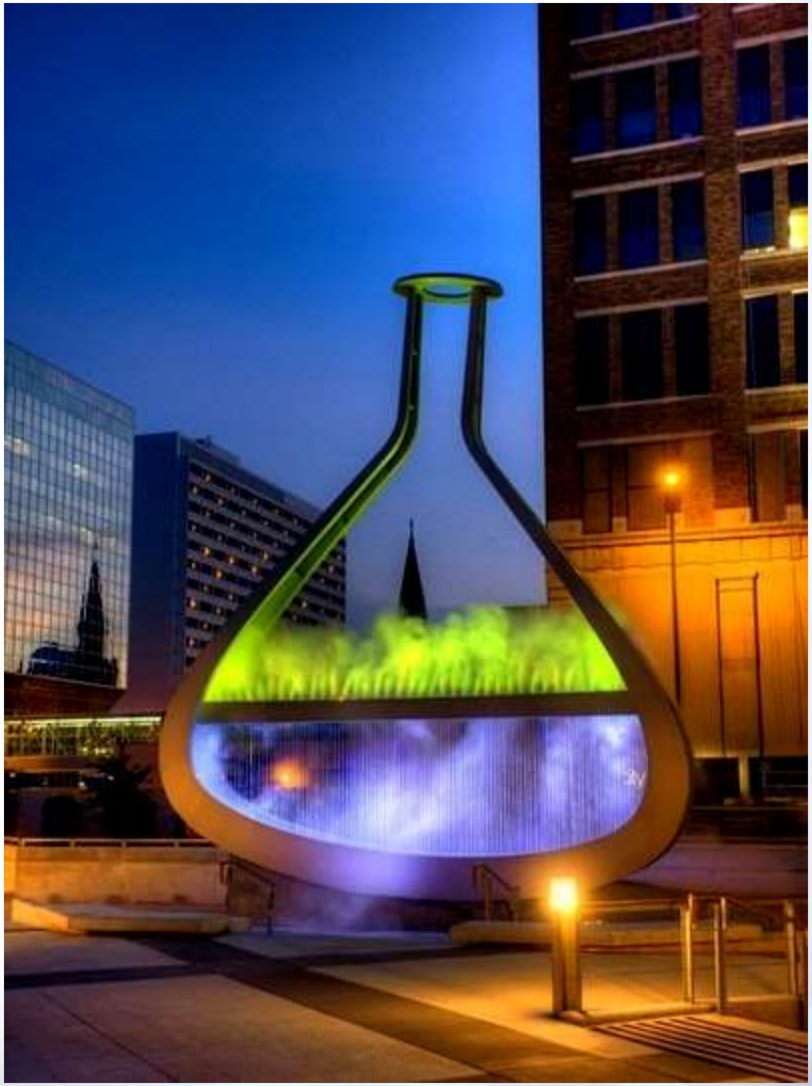
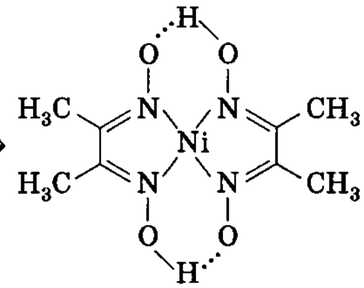
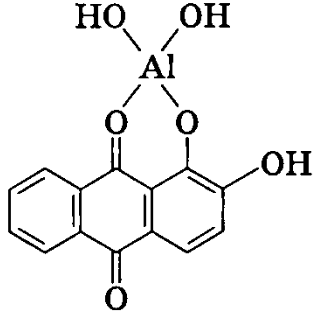
Analytical chemistry

