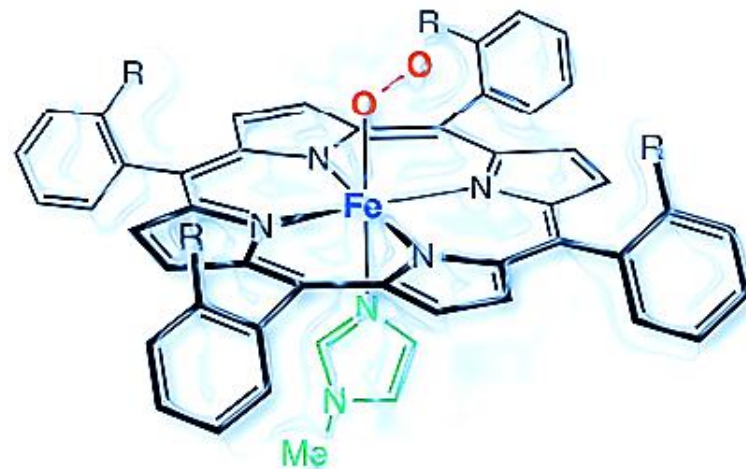
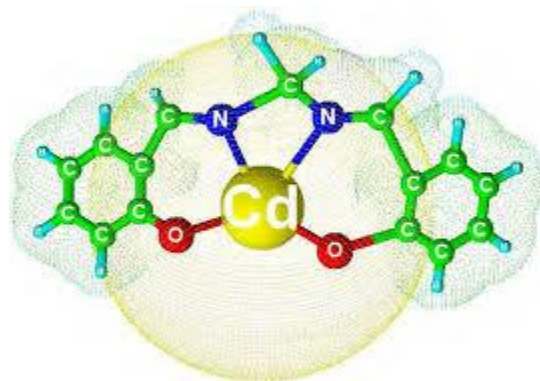
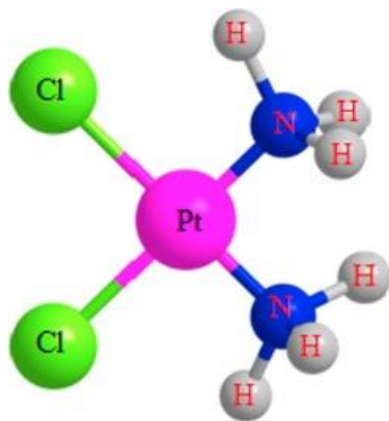


Coordinative and biocoordinative chemistry

Major in Pharmaceutical Chemistry - 2nd year

Assoc. Prof. Aurel Tăbăcaru, PhD



Curriculum

- 1. Introduction to coordinative and biocoordinative chemistry:** *Definition, role and importance of complex combinations; brief history of complex combination theory, Werner's coordination theory.*
- 2. Ligands and coordination number:** *Definition and classification of ligands; definition of coordination number; coordination numbers and corresponding geometries.*
- 3. Nomenclature, formulation and classification of complex combinations:** *General aspects; writing, formulating and classifying complex combinations.*
- 4. Formation and stability of complex combinations:** *Thermodynamic stability, stability constant, entropic effect, factors influencing the formation of complex combinations.*
- 5. Chemical bonding theories in complex combinations:** *Electrostatic model, covalent model, valence bond method, crystal field theory, ligand field theory, ligand spectrochemical series.*
- 6. Stereochemistry of complex combinations:** *Internal asymmetry or Jahn-Teller effect; isomerism of complex combinations.*
- 7. Reactivity of complex combinations:** *Hydrolysis reactions, addition reactions, anation reactions, trans effect of ligands.*
- 8. Biological implications of complex combinations:** *Biological role of metal ions; biocoordinating systems; metal complexes with nucleotides; role of metals in enzyme catalysis; synthetic chelates - models for biological systems; masking agents in heavy metal poisoning therapy; therapeutically active complexes - conditioned complexes in pharmaceutical forms, biologically active chelated complexes.*

Study bibliography

1. Marcu Gh., *Chimia compușilor coordinativi*, Editura Academiei Republicii Socialiste România, Bucharest, 1984.
2. Brezeanu M., Spacu P., *Chimia combinațiilor complexe*, Editura Didactică și Pedagogică, Bucharest, 1974.
3. Wilkinson G., *Comprehensive coordination chemistry*, Pergamon Press, 1987.
4. Lawrance G.A., *Introduction to coordination chemistry*, John Wiley & Sons, 2013.
5. Crichton R.R., *Biological inorganic chemistry*, Elsevier, 2012.
6. Străjescu M., Teodor F., *Elemente de chimie bioanorganică*, Editura Dacia, Cluj-Napoca, 1979.
7. Roman L., Bârză O., *Implicații biomedicale ale combinațiilor complexe*, Editura Dacia, Cluj-Napoca, 1979.

1. Introduction to coordinative and biocoordinative chemistry

"Nature solves some of its most complex problems using coordinative compounds."
(Academician Maria Brezeanu)

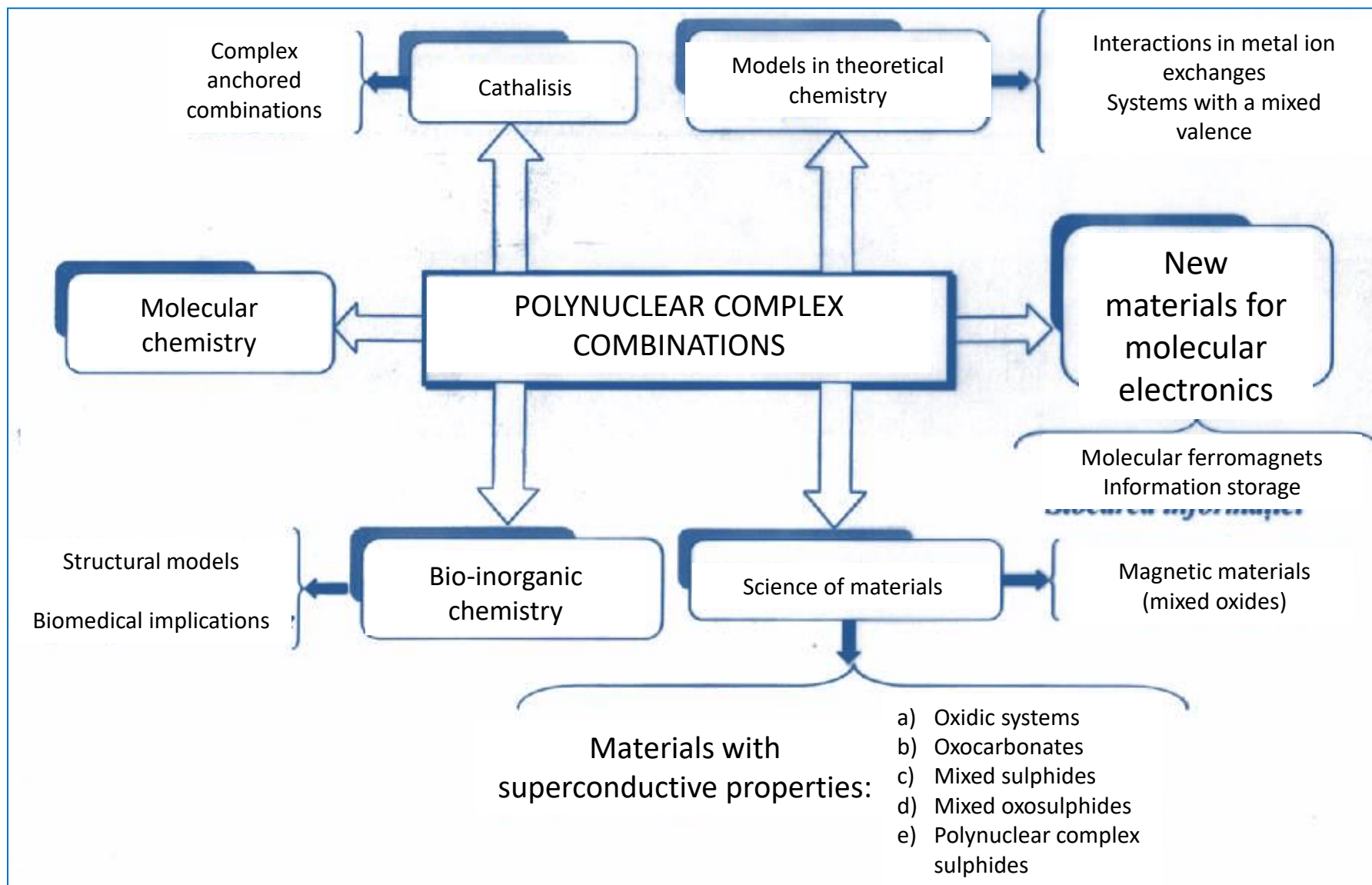
- Coordinative chemistry, also known as complex combination chemistry, is the branch of chemistry that deals with the study of coordinate compounds.
- Initially considered a chapter of inorganic chemistry, today a discipline in its own right, coordinative chemistry is one of the most important and highly topical areas of chemistry in general and inorganic chemistry in particular, a fascinating field that offers the researcher unsuspected satisfactions, a field that has attracted and continues to attract researchers from all over the world and from all fields of chemistry, a field that, in an extremely short period of time, has experienced one of the most impressive developments.
- In our country there is a strong school of coordinative chemistry, which has an old and solid tradition, illustrated by the work of prestigious personalities of Romanian chemistry (Nicolae Costăchescu, Gheorghe Spacu, Radu Cernătescu, Raluca Ripan, Petru Spacu, Gheorghe Marcu, Maria Brezeanu and others).

1. Introduction to coordinative and biocoordinative chemistry

The importance of this area lies in the following:

- Coordinate chemistry is a frontier discipline that involves in research, in addition to inorganic chemists, specialists from many areas of chemistry, both theoretical and experimental.
- Complex combinations, especially polynuclear ones, are nowadays having multiple and important practical applications in the most varied fields.
- The number of complex combinations is much higher than the number of so-called simple combinations (in the general sense: acids, bases, oxides, salts) and is increasing rapidly from year to year.
- Complex combinations are ubiquitous in both the systems that are the subject of chemical research and in living organisms.

1. Introduction to coordinative and biocoordinative chemistry



1. Introduction to coordinative and biocoordinative chemistry

Defining complex combinations

- According to the International Union of Pure and Applied Chemistry (IUPAC), *complex combinations or coordinative compounds are substances formed by the addition of one or more ions and/or molecules to one or more ions and/or molecules.*
- The coordination entity generally refers to molecules or ions in which there is one atom **(A)** - known as the central atom - to which other atoms **(B)** or groups **(C)** - known as coordinating atoms- are attracted.
- Each atom **(A)** has a characteristic *coordination number*, which is the number of atoms directly attracted to it. Atoms **(B)** and groups **(C)** are called *ligands*.
- In complex combinations each chemical element has its oxidation state satisfied, from the classical valence point of view.

1. Introduction to coordinative and biocoordinative chemistry

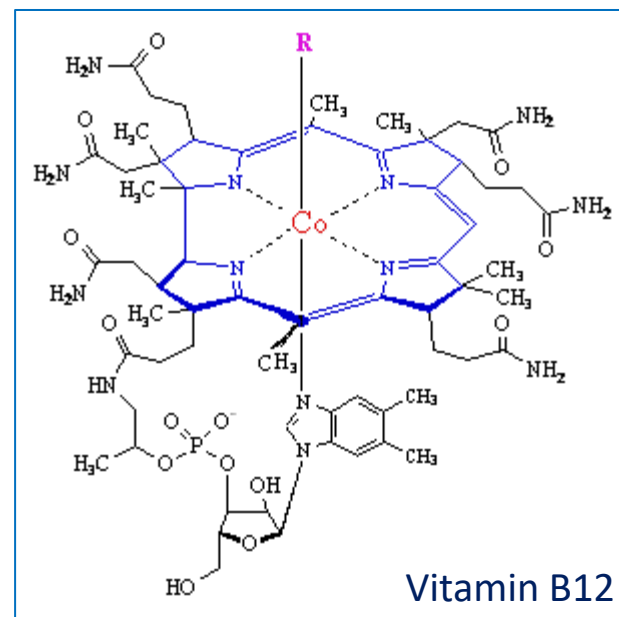
The role and importance of complex combinations

1. The emergence and development of spatial concepts of chemical structure led, at first, to the emergence of ***stereochemistry*** of complex combinations, later extended to all inorganic compounds.
2. Elucidation of solvent-solvent interactions with complex formation that occur in the dissolution process.
3. Explaining the formation of complex combinations led to the development of the electrostatic theory of acids and alkali.
4. The development of coordinative chemistry has enabled the development of analytical chemistry, since the latter is also based on the formation of complex combinations.
5. In catalytic processes, intermediates also form complex combinations.
6. Certain complex combinations also play a crucial role in the normal functioning of living organisms.

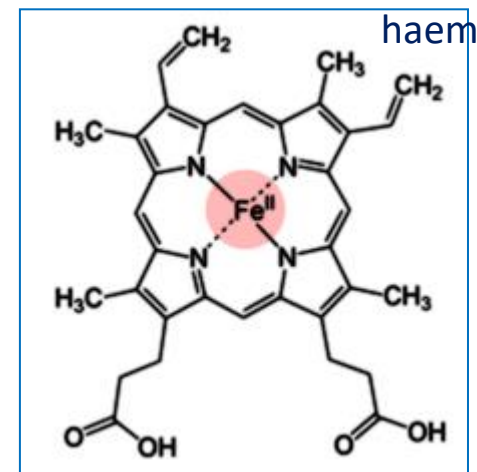
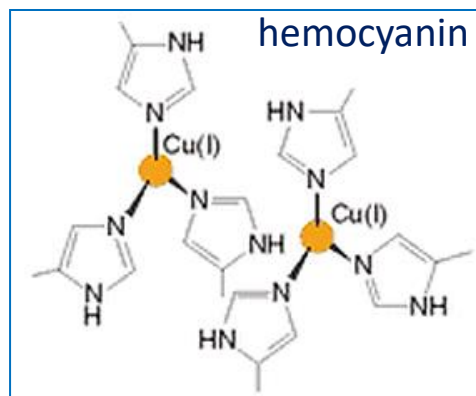
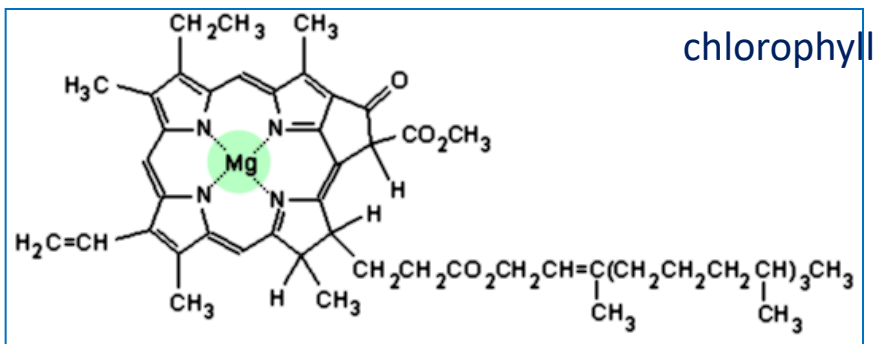
1. Introduction to coordinative and biocoordinative chemistry

Among the substances present in living organisms, known to us all, which are nothing but complex combinations or biocoordinating compounds, can be mentioned:

- chlorophyll, the green dye in plants, is a complex combination of magnesium;
- haem, a complex combination of Fe(II);
- vitamin B12, a complex combination of Co(II);
- hemocyanin, a complex combination of Cu(I).



