2-}$	oxalato		$\text{N}_2$	dinitrogen
	$\text{CO}_3^{2-}$	carbonato		$\text{C}_5\text{H}_5\text{N}$	pyridine
	$\text{CH}_3\text{COO}^-$	acetato		$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	ethylenediamine

C) The Greek prefixes di-, tri-, tetra-, etc. are used to designate the number of each type of ligand in the complex ion. If the ligand already contains a Greek prefix (e.g. ethylene diamine) or if it is a polydentate ligand (i.e. it can attach at more than one coordination site), the prefixes bis-, tris-, tetrakis-, and pentakis- are used instead. The numerical prefixes are listed in Table 3.

Table 3. Numerical Prefixes

Number	Prefix
1	mono
2	di (bis)
3	tri (tris)
4	tetra (tetrakis)
5	penta (pentakis)
6	hexa (hexakis)
7	hepta
8	octa
9	nona (ennea)
10	deca
11	undeca
12	dodeca

D) After naming the ligands, name the central metal. If the complex ion is a cation, the metal is named same as the element. For example, Co in a complex cation is called cobalt and Pt is called platinum. If the complex ion is an anion, the name of the metal ends with the suffix -ate. For example, Co in a complex anion is called cobaltate and Pt is called palatinate (Table 4). For some metals, the Latin names are used in the complex anions (e.g. Fe is called ferrate and not ironate).

Table 4: Name of Metals in Anionic Complexes

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

E) Following the name of the metal, the oxidation state of the metal in the complex is given as a Roman numeral in parentheses.

3. To name a neutral complex molecule, follow the rules of naming a complex cation.

Remember: Name the (possibly complex) cation BEFORE the (possibly complex) anion.

For historic reasons, some coordination compounds are called by their common names. For example,

$[\text{Fe}(\text{CN})_6]^{3-}$  and  $[\text{Fe}(\text{CN})_6]^{4-}$  are named ferricyanide and ferrocyanide respectively, and  $[\text{Fe}(\text{CO})_5]$  is called iron carbonyl.

#### Examples:

$[\text{Cr}(\text{OH})_4]^-$  tetrahydroxochromate(III) ion

$[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{Cl})_4]$  tetraammineplatinum(II) tetrachloroplatinate(II)

$[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]^+$  tetraamminechloronitrito-N-cobalt(III)

$[\text{Cr}(\text{H}_2\text{O})_4(\text{NH}_3)]^{2+}$  amminetetraaquachromium(II)

$[\text{Cr}(\text{SO}_4)(\text{NH}_3)]$  amminesulfatochromium(II)

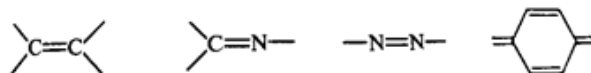
$[\text{Cr}(\text{H}_2\text{O})_4(\text{NH}_3)]\text{SO}_4$  amminetetraaquachromium(II) sulfate

$\text{K}_3[\text{Fe}(\text{CN})_6]$  potassium hexacyanoferrate(III)

#### The color of ligands and complexes

A significant part of the complex formation reactions are color reactions. There is a close relationship between the color of the substance and its electron structure. The molecule shows absorption in the visible or ultraviolet part when under the influence of radiation the electrons are transferred from the ground state to one of the excited states. The creation of a color or its change is always related to the deformation of the normal electronic structure of the molecule or atom.

Changes in electron energy under the influence of irradiation occur in molecules containing chromophore groups, i.e. atomic groups with multiple, unsaturated bonds. Examples of chromophore groups are:



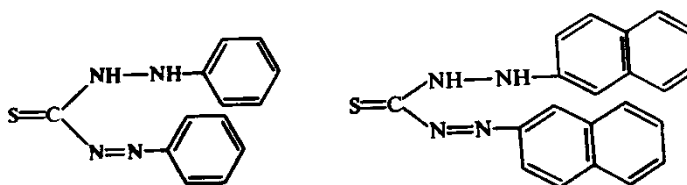
The strongest chromophore groups are the azo group and the p-quinoid ring.

If there is a chromophore group in the organic reagent molecule, then the reagent has its own color, and the color reaction with the metal ion is based on a change in color, often combined with an increase in intensity. The color change in the direction of longer wavelengths is called the deepening of color or offset, or bathochromic effect. The shifting of the maximum absorption in the direction from red to ultraviolet is defined as the increase in color or as a hypsochromic effect.

Colored complexes with colorless ligands create metal ions, which themselves have a chromophore effect. These are metals that can occur at various degrees of oxidation, e.g. Fe, Cu, Ni, Co, Cr, V, Mn, Ce. In this case, the appearance of color is observed, because in a high dilution of the ions of the mentioned group of metals appear colorless, and the formation of the complex is accompanied by the appearance of a much more intense color.