Lecture № 6

Complexation equilibria
Part II





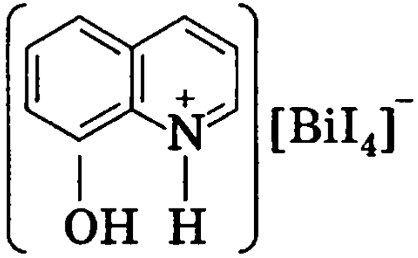


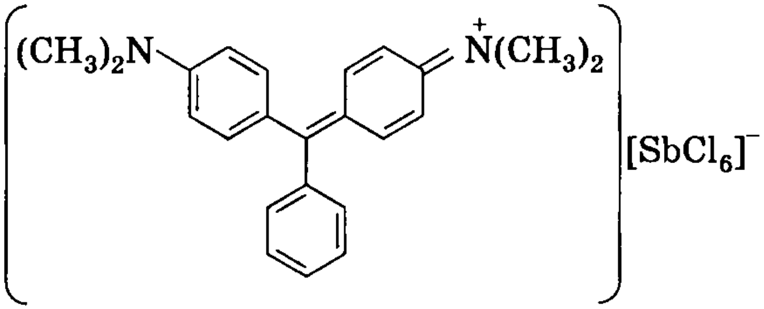
Coordination Compounds

In this case, ligands are ions or molecules that form covalent bonds with cations by donating a pair of electrons which are then shared by the ligand and the cation. The number of bonds formed per molecule is referred to as a “dentate” (meaning tooth-like). Unidentate reagents form a single bond per molecule, hexadentate form six, and so on... The chemical species formed as a result of these reactions leading to the formation of a covalent bond are called ***inner-sphere complexes***.

Outer-Sphere Complexes: In this case the attraction between “metals” (cations) and “ligands” (anions) is purely electrostatic and result in a new compound where each of the initial species retain part of or all of their water coordination shells. These type of complexes are also called ***ion pairs***.

Chelation (from the greek “claw”). Chelates are sometimes called ***internal complexes***.





Factors Influencing the Stability of Complexes

1

Ability of metallic ions to form complexes

Gerold Schwarzenbach

classes A

Lewis's acids that exhibit an affinity for halide ions according to the following sequence

$$\mathrm{F^-} \gg \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}.$$

they form the most stable complexes with the first members of each group of donor atoms of the periodic table (N, O, F).

class B

metals form complexes far more easily with iodide ions than with fluoride ions and, in aqueous solutions, give the most stable complexes with the heaviest donor atoms of a group of the periodic table (P, S, Cl).

According to this classification, Schwarzenbach distinguishes three sorts of acceptor metallic ions:

- the cations exhibiting the electronic structure of the preceding noble gas. They are the alkaline cations, the alkaline earth cations, and also the Al^{3+} cation. They are all of class A. The bonds within these complexes are essentially of an *electrostatic origin*. Interactions between ions of a small size and of high electrical charges are particularly strong. For example, the aluminum cation forms very stable complexes with fluoride anions and very weak ones with iodide ions. With these cations, water gives stable complexes than ammonia does;
- the cations that have their d-shell totally filled. Typical cations are Cu, Ag, and Au. They are of class B. The bonds they form with ligands exhibit a noticeable *covalent character*. The more noble (the less oxidizable by air) the metal is and the less electronegative the donor atom of the ligand is, the more stable the complex is. For example, Cd^{2+} and Hg^{2+} form very stable complexes with iodide and cyanide ions but very weak ones with fluoride ions;
- transition cations with an incomplete d-shell. They belong either to class A or to class B. They are on the borderline of the preceding two classes.

The concept of hard and soft acids and bases (*HSAB concept)*

The basic principle of the HSAB concept

Hard acids are located in class A and soft acids in class B. Ligands are also classed in two categories, A and B. Those located in class A are hard bases, while those of class B are soft bases.

**Ligands, whose donor atoms are *oxygen, nitrogen, or fluorine*, are hard bases. Those whose donor atoms are *sulfur, phosphorus, or halogens*, to the exclusion of fluorine,
are soft bases.**

! the homogeneous pairs hard acid/hard base, on the one hand, and soft acid/soft base, on the other, give the most stable complexes. The heterogeneous pairs hard acid/soft base and vice versa give the least stable ones.