In addition, in the vast majority of cases, the chemical elements present in living organisms perform their functions "via coordination".



1. Introduction to coordinative and biocoordinative chemistry

Brief history of complex combination theory

In the history of the complex combination there are three stages.

1. The trial phase

- The first works leading to the study of complex combinations belong to **Tassaert** (1798) on metal amines. He noted that leaving salts of cobalt amines at rest yields stable combinations containing six orange-yellow ammonia (NH_3) molecules, denoted $\text{CoCl}_2 \cdot 6\text{NH}_3$.
- The research was continued between 1802 and 1869 by a number of chemists such as **Proust**, **Thénar**, **Reist**, **Hoffmann**, etc. **Reist** attempted a classification of the combinations obtained by colour as follows:



luteosalts



praseosalts



purplesalts



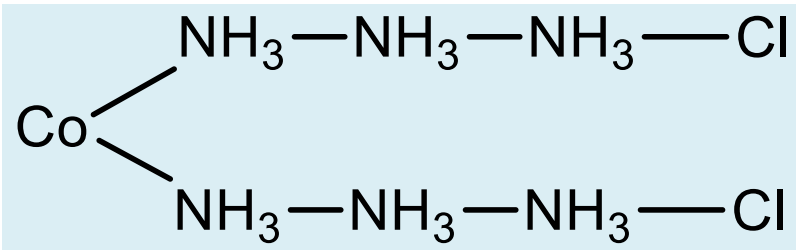
rosesalts

1. Introduction to coordinative and biocoordinative chemistry

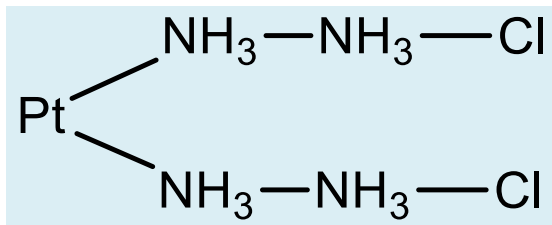
Brief history of complex combination theory

II. Stage dominated by Scandinavian chemists' ideas

- In 1869, **Blomstrand** proposed chained structures for Co(II) and Pt(II) compounds, assuming that their structure is planar and that ammonia molecules bond to each other like methylene groups in organic compounds.



for $\text{CoCl}_2 \cdot 6\text{NH}_3$



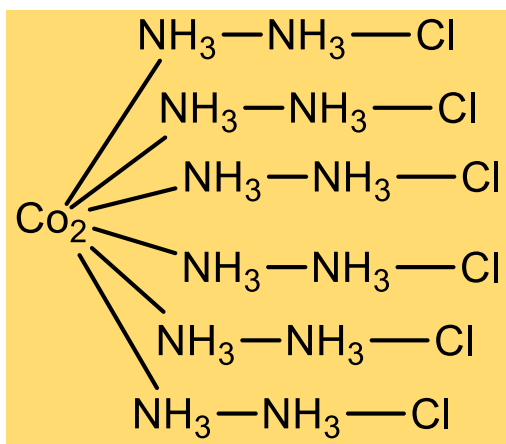
for $\text{PtCl}_2 \cdot 4\text{NH}_3$

1. Introduction to coordinative and biocoordinative chemistry

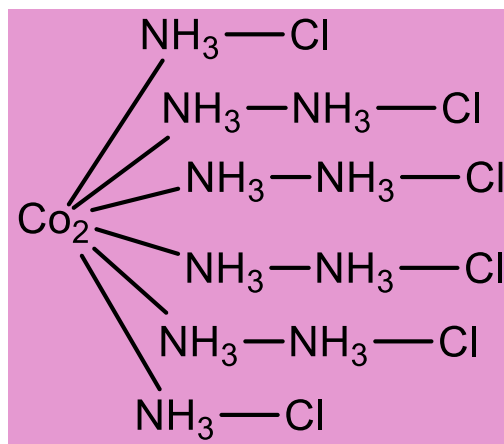
Brief history of complex combination theory

II. Stage dominated by Scandinavian chemists' ideas

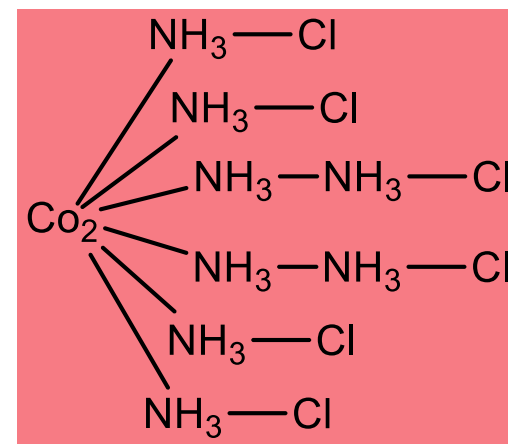
- Regarding Co(III) ammoniates, Blomstrand argues that they are dimeric compounds. Corresponding to the three prepared combinations - hexa ammoniate, penta ammoniate and tetra ammoniate, Blomstrand proposes the following structures:



for $\text{Co}_2\text{Cl}_6 \cdot 12\text{NH}_3$
Hexa ammoniate
(luteosalt)



for $\text{Co}_2\text{Cl}_6 \cdot 10\text{NH}_3$
Penta ammoniate
(purplesalt)



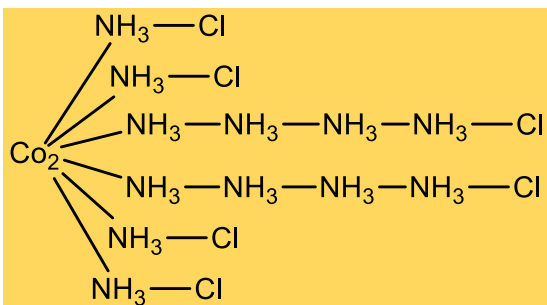
for $\text{Co}_2\text{Cl}_6 \cdot 8\text{NH}_3$
Tetra ammoniate
(rosesalt)

1. Introduction to coordinative and biocoordinative chemistry

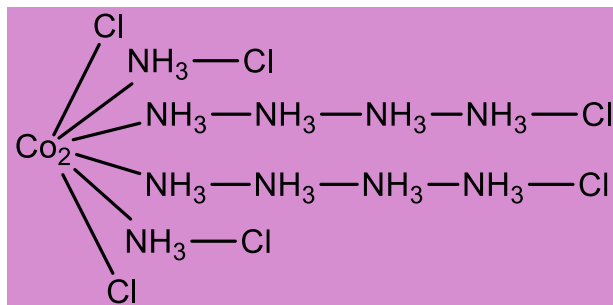
Brief history of complex combination theory

II. Stage dominated by Scandinavian chemists' ideas

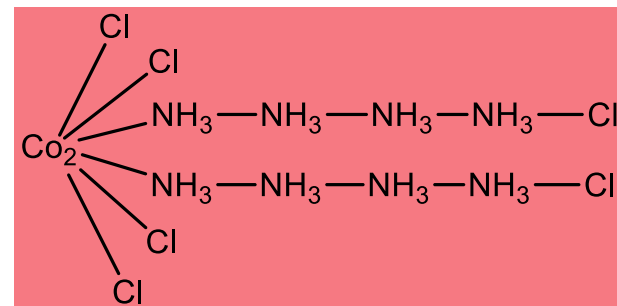
- **Jörgensen** notes that the chlorine atoms in purplesalt and rosesalt are not identical. As a result, Jörgensen assumes that these chlorine atoms are bound in two different ways: ionically and non-ionically (as masked atoms).



luteosalt



purplesalt



rosesalt

- Jörgensen's work lasted 15 years. However, he failed to explain the physicochemical properties of these compounds. His work was abandoned after **Werner**'s theory of coordination appeared in 1893.

1. Introduction to coordinative and biocoordinative chemistry

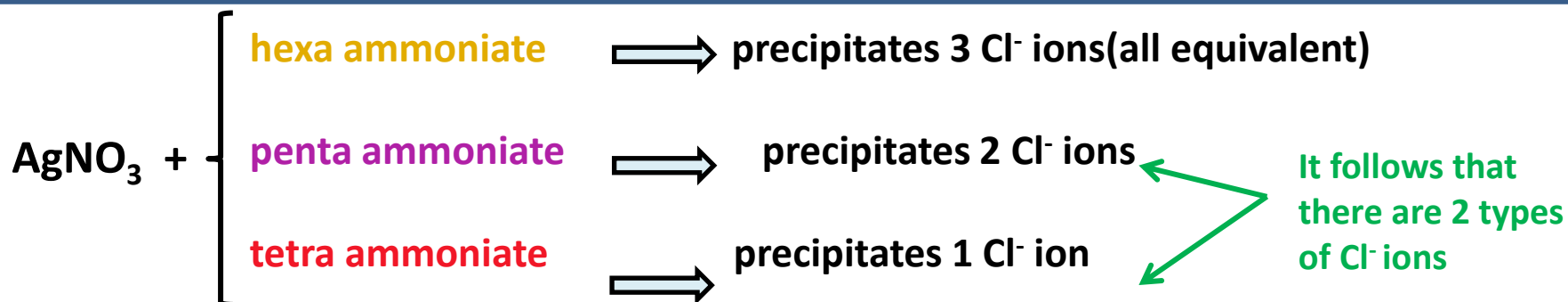
Brief history of complex combination theory

III. Werner's theory of coordination

- Werner abandoned the old valence theory from the start, because it could not explain the formation of combinations in which the combination ratio is greater than that given by the valences of the elements.
- Werner thus lays the foundations for a new theory of complex combination formation (1893), namely coordination theory.
- Experimental findings:



Alfred Werner
(Nobel Prize, 1913)

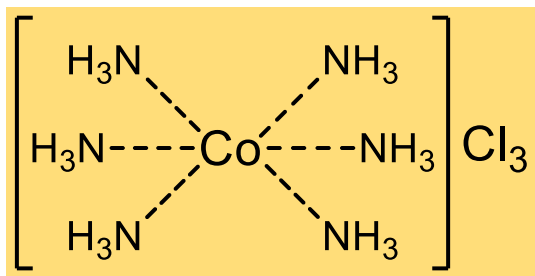


III. Werner's theory of coordination

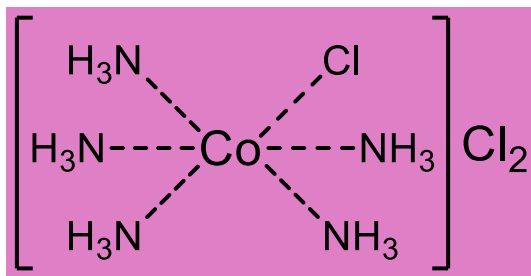
- According to Werner's coordination theory, in the formation of complex combinations some atoms possess, in addition to core valences (normal), valence bonds, while secondary (residual) valence bonds are spatially directed. Werner's theory is therefore based on two postulates:

1) The fundamental postulate of coordination theory: *the main (normal) valence forces are those manifestations of chemical affinity that lead to the formation of simple combinations, and the secondary (residual) valence forces ensure the bonding of the component molecules of complex combinations.*

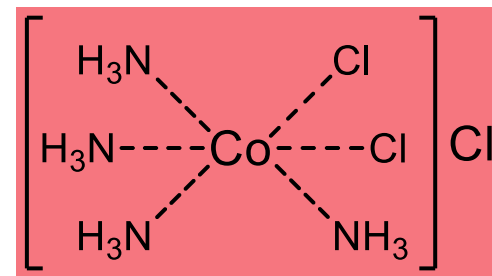
- The primary valence** corresponds to the **oxidation state of the central atom**, and the **secondary valence** corresponds to the **coordination number**.



$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
(luteosalt)



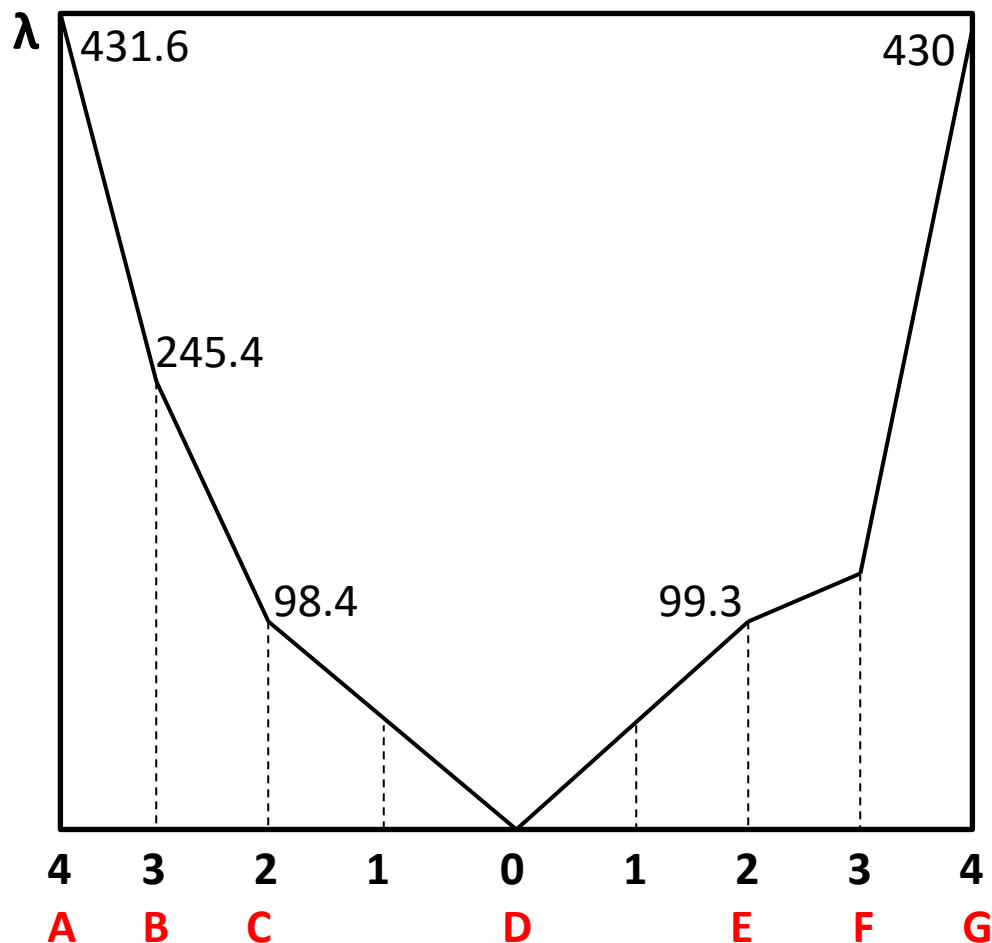
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
(purplesalt)



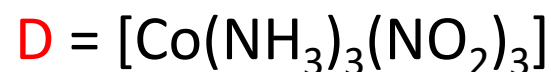
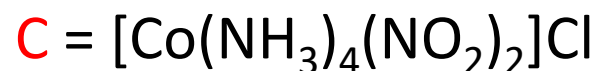
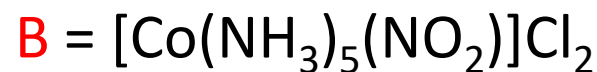
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$
(rosesalt)

III. Werner's theory of coordination

- Through conductometric work, Werner established the correlation between the composition of complex combinations and the type of ionic dissociation.