Known reactions are colorless between the ligand and the metal ion not having chromophoric properties, which result in colored complexes. In this case, a secondary reaction can occur, wherein the chromophore moiety is formed. A colored complex can also arise when the colorless ligand absorbs radiation in the near ultraviolet, followed by reaction with metal ion absorption shifts to the visible spectrum.

In the case of interaction of chromophore groups of the ligand molecule with metal ions with chromophore properties, complexes of particularly intense color are formed. The presence of the organic ligand in addition to the chromophore groups also to auxochrome groups, e.g.  $-\text{NH}_2$ ,  $-\text{OH}$ ,  $-\text{SH}$ ,  $-\text{NO}_2$ ,  $=\text{CO}$ , affects the color, enhancing it or changing its shade. Increasing the molecular weight of the ligand, e.g. by replacing the phenyl group with a naphthyl group, generally results in an increase in the color intensity of the ligand and its colored complexes. As an example, dithizone (diphenylthiocarbazone) can be mentioned, whose color is less intense than its analog, di- $\beta$ -naphthylthiocarbazone:



### Masking reactions

In order to increase the selectivity of analytical reactions (selectivity of reagents), complexation reactions are often used to mask the interfering ions. It is one of the most important applications of complex formation reactions in analytical chemistry.

Masking the interfering ion is the carrying of this ion, as a result of the complexation reaction, into a complex of adequate stability. The ion bound in this form is unable to react and does not interfere with the detection or determination of another ion. For example, if only cadmium (by precipitating it in the form of sulphide) needs to be separated from the mixture of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions, both ions should be converted into cyanide complexes  $\text{Cd}(\text{CN})_4^{2-}$  and  $\text{Cu}(\text{CN})_2^-$ . From the cyanide environment, hydrogen sulphide will only precipitate cadmium sulphide; the copper will remain in the solution masked in the form of a cyanide complex.

The concentration of  $\text{Cd}^{2+}$  ions resulting from the  $\text{CdS}$  solubility product is lower than the concentration determined by the stability constant of  $\text{Cd}(\text{CN})_4^{2-}$  complex, and the concentration of  $\text{Cu}^{2+}$  ions conditioned by the  $\text{Cu}_2\text{S}$  solubility product is higher than the concentration resulting from the constant  $\text{Cu}(\text{CN})_2^-$  stability.

Constants, on the basis of which the compared concentrations are calculated, should of course be conditional constants, calculated for the conditions prevailing in a given environment. If masking is to be quantitative, then the differences between constants (constants of stability and appropriate solubility products) must be quite significant. It should be added that only very few constants of stability have such precisely determined values, so that they can accurately predict the course of an appropriate reaction. Usually, after selecting a complexing factor, it should be tested experimentally whether in given conditions the reaction proceeds as predicted.

Before precipitation of nickel with dimethylglyoxime from a solution containing iron (III) ions,  $\text{Fe}^{3+}$  ions should be masked with tartaric acid. A durable water-soluble tartrate complex of iron is formed, which prevents the release of iron (III) hydroxide after the addition of  $\text{H}_2\text{Dm}$  and ammonia. For masking multivalent metal ions, another hydroxy acid, namely citric acid, is also used. Oxalic acid, also used for masking, forms less stable complexes with metals than tartaric and citric acids, especially in neutral or alkaline environments. Complexes of oxalic acid, unlike tartaric and citric acid complexes, do not easily decompose after acidification of solutions. This is related to the strength of these acids. Oxalic acid anions (and other stronger acids) bind hydride ions less well and therefore their metal complexes are generally quite stable in acidic solutions.

Among the inorganic masking agents, cyanides, thiosulphates, fluorides, chlorides and ammonia are most commonly used. The most common applications of organic reagents are: EDTA, tartaric, citric and oxalic acids (see Table 5.).

Particularly important role as a masking reagent plays in the chemical analysis of EDTA. In the presence of EDTA, hydroxides of titanium, beryllium, uranium (VI), niobium and tantalum can be precipitated with ammonia, while other metals of group III, such as iron (III) and aluminum, remain in solution. Their complexes with EDTA are more

stable than hydroxides. An example of the use of EDTA as a sequestering agent in color reactions is the detection or determination of copper with sodium diethyldithiocarbamate in the presence of Co, Ni, Fe, Mn, Cd, Pb and Zn, which are masked by EDTA. Sodium thiosulphate is an effective masking agent for many metals during detection or determination of zinc using dithizone. In an ammonium-buffered medium, thiosulphates prevent the reaction of dithizone with Ag, Cu, Hg, Bi, Cd and Pb.