The softness is related to the electronegativity of the species, i.e., the ability of the ligand donor atoms to become better electron donors.

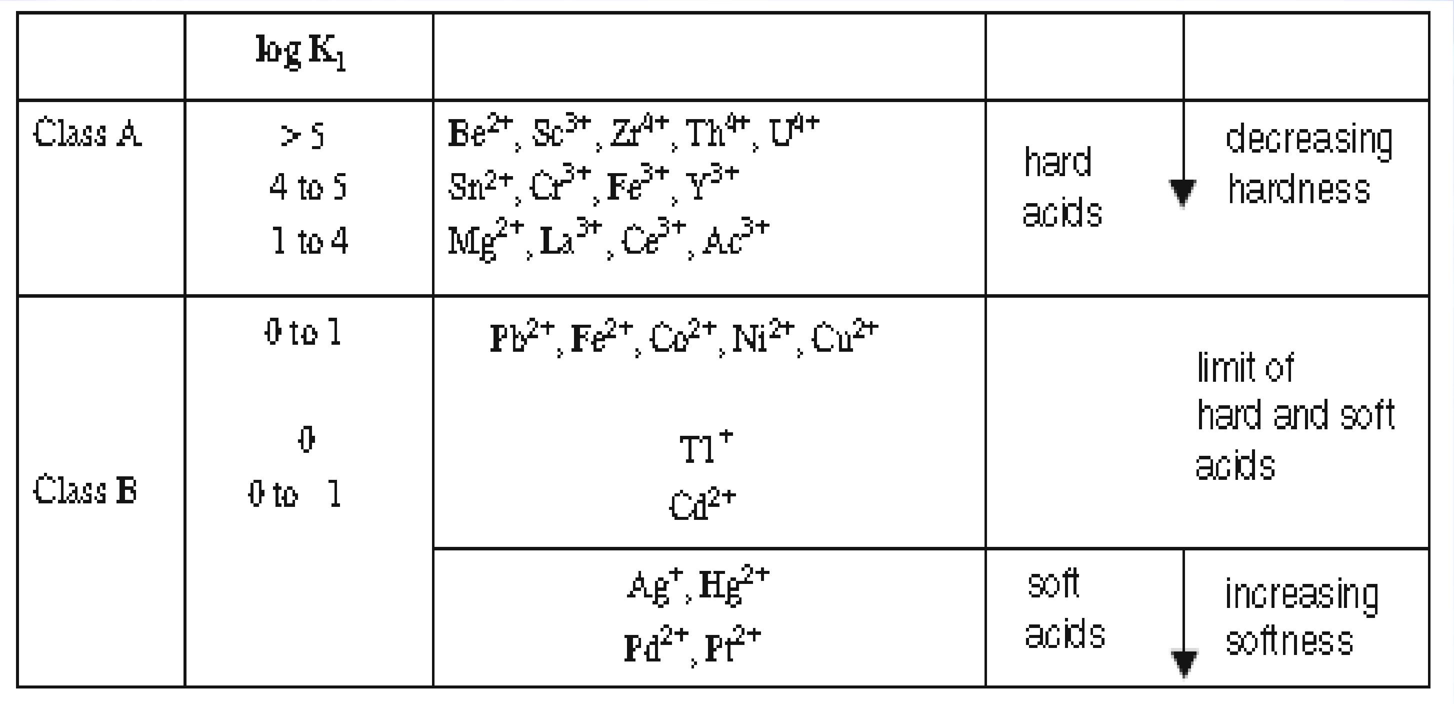
Hard (Predominantly, having the electron configuration of inert gases)
Acids: Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}
Bases: NH_3, RNH_2, H_2O, $OH^–$, CO_3^{2-} , SO_4^{2-} , $F^–$

Boderline (Intermediate character)
Acids: Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}
Bases: $Br^–$, $Cl^–$

Soft (Electron configuration in the outer shell similar to Ni, Pb, Pt)
Acids: Cu^+, Ag^+, Cd^{2+}, Hg^{2+}, Au^+
Bases: $CN^–$, $SCN^–$, RSH, $RS^–$
The hard and soft characters are not absolute but gradually vary.