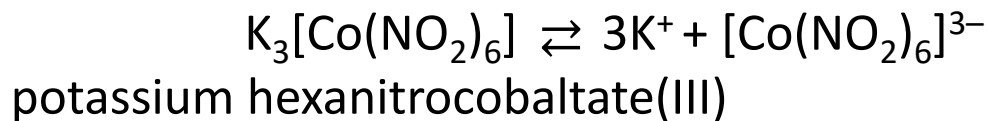
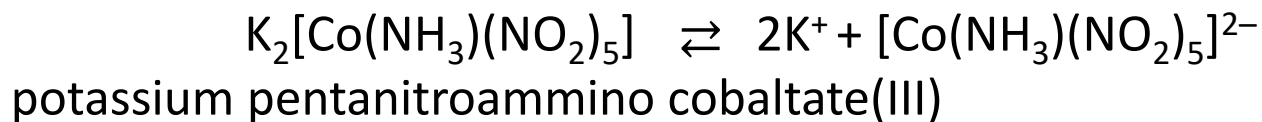
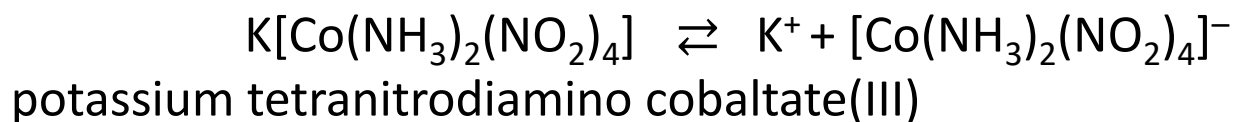
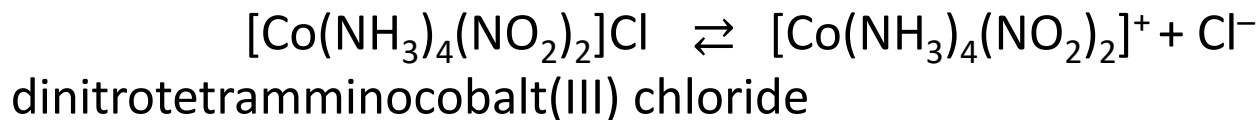
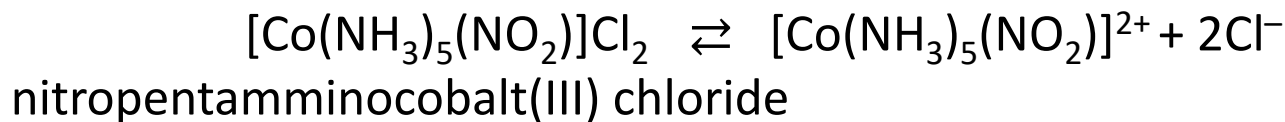
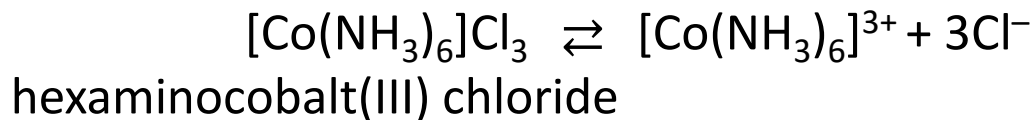


- Werner - Miotti diagram for complex combinations of Co(III) in which NH_3 is progressively substituted with NO_2^- groups:



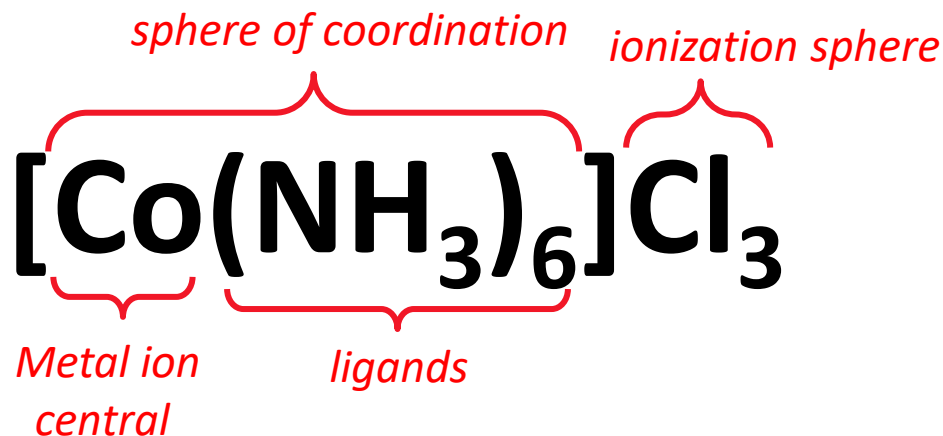
III. Werner's theory of coordination

- Werner believes that ionic dissociation of the complex combinations considered occurs as follows:



III. Werner's theory of coordination

- On the basis of the results obtained from chemical and conductometric analyses, Werner established the formulae for complex combinations, **indicating in square brackets the unit that functions as a complex.**
- In a complex combination they are distinguished as follows:
 - a) the **coordination sphere**, which contains ions or molecules directly bound to the central metal ion;
 - b) **ionization sphere**, which contains more weakly bound ions.



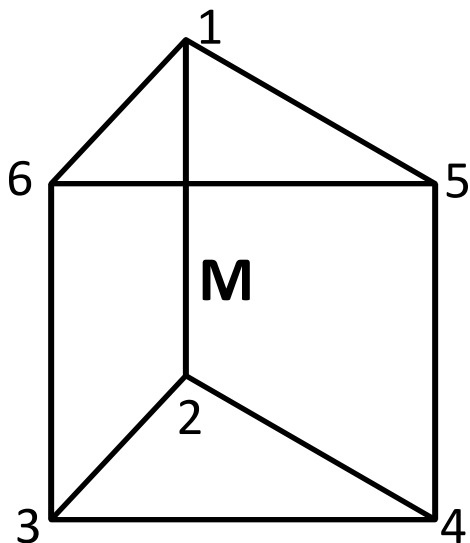
III. Werner's theory of coordination

2) The postulate concerning the spatial orientation of valences

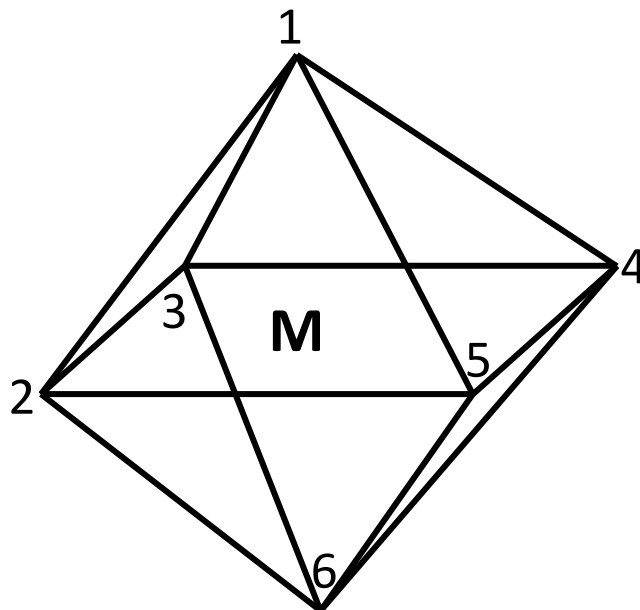
- Assuming that valence secondary bonds are spatially directed, Werner brings a new element to inorganic chemistry by introducing spatial representations of inorganic compounds.
- In this way, Werner lays the foundations of inorganic stereochemistry.
- Werner assumes that these combinations have a spatial structure. To identify this structure, he proceeded to compare the number of known geometric and optical isomers for a given combination with the number of isomers predicted by the various models considered.

III. Werner's theory of coordination

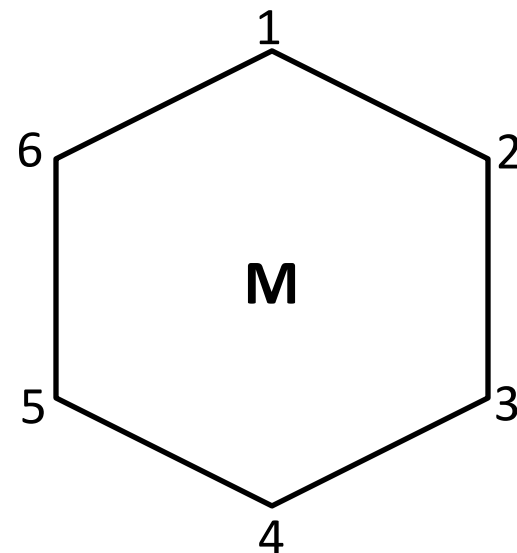
- Hexacoordinate combinations of type Ma_4b_2 - 3 models:



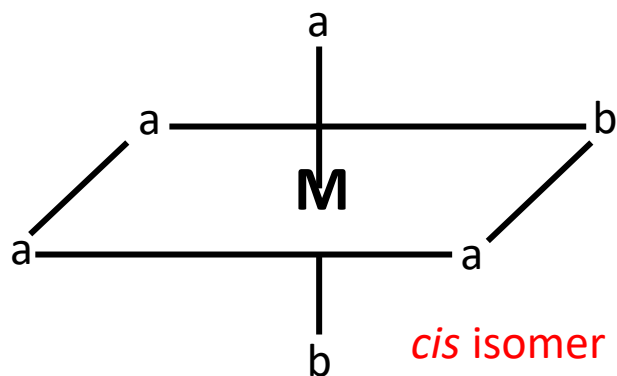
(prismatic model)
3 geometric isomers
(1,2), (1,3) and (1,6)



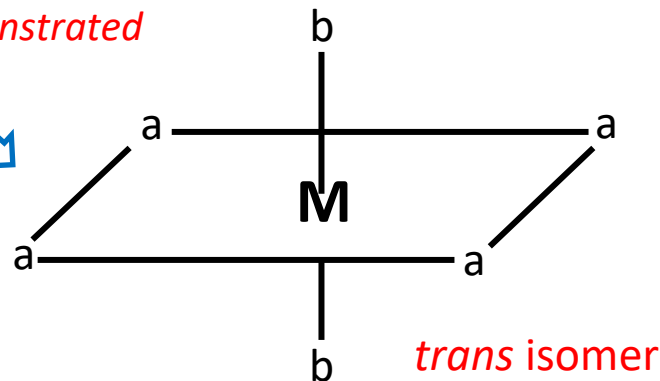
(octahedral model)
2 geometric isomers
(1,2) and (1,6)



(hexagonal model)
3 geometric isomers
(1,2), (1,3) and (1,4)

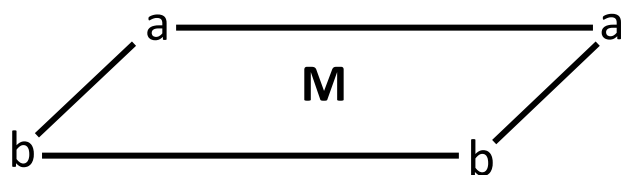


experimentally demonstrated

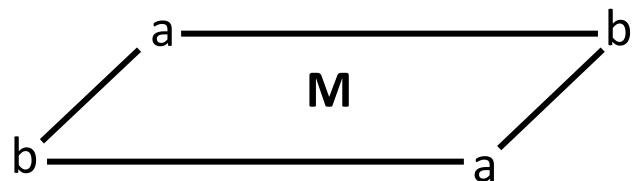


III. Werner's theory of coordination

- Werner assigned the planar-square model (the tetrahedral model does not admit isomerism) **to complex tetra-coordinate combinations of the type Ma_2b_2** , especially those of Pt and Pd, which have two geometric isomers:



cis isomer



trans isomer

- The predictions of this model have been confirmed by a number of experimental data, such as X-ray diffraction spectra or infrared (IR) spectra of complex combinations.
- It should be pointed out that Werner made only a formal distinction between the two types of valence - primary valence and secondary valence - without considering that there is a deep distinction between them.
- Although the structure of atoms and the notion of valence were not known when Werner developed coordination theory, his theory succeeded. Nowadays one cannot approach the problem of complex combinations without knowing the theory of complex combinations.

2. Ligands and coordination number

Definition of ligands

- *Ligands are ions or molecules containing one or more atoms, called **donor atoms**, which possess at least one non-participating electron doublet capable of forming a donor-acceptor bond (coordinative or dative bond) with the central metal ion.*
- *When a ligand binds to the central metal ion via two or more donor atoms, it closes cycles of atoms and is called a **chelating ligand (chelating agent)**.*

Classification of ligands

- **According to their chemical nature**, ligands are divided into:
 1. inorganic ligands
 2. organic ligands
- **According to the number of donor atoms**, ligands are classified into:
 1. monodentate ligands
 2. bidentate ligands
 3. tridentate ligands
 4. Tetradentates, etc.

2. Ligands and coordination number

Monodentate ligands

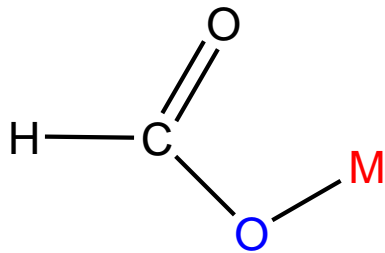
They are ions or molecules that coordinate to the metal centre through a single donor atom. The following types of inorganic and organic ligands fall into this category:

1. Monoatomic anions, such as halide ions: F^- , Cl^- , Br^- , I^-

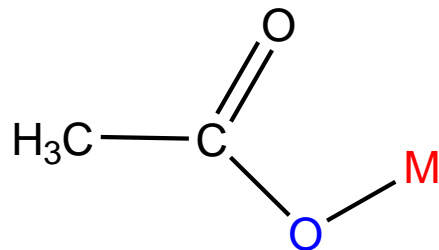
2. Polyatomic anions: CN^- , SCN^- , NO_2^- , NO_3^- , HO^- etc.