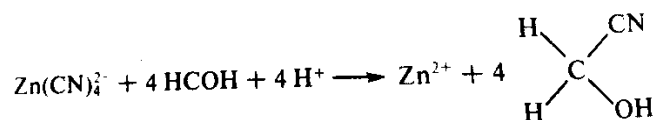
Table 5. Effective masking agents for metals.

Metal masked	Masking reagents
Sb	tartrates, citrates, $S^{2-}$ , $OH^-$ , $F^-$ , $I^-$ ,
Be	$F^-$ , $OH^-$ , tartrates, citrates
Bi	tartrates, citrates, EDTA, $I^-$ , thioureas
Cr(III)	oxalates, tartrates, citrates, EDTA
Sn	tartrates, citrates, $S^{2-}$ , $OH^-$ , $F^-$ , oxalates
Zn	$CN^-$ , $NH_3$ , $SCN^-$ , tartrates, citrates, EDTA, $OH^-$
Zr	tartrates, citrates, EDTA, $H_2O_2$ , $F^-$
Al	$F^-$ , $OH^-$ , tartrates, citrates, oxalates, EDTA, TEA
Cd	tartrates, citrates, EDTA, $CN^-$ , $I^-$ , $S_2O_3^{2-}$
Co	tartrates, citrates, EDTA, $CN^-$ , $NO_2^-$ , $S_2O_3^{2-}$
Mg	tartrates, citrates, EDTA
Mn	oxalates, tartrates, citrates, TEA, $CN^-$ , $P_2O_7^{4-}$ , $PO_4^{3-}$ , $F^-$
Cu	tartrates, citrates, EDTA, $CN^-$ , $S_2O_3^{2-}$
Mo	tartrates, citrates, oxalates, $F^-$ , $SCN^-$ , $H_2O_2$
Ni	tartrates, citrates, EDTA, $CN^-$ , $NH_3$
Pb	$OH^-$ , citrates, EDTA, $OH^-$ , $S_2O_3^{2-}$ , acetates
Pt	oxalates, $CN^-$ , $NH_3$ , $I^-$ , $S_2O_3^{2-}$ , $SCN^-$ , $NO_2^-$
Hg	$CN^-$ , $I^-$ , $Cl^-$ , $NO_2^-$
Ag	$CN^-$ , $NH_3$ , $Cl^-$ , $S_2O_3^{2-}$
Th	tartrates, citrates, EDTA, $F^-$ , $CO_3^{2-}$
Ti	tartrates, citrates, $H_2O_2$ , TEA, $F^-$
U	tartrates, citrates, oxalates, $H_2O_2$ , $F^-$ , $CO_3^{2-}$
V	$H_2O_2$ (for $V^V$ ), EDTA, $F^-$ , oxalates (for $V^{IV}$ )
Ca	Citrates, EDTA, $P_2O_7^{4-}$
W	tartrates, citrates, oxalates, $F^-$ , $H_2O_2$
Au	$CN^-$ , $Cl^-$ , $S_2O_3^{2-}$
Fe(II)	$CN^-$ , $S_2O_3^{2-}$ , 1,10-phenanthroline
Fe(III)	tartrates, citrates, oxalates, TEA, $PO_4^{3-}$ , $F^-$

Unmasking is the reverse of masking in chemical analysis. It consists in the release of the ion from the complex formed during masking in order to carry out further reactions with it. For example, zinc, masked by binding to



cyanide ions, is unmasked with formaldehyde. The aldehyde binds cyanides to stable cyanohydrin, releasing zinc ions:



Unmasking reactions are also used to detect or determine formaldehyde. First nickel ions are precipitated by adding excess of dimethylglyoxime (ammonia medium). Part of the nickel dimethylglyoxate precipitate dissolves after the addition of potassium cyanide and a cyanide complex of nickel  $[\text{Ni}(\text{CN})_4]^{2-}$  that is more stable than the  $\text{Ni}(\text{HDm})_2$  is formed. The remaining part of the  $\text{Ni}(\text{HDm})_2$  sediment is filtered off. The filtrate contains free  $\text{H}_2\text{Dm}$  and  $[\text{Ni}(\text{CN})_4]^{2-}$ . After this solution has been added to the test solution containing formaldehyde, the unmasking (releasing) of the nickel ion from the cyanide complex occurs. The free nickel ions react immediately with  $\text{H}_2\text{Dm}$ , whereby the amount of  $\text{Ni}(\text{HDm})_2$  that is equivalent to  $\text{HCOH}$  is released.

In order to release many elements from the fluoride complexes (e.g.  $[\text{FeF}_6]^{3-}$ ,  $\text{SiF}_4$ ), boric acid is used as the unmasking agent. A more stable  $\text{BF}_4^-$  ion is formed. Thanks to this reaction, traces of silicon in  $\text{HF}$  acid can be detected by spectrophotometric method with molybdate method.