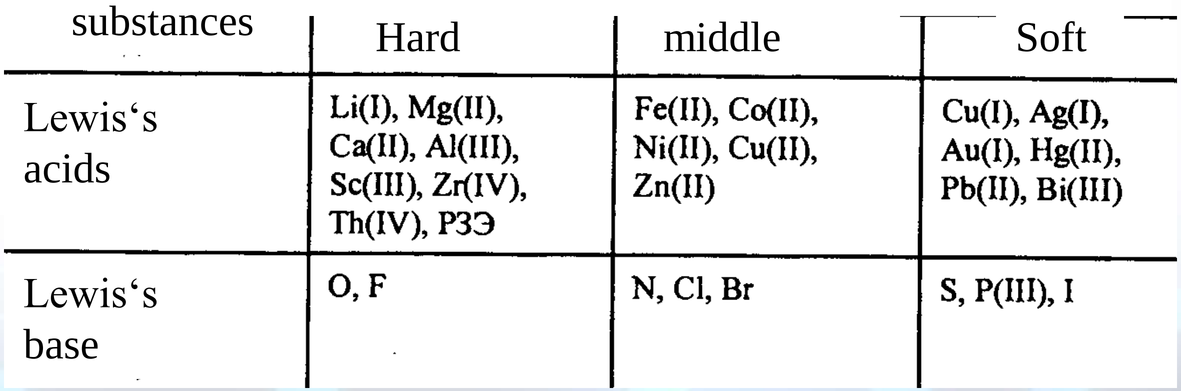
HSAB RULES: Thermodynamic equilibrium: Hard acids prefer to associate with hard bases and soft acids with soft bases. Kinetics: Hard acids react readily with hard bases and soft acids with soft bases.

Hardness and softness of some metallic ions



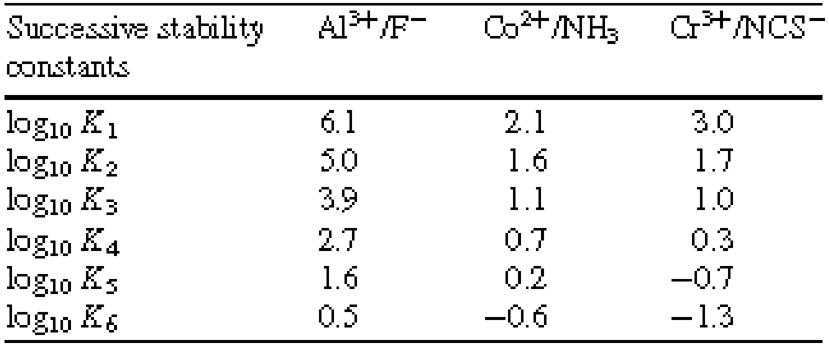
	$\log K_1$			
Class A	> 5 4 to 5 1 to 4	Be^{2+}, Sc^{3+}, Zr^{4+}, Th^{4+}, U^{4+} Sn^{2+}, Cr^{3+}, Fe^{3+}, Y^{3+} Mg^{2+}, La^{3+}, Ce^{3+}, Ac^{3+}	hard acids	↓ decreasing hardness
Class B	0 to 1 0 0 to 1	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} Tl^{+} Cd^{2+}		limit of hard and soft acids
		Ag^{+}, Hg^{2+} Pd^{2+}, Pt^{2+}	soft acids	↓ increasing softness

The homogeneous pairs hard acid/hard base and soft acid/soft base and vice versa give the most stable complexes.