3. Oxoanions derived from carboxylic acids:

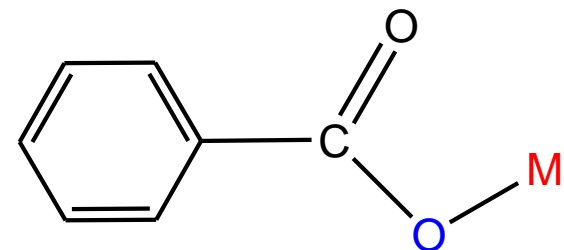
$HCOO^-$, CH_3COO^- , $CH_3CH_2COO^-$, $C_6H_5COO^-$ etc.



formiate



acetate

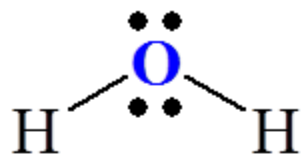


benzoate

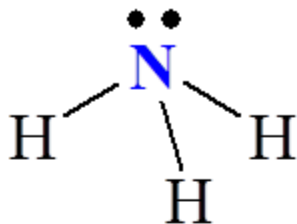
Monodentate ligands

4. Neutral molecules:

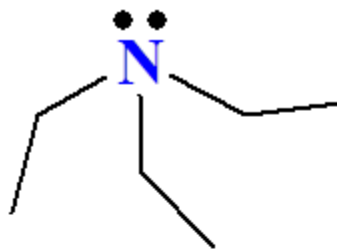
H_2O , NH_3 , CO , NO , PF_3 , monoamines (RNH_2 , R_2NH , R_3N), phosphines (R_3P , R_2PH , RPH_2), arsines (R_3As), pyridine (py) – $\text{C}_5\text{H}_5\text{N}$, urea – $\text{O}=\text{C}(\text{NH}_2)_2$ etc.



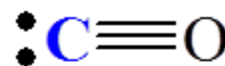
water



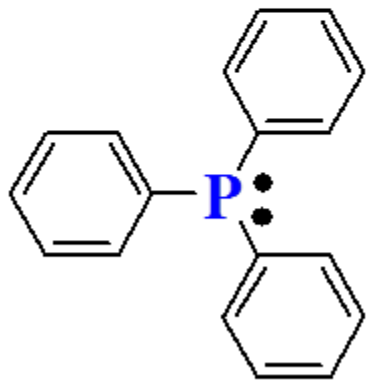
ammonia



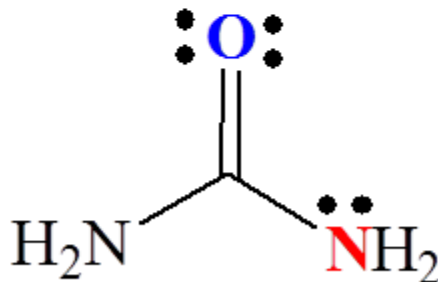
triethylamine



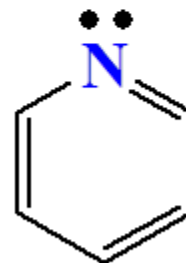
Carbon
monoxide



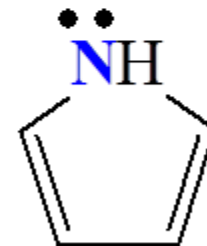
triphenylphosphine



urea



pyridine

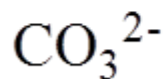
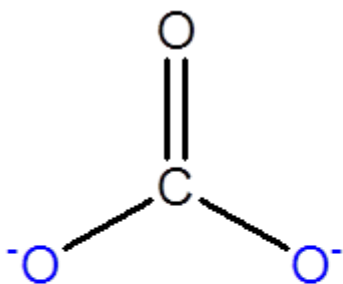


pyrrole

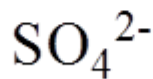
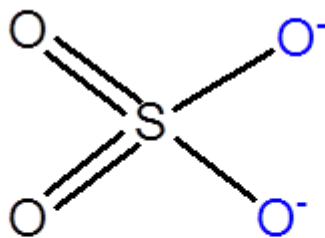
Bidentate ligands

They are ions or molecules that coordinate to the metal centre through two donor atoms.

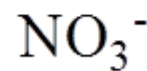
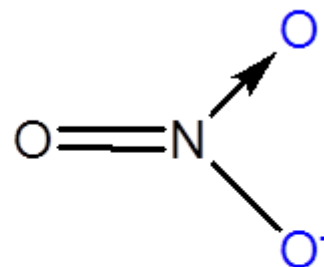
1. Inorganic bidentate ligands - oxygen radicals from inorganic acids, such as:



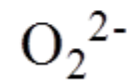
carbonate



sulphate



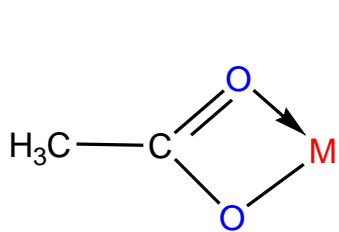
nitrite



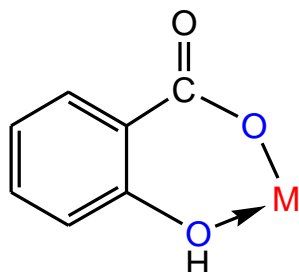
peroxide

Bidentate ligands

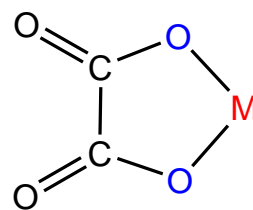
2. Organic bidentate ligands: carboxylic acids, hydroxy acids, amino acids, dioxymes, diamines, diketones, etc.



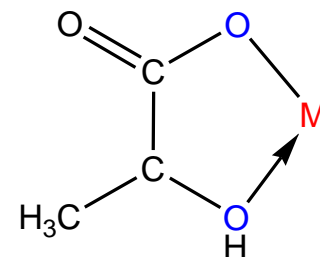
acetate



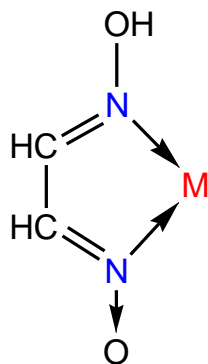
salicylate



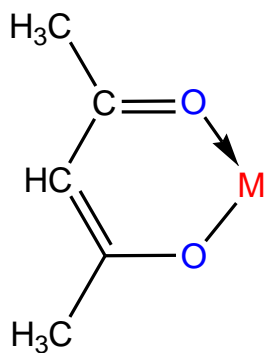
oxalate



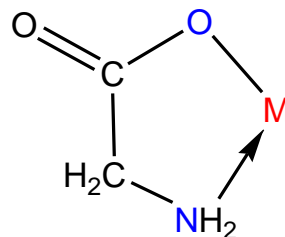
lactate



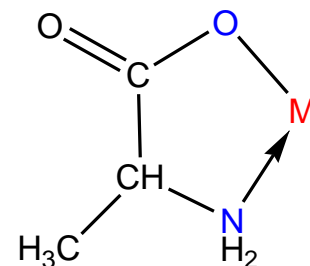
glyoximate



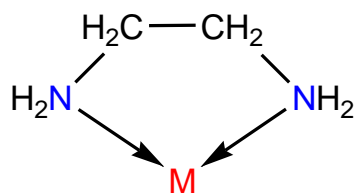
acetylacetonate



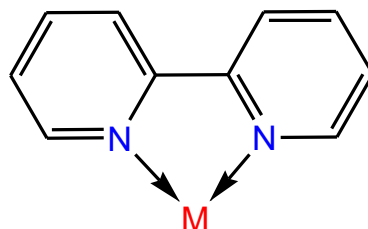
glycolate



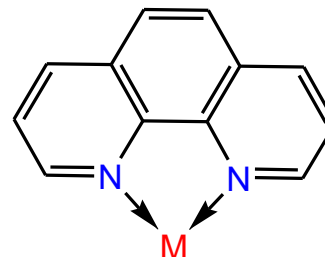
Alpha-alaninate



ethylenediamine



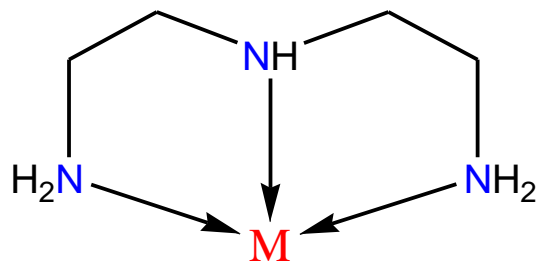
2,2'-dipyridine



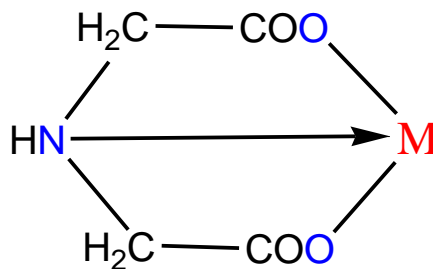
o,o'-phenantroline

Tridentate ligands

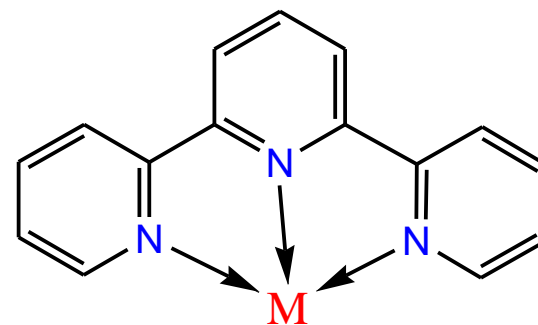
They are ions or molecules that coordinate to the metal centre through three donor atoms. They are **planar** and **non-planar**, as they occupy the three coordinate positions either in the same plane or in different planes.



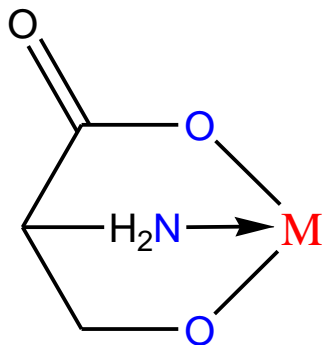
diethylentriamine



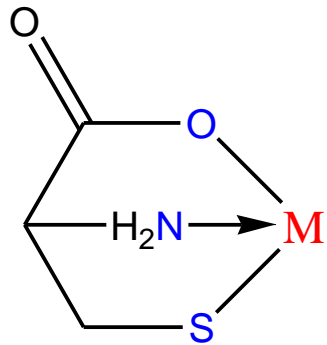
iminodiacetate



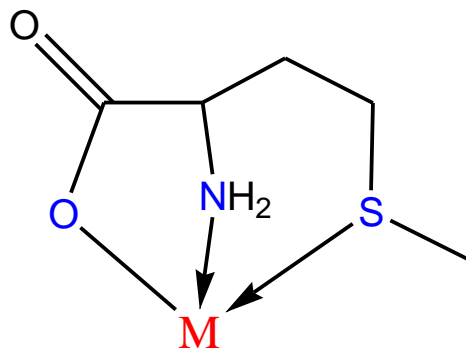
terpyridine



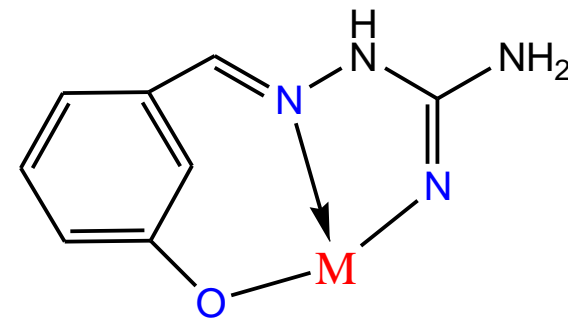
serine



cysteine



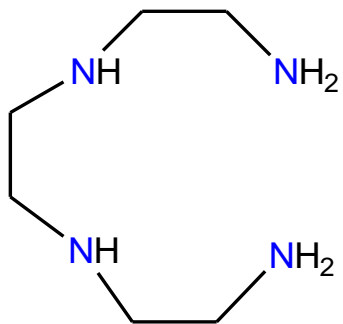
methionine



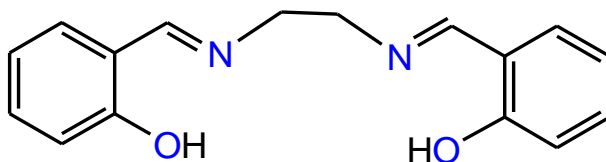
salicylidene-aminoguanidine

Tetradentate ligands

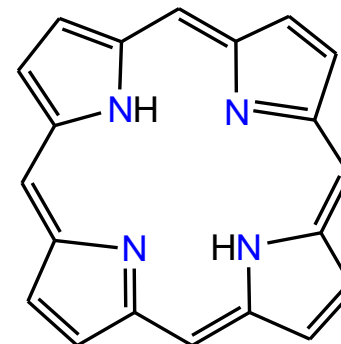
They are ions or molecules that coordinate to the metal centre through four donor atoms.



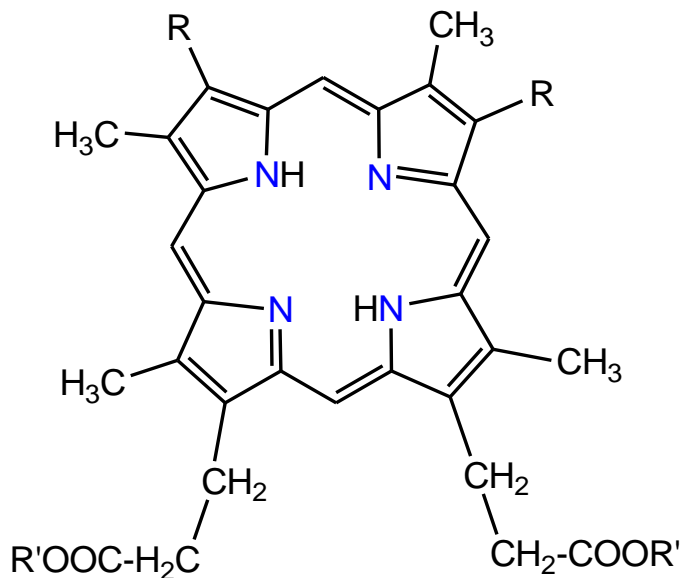
triethylenetetraamine



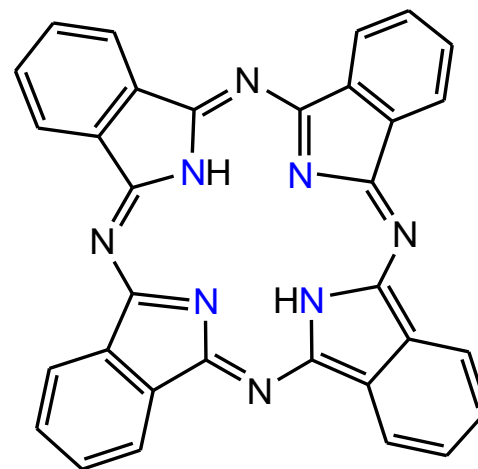
Bis(salicylidene)ethylidene
diamine



porphyrin



protoporphyrin



phthalocyanine

COORDINATION NUMBER

Defining the coordination number

- The concept of ***coordination number*** was introduced by Werner with coordination theory, when he referred to the ability of elements to have secondary valences in addition to primary valences, a property called coordination number.
- **Coordination number (CN)** *indicates the number of donor atoms by which one or more ligands can bind directly to the central metal atom in the coordination sphere of a complex combination.*
- The type and number of ligands determine the coordination number, the value of which is generally higher than the oxidation state of the central metal atom.

Defining the coordination number

- This is how the following complex combinations are formed:



diamino silver chloride



tetraamminocopper (II) chloride



tetrachloroauric acid

- A similar situation is found in the following complex combinations:

$\text{K}_4[\text{Fe}(\text{CN})_6]$ - potassium hexacyanoferrate (II)

$[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ - hexaminochromium (III) chloride

$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2$ - hexaaquacobalt (II) chloride

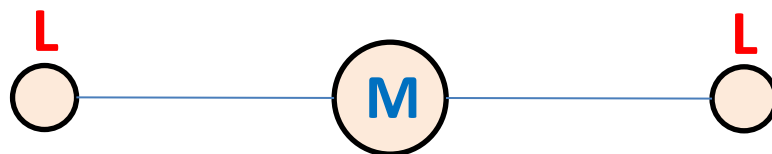
$\text{K}_2[\text{PtCl}_6]$ - potassium hexachloroplatinate (IV)

Defining the coordination number

- Under well-determined conditions, the coordination number depends essentially on the following factors:
 1. Nature of the central metal ion;
 2. Nature of ligands;
 3. Synthesis conditions of complex combinations;
 4. Temperature;
 5. pH of the environment;
 6. Ligand concentration in the environment;
 7. Nature of solvents.
- The coordination number has values between $2 \div 12$, but the most common values are between $4 \div 6$.

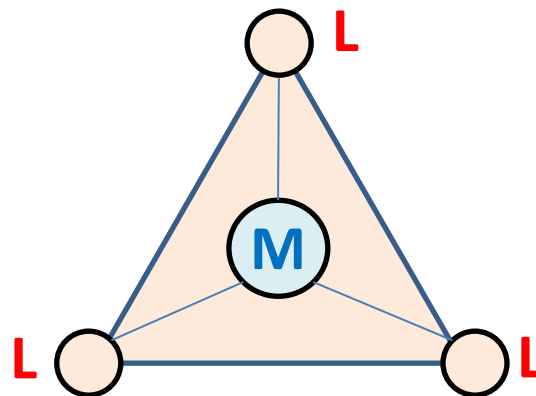
$$\text{CN} = 2$$

- Coordination number $\text{CN} = 2$ is adopted by few metal ions, occurring in complex combinations of Cu(I) , Ag(I) , Au(I) , Hg(I) and Hg(II) , which have the $(n-1)d^{10}$ electron configuration.
- As a result, the atomic orbitals involved in chemical bonding are the ns orbitals. For this reason, the compounds made are formed with sp , ds , dp or df hybrid orbitals.
- The molecule of the complex dicoordinated combination has a **digonal** (linear) **structure**, with two bonds placed at 180° .
- Such complex combinations in which $\text{CN} = 2$ are:
 - a) diamines**, such as $[\text{M}(\text{NH}_3)_2]\text{X}$, where: $\text{M} = \text{Ag}^+$, Cu^+ , and $\text{X} = \text{Cl}^-$, Br^- , I^- , HO^- , SCN^- ;
 - b) dicyanocomplexes**, such as $\text{M}^{\text{I}}[\text{M}(\text{CN})_2]$, where: $\text{M} = \text{Ag}^+$, Au^+ , and $\text{M}^{\text{I}} = \text{Na}^+$, K^+ .



$$\text{CN} = 3$$

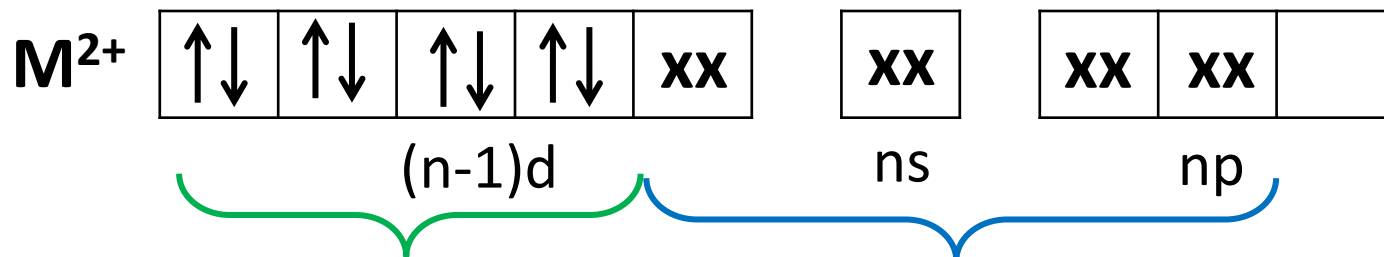
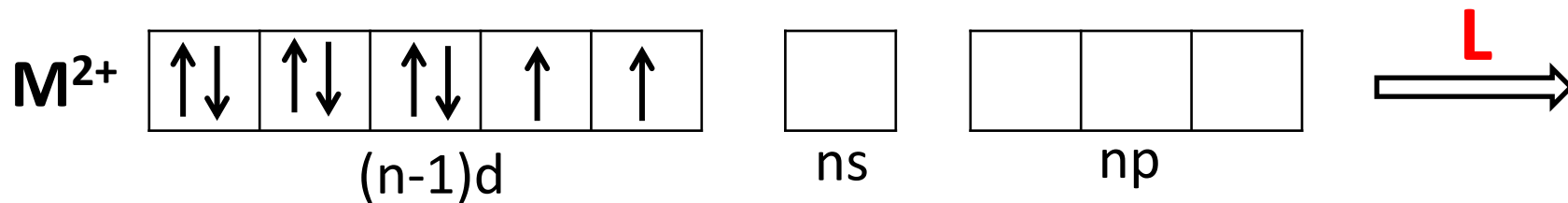
- It is expected, for geometrical reasons, that when a metal ion forms a complex trichordinate combination, the metal ion is at the centre of an equilateral triangle at the apex of which the ligands are located.
- Therefore, such a complex combination should adopt a **trigonal-planar structure**, in which the chemical bonds form angles of 120° to each other. This happens when the metal exhibits *sp²*, *d²s* or *dp²* hybridisation.
- CN = 3 is adopted by few metal ions, such as Ag(I), Cu(I), Zn(II), Cd(II) and Hg(II), for which, in aqueous solutions, a number of complex ions are evidenced, such as:
 - a) $[\text{AgX}_3]^{2-}$, where X = Cl⁻, Br⁻, CN⁻;
 - b) $[\text{MX}_3]^-$, where M = Zn²⁺, Cd²⁺, Hg²⁺, and X = F⁻, Cl⁻, Br⁻, I⁻, CN⁻.



$$\text{CN} = 4$$

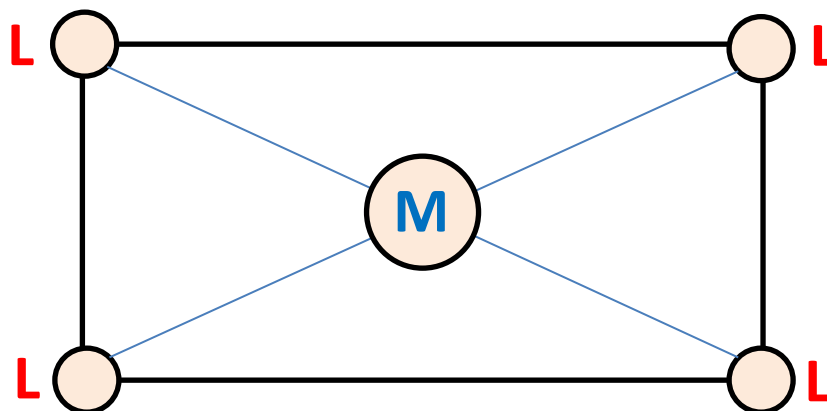
- Coordination number $\text{CN} = 4$ occurs in many complex combinations, especially those of transition metals.
- The **structure** of these complexes can be **square-planar** or **tetrahedral**.
- The **square-planar structure** is the result of ***dsp²*** hybridizations and is found in ions whose electron configuration is $(n-1)d^8$. This category includes the following species: **Ni(II), Pd(II), Pt(II), Au(III)**.
- In these ions, by rearranging the $(n-1)d$ electrons under the influence of the ligand field, one of the $(n-1)d$ orbitals becomes vacant.
- Such complex combinations are:
 - a) $\text{M}^{\text{I}}_2[\text{MX}_4]$** , where: $\text{M} = \text{Ni}^{2+}, \text{Pd}^{2+}, \text{Pt}^{2+}$; $\text{M}^{\text{I}} = \text{Na}^+, \text{K}^+, \text{Ba}^{2+}$;
 $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{CN}^-$.
 - b) $\text{M}^{\text{I}}[\text{AuX}_4]$** , where: $\text{M}^{\text{I}} = \text{Na}^+, \text{K}^+, \text{NH}_4^+, \text{Cs}^+, \text{Ag}^+$;
 $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{SCN}^-, \text{CN}^-$.

CN = 4



electrons of the metallic ion

ligand electrons

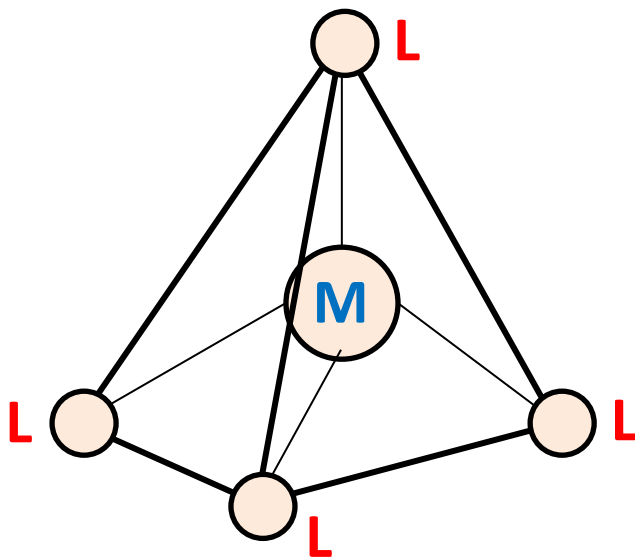
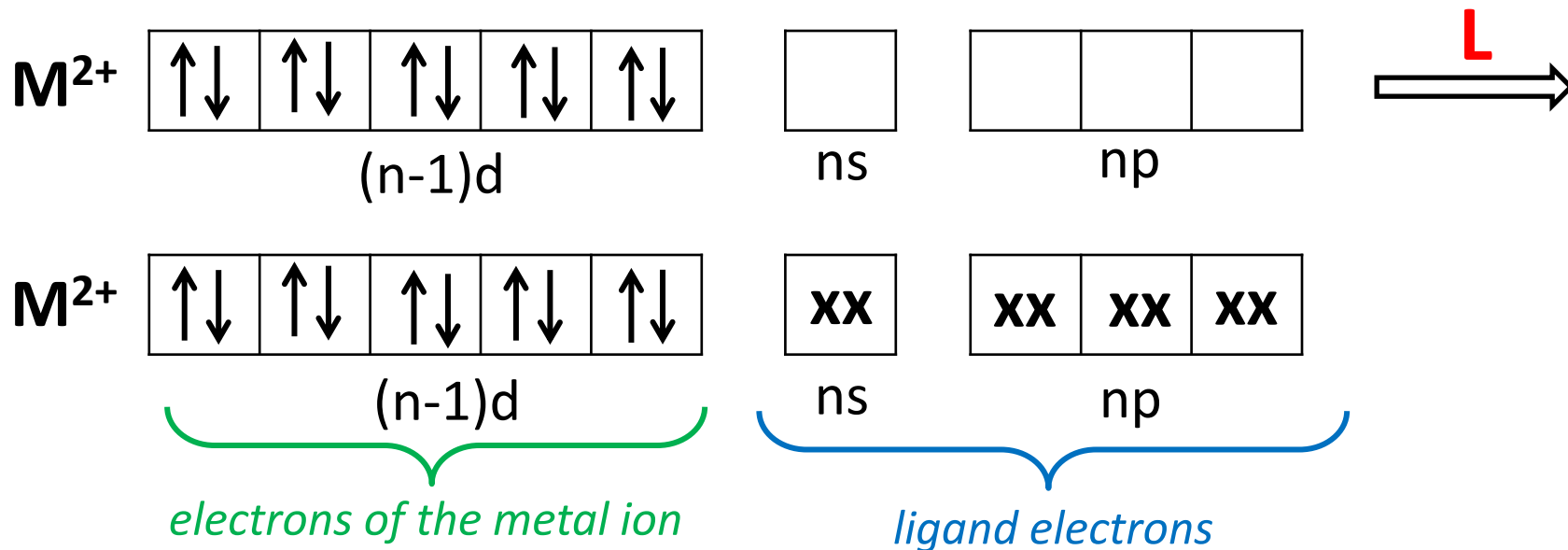


Square-planar structure corresponding to dsp^2 hybridization

CN = 4

- The **tetrahedral structure** is the result of sp^3 , spd^2 , d^3s , sf^3 hybridizations and is found in complex combinations of transition metals with $(n-1)d$ orbitals fully or almost fully occupied with electrons. This category includes the species: $Fe(II) - d^6$, $Co(II) - d^7$, $Cd(II) - d^{10}$, $Zn(II) - d^{10}$, $Hg(II) - d^{10}$, $Cu(I) - d^{10}$.
- The best known tetrahedral complexes are the halogens, cyanides and sulphocyanides of the form $[MX_4]^{2-}$. Such combinations can also form the main block elements, such as $Be(II)$, $In(III)$, $Pb(II)$.
- Tetrahedral tetracoordinated complex ions are:
 - a) $[M(OH)_4]^{2-}$, where $M = Be^{2+}, Zn^{2+}, Sn^{2+}, Pb^{2+}$
 - b) $[M(OH)_4]^-$, where $M = Al^{3+}, Ga^{3+}$
 - c) $[MX_4]^{2-}$, where $M = Fe^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}$;
 $X = Cl^-, Br^-, I^-, SCN^-, CN^-$
 - d) $[MX_4]^-$, where $M = In^{3+}, Tl^{3+}$; $X = Cl^-, Br^-, I^-$