substances	Hard	middle	Soft
Lewis‘s acids	Li(I), Mg(II), Ca(II), Al(III), Sc(III), Zr(IV), Th(IV), РЗЭ	Fe(II), Co(II), Ni(II), Cu(II), Zn(II)	Cu(I), Ag(I), Au(I), Hg(II), Pb(II), Bi(III)
Lewis‘s base	O, F	N, Cl, Br	S, P(III), I

generally, the numerical values of the successive stability constants *Kn decrease regularly as n increases*



Successive stability constants	Al^{3+}/F^-	Co^{2+}/NH_3	Cr^{3+}/NCS^-
$\log_{10} K_1$	6.1	2.1	3.0
$\log_{10} K_2$	5.0	1.6	1.7
$\log_{10} K_3$	3.9	1.1	1.0
$\log_{10} K_4$	2.7	0.7	0.3
$\log_{10} K_5$	1.6	0.2	−0.7
$\log_{10} K_6$	0.5	−0.6	−1.3

Complexes of metallic ions at oxidation state + III are more stable than those of the same metals at oxidation state + II.

The stability of complexes of bivalent metals of the first series of transition metals, for a same ligand, changes according to the order:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

This is the Irving–Williams's series.

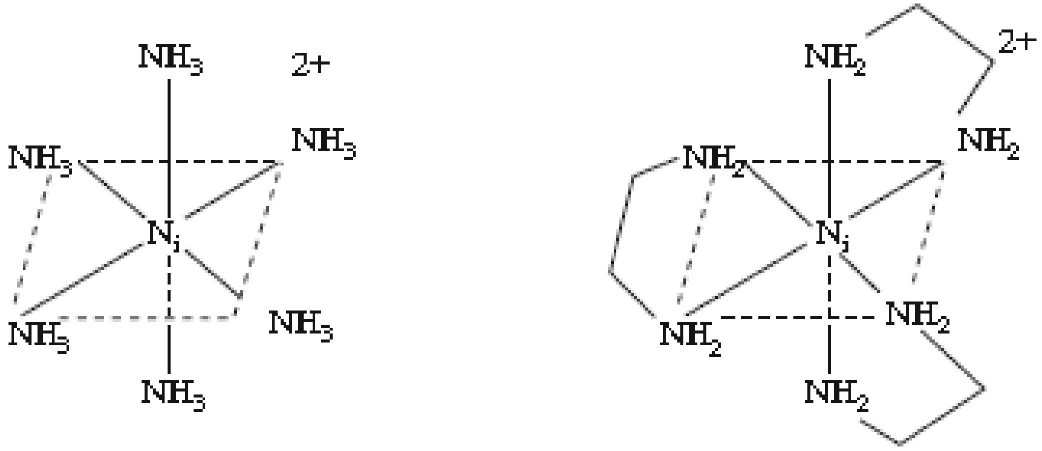
Stability of Chelates: Chelate and Macrocyclic Effects

chelates **are particular complexes in which a multidentate coordinate consisting of an ion or organic molecule contracts all its bonds with the same central ion. The latter is therefore tied in a cyclic structure as if it were in a claw (*chelatos* = claw). Chelates are sometimes called *internal complexes.***

A chelate is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring.

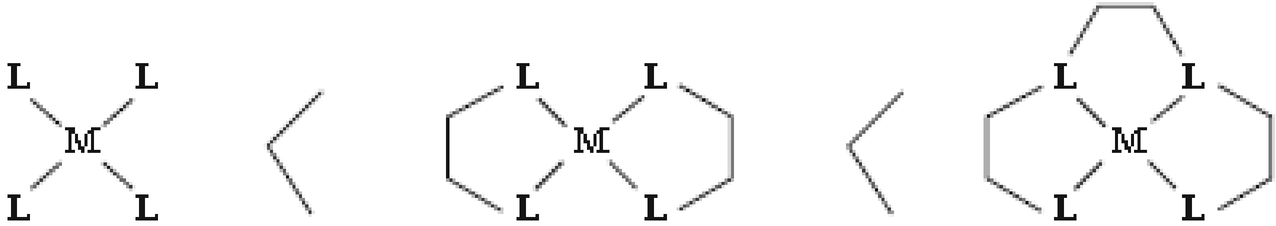
chelate effect

The difference in stabilities exhibited by the complex that could, a priori, be considered analogous to the chelate and by the chelate itself is called the ***chelate effect.***