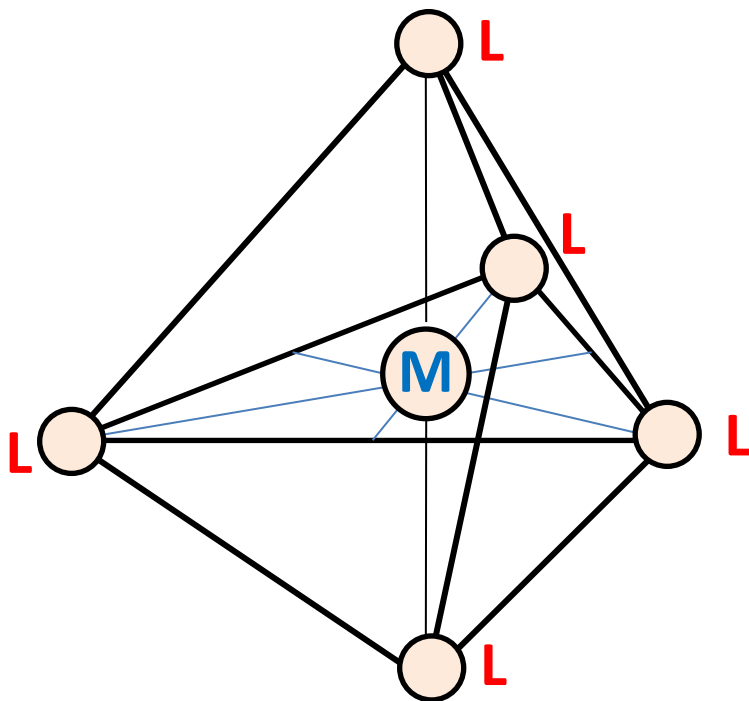
CN = 4



Tetrahedral structure
related
 sp^3 hybridization

CN = 5

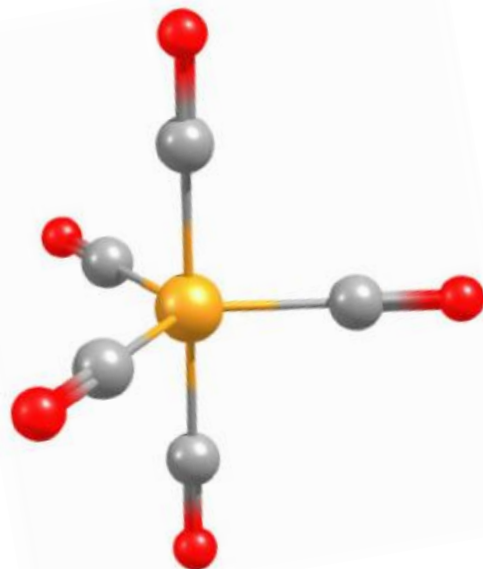
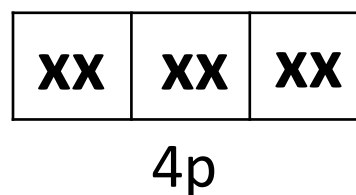
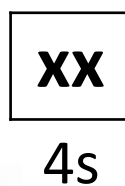
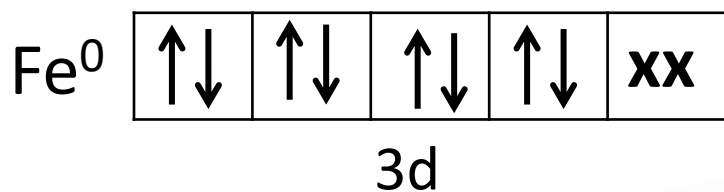
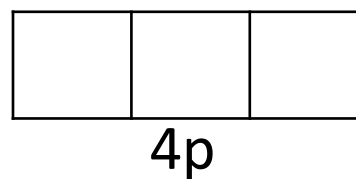
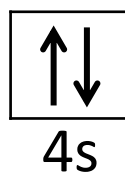
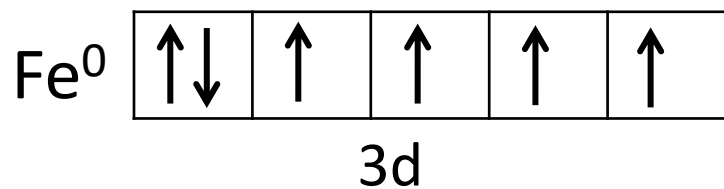
- Few complex pentacoordinate combinations are known. They can adopt two types of spatial conformation: **trigonal bipyramid** and **quadratic pyramid**.
- In the case of the **trigonal bipyramid** conformation, the central metal ion has dsp^3 or d^3sp hybridization. Such complex combinations are metal pentacarbonyls of the form $M(CO)_5$, where $M = Ru, Os, Fe$.



CN = 5

$\text{Fe}(\text{CO})_5$

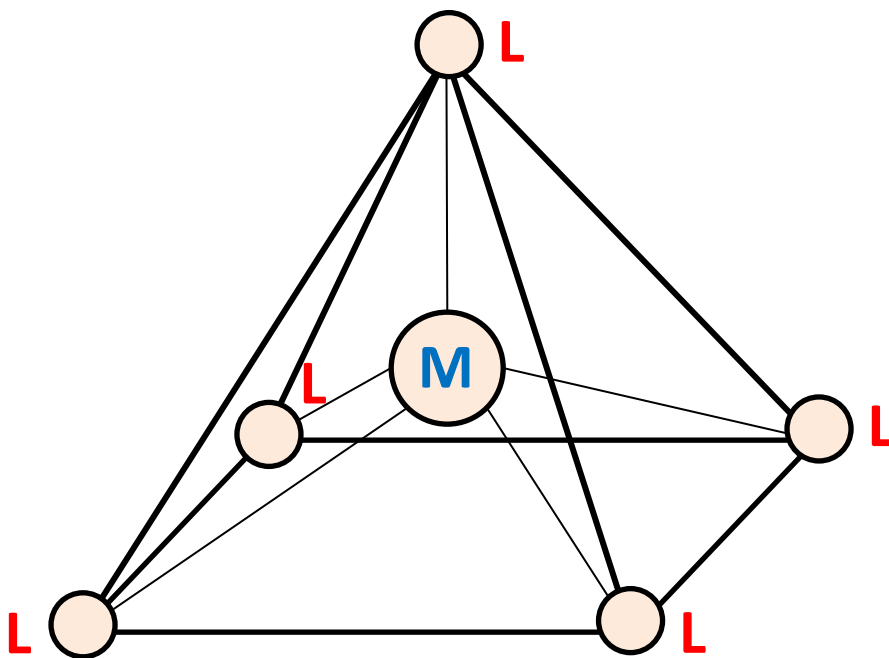
Fe (Z = 26): $[\text{Ar}] 3d^6 4s^2$



The trigonal bipyramid structure of $\text{Fe}(\text{CO})_5$ related to the dsp^3 hybridization

CN = 5

- The *quadratic pyramid* conformation occurs in complex combinations of metal ions that exhibit $d4s$ or $d2sp2$ hybridization. This category includes Co(II), Ru(III) and In(III). They form complexes such as: $K_3[Co(CN)_5]$, $K_2[MCl_5]$, where M = Co^{2+} , Ru^{3+} , In^{3+} .



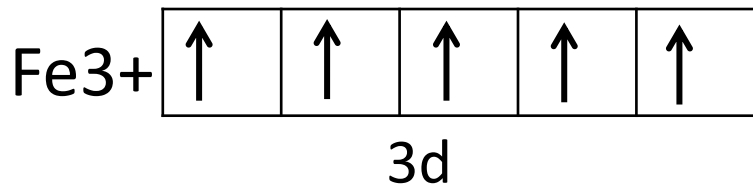
CN = 6

- Hexacoordinate combinations are the most common and can adopt two types of spatial conformation: **octahedral** and **trigonal prism**.
- Most complex combinations in which the central metal ion is hexacoordinate adopt a **octahedral conformation**, generally exhibiting $d2sp3$ hybridization, but sometimes also $sp3d2$ or $d2sf3$ hybridization.
- Among the transition metals that have the ability to form complexes with CN = 6 include **Cr(III), Fe(III), Co(III), Co(II), Ni(III), Ru(II), Rh(III), Ir(III), Pd(IV), Pt(IV)**. Such complexes are:
 - a) $[ML_6]X_3$, where: $M = Cr^{3+}, Co^{3+}$; $L = H_2O, NH_3$; $X = Cl^-, Br^-, I^-$
 - b) $M^I_3[MX_6]$, where $M = Fe^{3+}, Cr^{3+}$; $M^I = Na^+, K^+$; $X = SCN^-, CN^-$

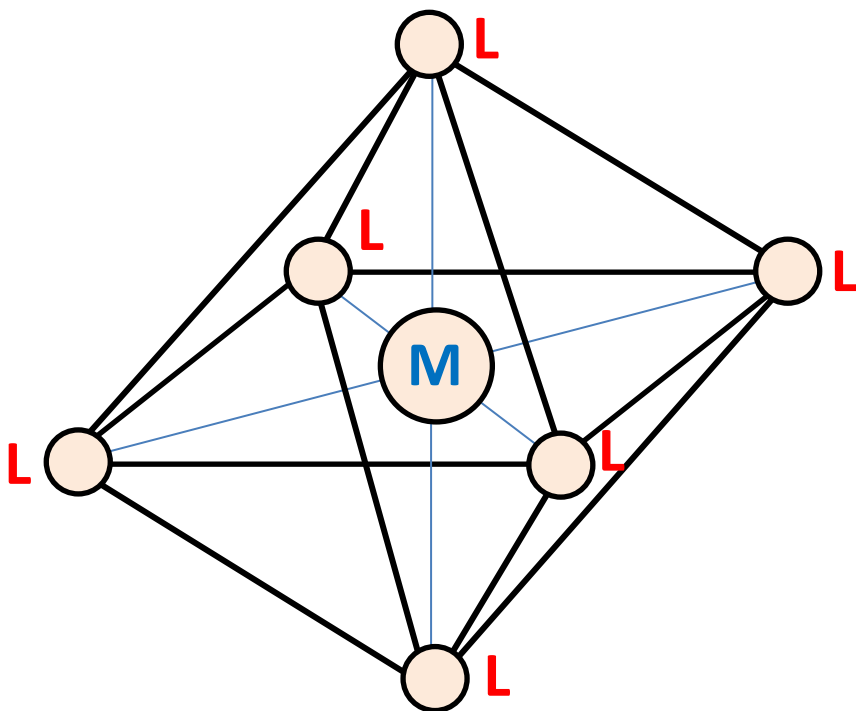
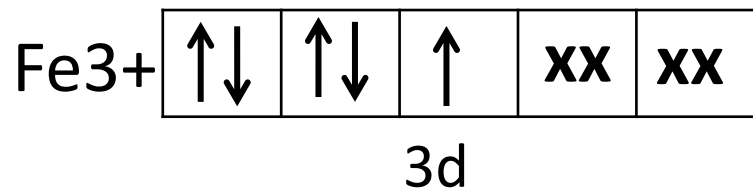
$K_3[Fe(CN)_6]$

Fe (Z = 26): $[Ar] 3d^6 4s^2$

CN = 6



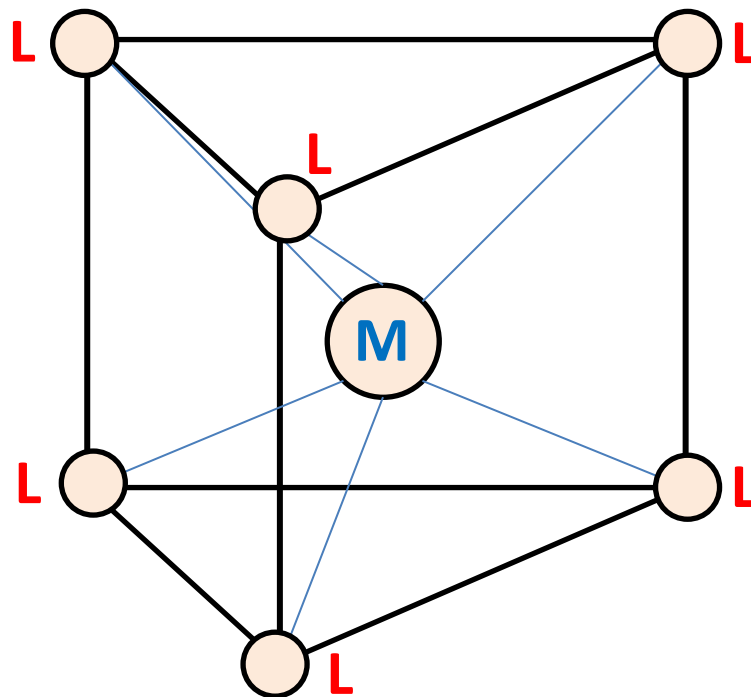
CN
→



Octahedral structure related to the d^2sp^3 hybridization

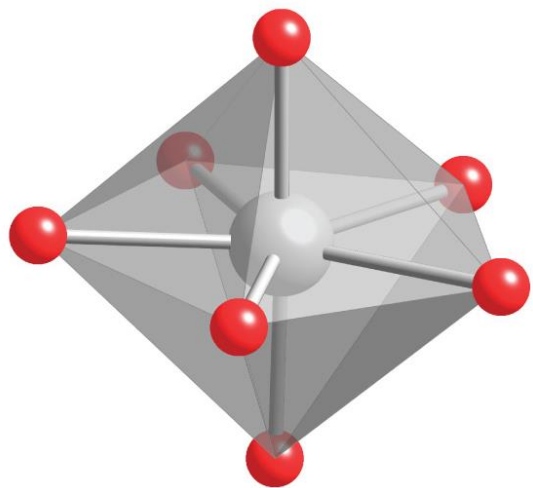
CN = 6

- Apart from the transition metals, a significant number of main-block metals form complex combinations with octahedral structure, such as: Al(III), Ga(III), Tl(III), In(III), Sn(IV), Pb(IV), Ge(IV), Sb(III).
- The *trigonal prism structure* is very rare, the metal ion having *d₄sp* hybridization.

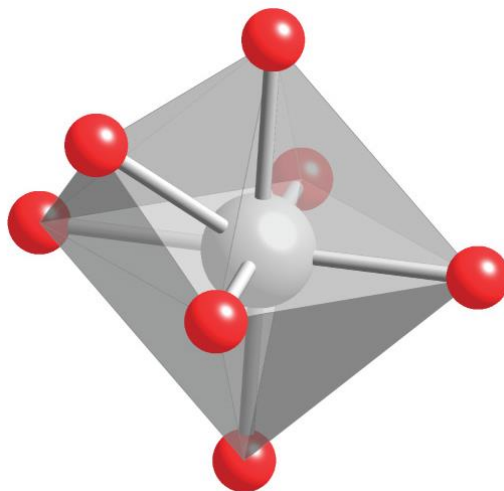


CN = 7

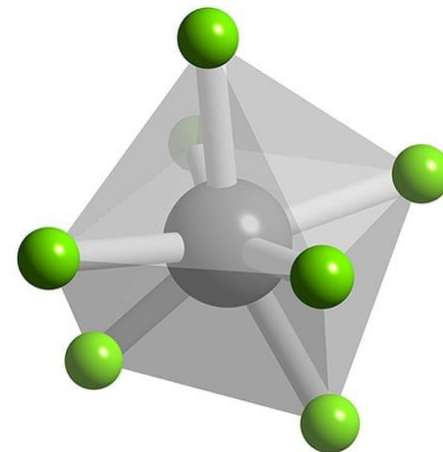
- Relatively few complex heptacoordinate combinations occur. Such complexes form in particular Zr(IV), Hf(IV), V(V), Nb(V), Ta(V), U(V), Np(V), Pu(V).
- In the presence of alkaline fluorides, these ions form $[\text{MF}_7]^{2-}$ and $[\text{MF}_7]^{3-}$ complexes. The complex combinations formed can exhibit three types of coordination polyhedra:



pentagonal bipyramid



pyramidal (mono)
octahedron



trigonal (mono)
pyramidal prism

3. Nomenclature, formulation and classification of complex combinations

Nomenclature and formulation of complex combinations

Names of some neutral and anionic inorganic ligands

| Chemical formula | Designation | Chemical formula | Designation | Chemical formula | Designation |
|------------------------------|-------------|------------------|-------------|---|----------------|
| H ₂ O | aqua | F ⁻ | fluoro | NO ₂ ⁻ | nitro |
| NH ₃ | ammino | Cl ⁻ | chloro | ONO ⁻ | nitrito |
| CO | carbonyl | Br ⁻ | bromine | CO ₃ ²⁻ | carbonate |
| NO | nitrozil | I ⁻ | iodo | SO ₄ ²⁻ | sulphate |
| HO ⁻ | hydroxo | CN ⁻ | cyano | SO ₃ ²⁻ | sulphite |
| O ²⁻ | oxo | CNO ⁻ | cyanate | S ₂ O ₃ ²⁻ | thiosulphate |
| O ₂ ²⁻ | peroxo | SCN ⁻ | thiocyanate | NCS ⁻ | isothiocyanate |

Nomenclature and formulation of complex combinations

Abbreviations of neutral and anionic organic ligands

| Designation | Abbreviation | Designation | Abbreviation |
|-----------------------|-------------------|---------------------------------|-------------------------------|
| urea | ur | ethylenebis(diphenylphosphine) | diphos |
| pyridine | py | cyclopentadienyl | C ₅ H ₅ |
| 2,2'-dipyridine | dpy | oxalic acid | H ₂ ox |
| terpyridine | tpy | oxalate | ox |
| 1,10-Phenanthroline | phen | acetylacetonone | Hacac |
| ethylenediamine | en | acetylacetonate | acac |
| diethylenetriamine | dien | dimethylglyoxime | H ₂ dmg |
| triethylenetetraamine | trien | dimethylglyoxylate | dmg |
| triethylamine | Et ₃ N | ethylenediaminetetraacetic acid | H ₄ edta |
| triphenylphosphine | Ph ₃ P | ethylenediaminetetra acetate | edta |

Nomenclature and formulation of complex combinations

Some general issues

Two kinds of multiplicative affixes are used to indicate stoichiometry and the structure of complex combinations:

- *Simple multiplicative affixes*: di, tri, tetra, penta, hexa, hepta, nona, deca, etc., to indicate stoichiometric proportions, number of identical coordinate groups or number of identical central atoms. For example:



- *Multiplicative affixes*: bis, tris, tetrakis, pentakis, hexakis, etc., are used to indicate a grouping of identical organic radicals. For example:



In complex combination formulas, the separation of complex ions and neutral entities is done by square brackets, which can be: $[()]$, $\{ \{ () \} \}$, $\{ \{ \{ () \} \} \}$, $\{ \{ \{ \{ () \} \} \}$. For example:



Nomenclature and formulation of complex combinations

Some general issues

- Arabic numerals followed by a + or - sign as an exponent are used to indicate the charge of a complex ion, and Roman numerals enclosed in round brackets are used to indicate the valence of the central metal ion. For example: $[\text{PtCl}_6]^{2-}$ hexachloroplatinate(IV)
- To write the oxidation state or zero valence, the number 0 is used.
- The electropositive constituent (cation) in the formula is placed first, as in the case of simple combinations. For example: $\text{K}_3[\text{Fe}(\text{CN})_6]$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- The number of identical atoms or groups of identical atoms, in the latter case enclosed in round brackets, is indicated by Arabic numerals placed at the bottom right of the symbol or brackets enclosing groups of atoms. For example:
 $\text{Na}_3[\text{AlF}_6]$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Fe}_2(\text{CO})_9]$
- Structural prefixes (*cis*, *trans*, *fac*, *mer*, etc.) are written in italics and linked with a formula dash. For example:
cis- $[\text{PtCl}_2(\text{NH}_3)_2]$, *trans*- $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$

Nomenclature and formulation of complex combinations

Writing and formulating complex combinations

- To write an ion or complex entities, inside the square brackets first write the symbol of the central metal atom and then the anionic ligands in order: H^- , O_2^{2-} , HO^- , F^- , Cl^- , Br^- , I^- , CN^- , NO_2^- , SCN^- , CO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$.
- Next come the neutral ligands in order of H_2O , NH_3 , CO , NO and then the organic ligands in alphabetical order: acac, dpy, en, ox, py, ur and others.
- Organic ligands derived from carboxylic acids (by loss of protons) are given the **-ate** termination. For example: HCOO^- (formiate), CH_3COO^- (acetate), $\text{C}_2\text{O}_4^{2-}$ (oxalate).
- ***Ligand names are written in alphabetical order, without considering the numerical prefixes indicating the number of ligands.***
- When the name of the ligand ends with the letter *e*, it is deleted. For example:
 $[\text{Pd}(\text{Ph}_3\text{P})_4]$ tetrakis(triphenylphosphin)palladium(0)

Nomenclature and formulation of complex combinations

Writing and formulating complex combinations

- *Name of anionic complex ions.* In formulating an anionic complex ion, first read the ligands in alphabetical order and then the central atom by adding the suffix **-ate** to its name, while indicating the valence of the metal in Roman numerals in round brackets. For example:

K₃[Fe(CN)₆] potassium hexacyanoferrate(III)

Sodium Na₃[Ag(S₂O₃)₂] dithiosulphatoargentate(I)

Potassium K[AuCl₄] tetrachloro(III) alkoxide

- *Cationic complex ions are named* in a similar way, except that the preposition **of** is added before the name and the suffix *-ate* is not added to the name of the central atom. For example:

[Co(NH₃)₆]Cl₃ hexaamminocobalt(III) chloride

[Fe(dpy)₃]Cl₂ tris(2,2'-dipyridine)iron(II) chloride

[Co(ONO)(NH₃)₅]SO₄ pentaamminonitritocobalt(III) sulphate

[Co(SCN)(NH₃)₅]Cl₂ pentaamminothiocyanatocobalt(III) chloride

Nomenclature and formulation of complex combinations

Writing and formulating complex combinations

- *Name of neutral compounds* is done in the same way as for cationic compounds, except that the preposition *of* is not used. For example:

[Co(NO₂)₃(NH₃)₃] triamminotrinitrocobalt(III)

[Ni(CO)₂(Ph₃P)₂] dicarbonylbis(triphenylphosphine)nickel(0)

[PtCl₂(ox)] dichlorooxalatoplatinum(IV)

[Cu(CH₃COO)₂(py)₂] bis(acetate)bis(pyridine)copper(II)

- If both the anion and the cation are complex, the formulation is done by applying the express rules for each. For example:

[Co(NH₃)₆][Cr(CN)₆] hexaamminocobalt(III) hexacyanochromate(III)

[Pt(NH₃)₄][CuCl₄] tetraaminoplatinum(II) tetrachlorocuprate(II)

[CrCl₂(NH₃)₄][CrCl₄(NH₃)₂] diamminotetrachlorochromate(III)
tetraamminodichlorochromate(III)

[Co(NO₂)(NH₃)₅][Co(NO₂)₄(NH₃)₂]₂ pentaamminonitrocobalt(III)
bis(diamminotetranitrocobaltate(III))

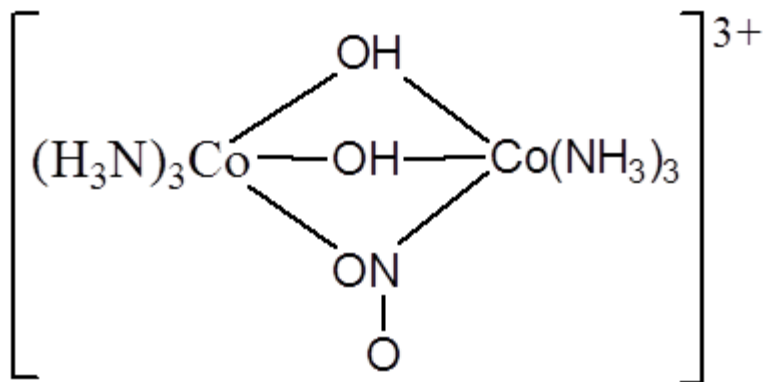
Nomenclature and formulation of complex combinations

Writing and formulating complex combinations

- Naming of di- and polynuclear complexes with bridging ligands.* The specification of *bridging* ligand, connecting two metal centres, is made by adding the Greek letter μ before its name. Two or more bridge ligands of the same kind are denoted by *di- μ* , *tri- μ* etc.:



μ -hydroxo-bis(pentaaminochrom(III)) chloride



hexaamino-di- μ -hydroxo- μ -nitrite(*O,N*)-dicobalt(III) ion

- If a bridging ligand binds more than two metal centres, this number is indicated by adding a numerical subscript to the letter μ :



Nomenclature and formulation of complex combinations

Writing and formulating complex combinations

- *Naming of di- and polynuclear complexes without bridging ligands.* Symmetric compounds with metal-metal bonds are defined using multiplicative prefixes:



- In the case of asymmetric ones, one central atom and the ligands attached to it are considered as one ligand attached to the other central atom:



pentacarbonyl[(triphenylphosphinyl)aurium]manganese

- *Clusters of identical central atoms (clusters).* In the case of these types of complex combinations it is necessary to indicate the shape of the polyhedron formed by the metal atoms, which is designated by *triangle*, *tetrahedron*, *octahedron*, etc.:



dodecacarbonyl-triangulo-trifer



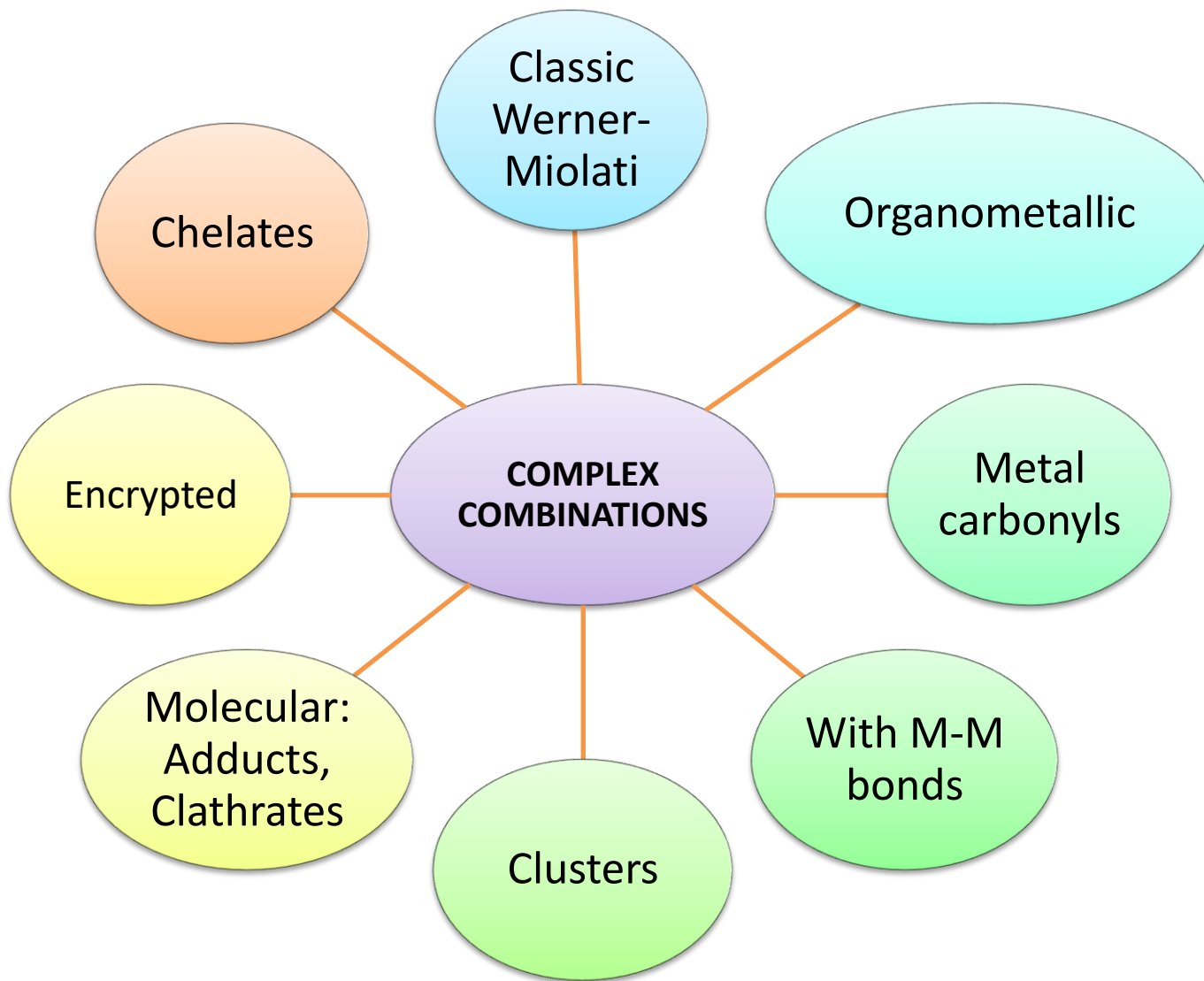
octa- μ_3 -chloro-octahedral-hexawolfram(II) ion

Classification of complex combinations

- In a first approximation, according to the number of central atoms, complex combinations are classified into ***mononuclear*** and ***polynuclear***.
- According to the complex ion charge criterion, we distinguish the following complexes:
 - anionic*** $[\text{Co}(\text{CN})_6]^{3-}$
 - cationic*** $[\text{Co}(\text{NH}_3)_6]^{3+}$
 - neutral*** $[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$
- Other classifications can be made by coordination number (C.N.), or by the oxidation state of the central atom. Depending on whether the coordinated ligands are of the same or different species, we distinguish complex combinations:
 - homogenous*** $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $\text{K}_2[\text{NiCl}_4]$, $\text{Na}_2[\text{Zn}(\text{OH})_4]$ etc.
 - heterogeneous*** $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]\text{Cl}$, $[\text{Cu}(\text{SCN})(\text{py})_2(\text{Ph}_3\text{P})]$ etc.

Classification of complex combinations

- According to the most important structural types, an acceptable classification is shown in the scheme below.



Classic Werner-Miolati

Classical Werner-Miolati complexes comprise a large number of mono- or polynuclear, homogeneous and micronuclear representatives, among which Co(III), Cr(III), Ni(II) and Pt(II/IV) compounds are prominent.

- Essentially they are anionic, cationic or neutral (non-electrolyte) type complexes, with C.N. ranging from 2 to 8, the most frequent being the hexacoordinated ones.
- These complexes contain mostly ionic (F^- , Cl^- , Br^- , I^- , CN^- , SCN^- , NO_2^-) or neutral (H_2O , NH_3 , CO , NO) inorganic ligands as well as organic ligands (py, monoamines, monocarboxylic acids).
- Classical complex combinations have found many practical applications, especially in qualitative and quantitative chemical analysis. For example:
 - ✓ Co(III) complex amines - determination of Hg, Cd, Cu, Bi, Ag, Sb etc.;
 - ✓ metal-templated reactions and in biochemical research, as vitamin B12 is known to be a cobalt cyanocomplex (cyanocobalamin);
 - ✓ isothiocyanates, in particular Cr(III), among which the *Reinecke salt* $(NH_4)[Cr(NCS)_4(NH_3)_2]$ stands out, with remarkable uses in analytical chemistry in the determination of Cu, Hg, Au, Tl, Ag, Cd, Bi, etc., in the analysis of pharmaceutical preparations, N-alkali and in the isolation of antibiotics.



Chelates

Metal chelates form a special class of complex combinations, containing bi- or polydentate cyclic ligands, which have developed and diversified exhaustively thanks to the use of special organic ligands, such as Schiff bases, linear and cyclic tetraamines, macrocyclic polyethers, etc.

- In analytical chemistry alone, over 30% of reactions rely on the use of chelates.
- α -Dioxime is used in various biochemical processes and in organic synthesis.
- β -Diketonates are stable and readily soluble in organic solvents and are used for the separation and determination of elements by spectrophotometry.
- The application of ligand complexes of the semicarbazide, thiosemicarbazide, thiosemicarbazone class and their derivatives in bioanorganics and pharmacology is very successful. The action of such complexes on viruses and tumours is well known, and they are used as pesticides and fungicides in agriculture.
- Of particular importance have been chelates with macrocyclic ligands of the type formed in plant and animal organisms (porphyrins, chlorophyll, hemin, cobaloxime), which can constitute *in vitro* biochemical reactions occurring in organisms *in vivo*.

With M-M bonds

- A particular development is in the class of complex combinations of transition metals that include metal-metal bonds.
- The great variety of types and binding modes, the possibilities of practical use in synthesis and catalysis, stimulate the passion of researchers, as evidenced by the production of thousands of scientific papers.

Clusters

- Linked to these are *clusters*, complexes in which the central atom is replaced by a cage of metal atoms, a polyhedron surrounded by ligands such as halogens, carbon monoxide, etc.
- In fact, some oligomeric metal-organic compounds and polynuclear metalcarbonyls also fit perfectly into this class.

Organometallic

Great interest has been aroused by organometallic complex combinations, especially with transition metals, and among them metalloolefin, π -allyl and related complexes, with wide applications in organic synthesis and homogeneous and heterogeneous catalysis.

Metal carbonyls

Metal carbonyls having as ligands carbon monoxide groups with the most diverse structures, mononuclear, polynuclear, heteronuclear and their derivatives hydrides and metal carbonyl halides, are of particular interest because of their spectacular practical implications in problems of synthesis, catalysis, refining and many others.

Encrypted

Among the current cutting-edge research are those related to the *crypt* class which have aroused a keen interest among specialists due to their involvement in analytical chemistry, biology and biochemistry. Generated by macrocyclic ligands, such as polycyclic ethers, they form stable complexes with alkali and alkaline earth metals.

Molecular: Adducts, Clathrates

Another special class that has seen strong development is that of *molecular complexes*, also known as adducts.

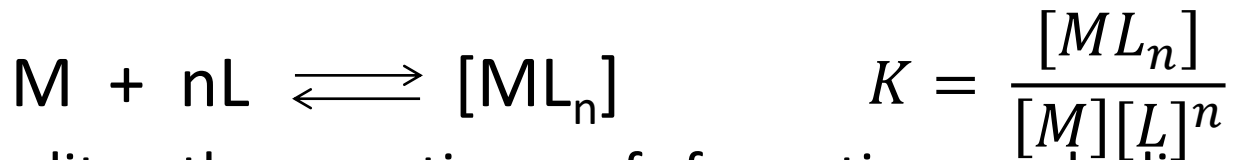
- They are obtained through donor-acceptor interaction and play an important role in a number of reactions that take place in the gas phase or in solutions.
- In particular, *adducts* formed from a complex unsaturated coordinative combination, such as those with planar-square geometry and donor molecules of the phosphine type, are at the forefront of studies undertaken by many specialist groups.
- Such hydrogen, oxygen or molecular nitrogen adducts are likely to underlie unconventional processes for separating hydrogen, oxygen and nitrogen from water and air, respectively, and activating them to produce ammonia and derived fertilisers, hydrogen fuel and oxygen fuel.
- Clathrates are solid molecular compounds in which the molecules of one component are enclosed in the crystal lattice of the other component, as in a cage.

4. Formation and stability of complex combinations

Thermodynamic stability

Stability constant

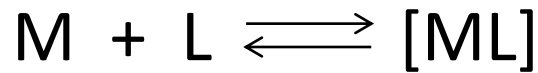
- The most important criterion for assessing the thermodynamic stability of a complex combination is the determination of **the equilibrium constant K** of the formation reaction, i.e. the ***stability constant*** based on the law of mass action:



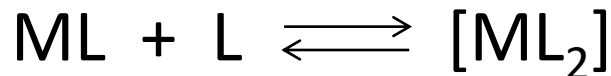
- In reality, the reactions of formation and dissociation of complex combinations can be expressed by a series of stepwise reactions, each with a corresponding equilibrium constant:

Thermodynamic stability

Stability constant

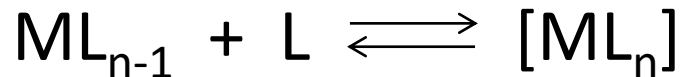


$$K_1 = \frac{[ML]}{[M][L]}$$



$$K_2 = \frac{[ML_2]}{[ML][L]}$$

⋮



$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

- The formation constant K_t will be given by the product of the constants:

$$K_t = K_1 \cdot K_2 \cdot \dots \cdot K_n$$

- The stability constant is a measure of species concentrations under equilibrium conditions.

Thermodynamic stability

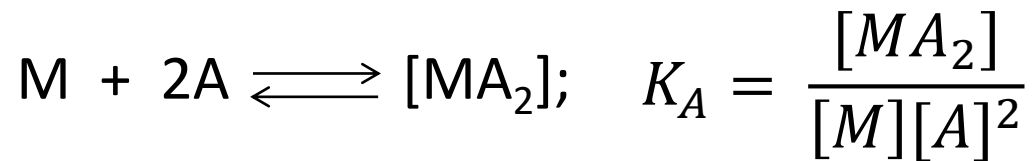
Stability constant

- The determination of stability constants is of great use in the study of complex combinations, because on their basis it is possible to obtain information about the type of metal-ligand bond, to predict the optimal conditions of formation, and to classify them into stable (strong) and unstable (weak) complexes.
- Various physical-chemical methods are used to study the formation of complex combinations, such as:
 - Electrochemical methods (potentiometric, polarographic, conductometric, amperometric);
 - Optical methods (photocolorimetric, spectrophotometric);
 - Ion exchange method;
 - Chromatographic and electrophoretic methods.

Thermodynamic stability

The entropic effect

- Calvin and Bailes energetically studied the formation reactions and stability constants of chelates with polydentate ligands (K_e) in comparison with classical complexes with monodentate ligands (A), with donor atoms in both cases:



$$\Delta G_A = -RT \ln K_A = -RT \ln \frac{[MA_2]}{[M][A]^2}$$



$$\Delta G_{K_e} = -RT \ln K_{K_e} = -RT \ln \frac{[MK_e]}{[M][K_e]}$$

Thermodynamic stability

The entropic effect

- Based on the following thermodynamic expressions:

$$\Delta G_A = \Delta H_A - T \cdot \Delta S_A = -RT \ln K_A$$

$$\Delta G_{Ke} = \Delta H_{Ke} - T \cdot \Delta S_{Ke} = -RT \ln K_{Ke}$$

and the assumption that in first approximation the metal-ligand bonds have the same enthalpy value, i.e. $H_A = H_{ke}$, under these conditions:

$$\Delta S_{Ke} - \Delta S_A = R \ln K_{Ke} - R \ln K_A$$

it is established that in the formation processes of chelated compounds the increase of their stability constants, i.e. their stability, is due to entropy. In other words, the balancing effect is essentially an entropic effect.

- Spike and Parry's work confirmed these findings for the formation of zinc and cadmium ethylenediamines.

Factors influencing the formation of complex combinations

Nature of the metal ion

- Research has shown that what essentially influences the ability of metal ions to form complex combinations is their electronic structure and their radius and charge.
- Based on the structural criterion, metal ions can be classified into:
 - ✓ alkali and alkaline earth metal cations, which have the lowest capacity to form complex combinations.
 - ✓ the cations of the elements of groups III A - VI A (periods 4-6) and subgroups I B and II B, which have a greater tendency to form complex combinations with CN 2, 4 or 6.
 - ✓ cations of transition metals, with *d* or *f* orbitals partially occupied by electrons, which exhibit the greatest ability to form complex combinations of the most diverse classes (CN = 2÷8).
- Martel and Calvin showed that, in general, the stabilities of complex combinations increase in proportion to the square of the charge of the central metal ion and inversely proportional to its radius (e^2/r), which is consistent with the low ability of alkali metals to form complexes.

Factors influencing the formation of complex combinations

Classification of metal ions and ligands based on relative coordination affinities

- A first attempt to classify metal ions was made by Ahrland, Chatt and Davies, who divide metal ions into two classes:
 - ✓ cations of class (a), which generate the most stable complexes with ligands having as donor atom the first element of one of the main groups V, VI or VII (i.e. N, O or F): $N \gg P > As > Sb > Bi$; $O \gg S > Se > Te$; $F \gg Cl > Br > I$.
 - ✓ cations of class (b), which generate the most stable complexes with ligands having as donor atom the second or next element of one of groups V, VI or VII: $N \ll P > As > Sb > Bi$; $O \ll S \sim Se > Te$; $F < Cl < Br \ll I$.
- Later, Pearson gives a new classification of complex-generating metal ions and ligands, according to which the formation of donor-acceptor metal-ligand bonds can be interpreted as the result of Lewis acid-base reactions: $A + : B = A : B$, where A is Lewis acid or electron acceptor (metal ion) and B is Lewis base or electron donor (ligand).

Factors influencing the formation of complex combinations

Classification of metal ions and ligands based on relative coordination affinities

- According to the theory of *hard* and *soft* acids, Pearson classifies complex-forming metal ions and ligands as follows:

| Class (a) or hard | Intermediaries | Class (b) or soft |
|--|--|---|
| Metal complex-generating ions | | |
| Li ⁺ , Na ⁺ , K ⁺ , Be ²⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Mn ²⁺ , Al ³⁺ , Sc ³⁺ , Ga ³⁺ , In ³⁺ , La ³⁺ , Cr ³⁺ , Co ³⁺ , Ce ³⁺ , Ti ⁴⁺ , Zr ⁴⁺ , Th ⁴⁺ , Pu ⁴⁺ , Ce ⁴⁺ , Sn ⁴⁺ , WO ₂ ⁴⁺ , VO ²⁺ | Fe ²⁺ , Co ²⁺ , Ni ²⁺ , Cu ²⁺ , Zn ²⁺ , Pb ²⁺ , Sn ²⁺ , Sb ³⁺ , Bi ³⁺ | Cu ⁺ , Ag ⁺ , Au ⁺ , Te ⁺ , Hg ₂ ²⁺ , Hg ²⁺ , Pd ²⁺ , Pt ²⁺ , Rh ²⁺ , Pt ⁴⁺ , Tl ³⁺ |
| Ligands | | |
| HO ⁻ , F ⁻ , Cl ⁻ , ClO ₄ ⁻ , NO ₃ ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ , PO ₄ ³⁻ , CH ₃ COO ⁻ , H ₂ O, NH ₃ , N ₂ H ₄ , ROH, R ₂ O, RNH ₂ | N ₃ ⁻ , Br ⁻ , NO ₂ ⁻ , SO ₃ ²⁻ , C ₆ H ₅ NH ₂ , C ₅ H ₅ N | I ⁻ , CN ⁻ , SCN ⁻ , S ₂ O ₃ ²⁻ , CO, PH ₃ , C ₂ H ₄ , R ₃ P, (RO) ₃ P, H ⁻ |

Factors influencing the formation of complex combinations

Classification of metal ions and ligands based on relative coordination affinities

- Class (a) ions are characterized by small volume, high oxidation state, low polarizability, absence of easily excited outer electrons, preferably coordinating bases capable of strong proton binding.
- Class (b) ions have large volume, low or zero positive charge, high polarizability, large number of easily excited electrons, preferably coordinating alkali with negligible basicity (CO, olefins, arenes).
- Class (a) alkali are weakly polarizable donor atom ligands that are strongly electronegative and possess high-energy vacant orbitals that are difficult to access.
- Class (b) alkali are ligands with slightly polarizable donor atoms of low electronegativity possessing low energy vacant orbitals.

Factors influencing the formation of complex combinations

Classification of metal ions and ligands based on relative coordination affinities

- When forming complex combinations, the class (a) metal ions coordinate the *hard* ligands with priority, in order: $F > Cl > Br > I$ and $O \gg S \sim Se; N \gg P > As > Sb$, and class (b), *soft* ligands, in the order: $S \sim C > I > Br > Cl > N > O > F$.
- Studying mixed complex combinations such as $[CoX(NH_3)_5]^{2+}$ and $[Co(CN)_5X]^{3-}$, where $X = F$ or I , Jörgensen observes that:
 - ✓ in the case of the combination $[CoX(NH_3)_5]^{2+}$, the fluorine derivative is more stable than the chlorine derivative because ammonia (hard base) prefers the fluorine ion (hard);
 - ✓ in the case of the combination $[Co(CN)_5X]^{3-}$, the iodine derivative is stable, due to the character of the CN^- (soft alkali) group.
- Based on these observations, Jörgensen calls the tendency of soft ligands to gather within the coordination sphere, *symbiotic* ligand behaviour.

Factors influencing the formation of complex combinations

Nature of the donor atom

- Considering the stability of halogen-complexes in solution, Ahrlund classifies metal ions into two groups:
 - ✓ group I (order of stability $F^- \gg Cl^- > Br^- > I^-$): Fe^{3+} , Be^{2+} , Cu^{2+} , Zn^{2+} , Sn^{2+} , Al^{3+} .
 - ✓ group II (order of stability $F^- \ll Cl^- < Br^- < I^-$): Cu^+ , Ag^+ , Cd^{2+} , Hg^{2+} , Pb^{2+} , Pt^{2+} , Pt^{4+} .
- According to the ability of metal ions to coordinate oxygen or nitrogen donor atoms, they can be grouped into three classes:
 - a) $O > N$: Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Mo^{5+} , Fe^{3+} , Co^{2+} ;
 - b) $O \approx N$: Be^{2+} , Cr^{3+} , Fe^{2+} , platinum metals;
 - c) $N > O$: Cu^+ , Ag^+ , Au^+ , Cu^{2+} , Cd^{2+} , Co^{3+} , Ni^{2+} .
- Although there is an analogy between oxygen and sulphur atoms, as donor atoms they behave differently:
 - a) $S > O$: Cu^+ , Ag^+ , Au^+ , Hg^+ ;
 - b) $O > S$: Be^{2+} , Cu^{2+} , Au^{3+} etc.

Factors influencing the formation of complex combinations

Nature of the donor atom

- In ligands containing oxygen as donor atom, the coordination capacity decreases in order: $\text{H}_2\text{O} > \text{R-OH} > \text{ROR}'$, and in the case of nitrogen: $\text{NH}_3 > \text{R-NH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$.
- In the case of sulphur ligands, it has been observed that the donor property of sulphur is greater the stronger the influence of the substituents and the order of the derivatives: $\text{R}_2\text{S} > \text{RSH} > \text{H}_2\text{S}$.
- Donor atoms can be classified according to their ability to generate chelates in the following order: nitrogen, oxygen, sulphur.
- The main factors influencing the stability of complex combinations are: ligand basicity, steric factors, cycle size and number of cycles in the case of chelates.
- Experimentally, it has been observed that chelated ligands, unlike monodentate ligands containing the same types of donor atoms, form more stable complex combinations (*chelation effect*).