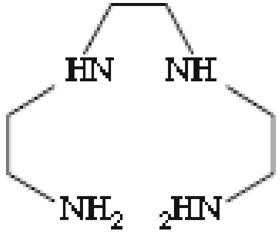


β_6 $3{,}1 \cdot 10^8$ β_3 10^{18}

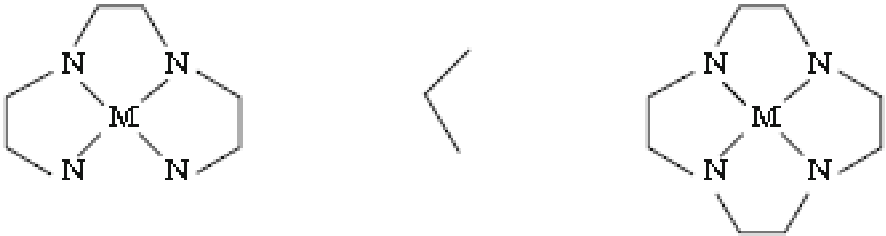
Overall stability constants of complexes $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$



Stability of complexes and chelates as a function of the number of pentagonal cycles



macrocyclic effect



The stability of the chelate possessing the maximal number of pentagonal cycles is higher than that of the structurally analogous chelate, notably endowed with the same denticity but with one fewer pentagonal cycle

entropic effect

Stability of the chelates (stability factors)

1. The number of pentagonal cycles in which the metallic ion is engaged. The greater their number is, the higher the chelate stability is.

2. The nature of the atoms that donate electronic pairs. Oxygen and nitrogen atoms give the most stable chelates;

3. The ratio of the number of chelator molecules/number of coordinating ions existing in the chelate once formed.

2

Concentration of reagent

$$C_M = [M] + [ML] + [ML_2] + ... + [ML_n]$$

$$[ML] = \beta_1 [M][L]$$

...

$$[ML_2] = \beta_2 [M][L]^2$$

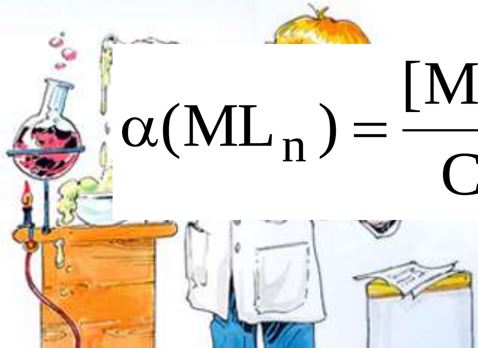
$$[ML_n] = \beta_n [M][L]^n$$

$$C_M = [M] + \beta_1 [M][L] + \beta_2 [M][L]^2 + ... + \beta_n [M][L]^n =$$

$$= [M](1 + \beta_1 [L] + \beta_2 [L]^2 + ... + \beta_n [L]^n$$

$$\alpha(M) = \frac{[M]}{C_M}$$

$$\alpha(M) = \frac{1}{1 + \beta_1 [L] + \beta_2 [L]^2 + ... + \beta_n [L]^n}$$



$$\alpha(ML_n) = \frac{[ML_n]}{C_M}$$

$$\alpha(ML_n) = \frac{\beta_n [L]^n}{1 + \beta_1 [L] + \beta_2 [L]^2 + ... + \beta_n [L]^n}$$

$$\alpha_{M} = \frac{1}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n}$$

$$\alpha_{ML} = \frac{\beta_1[L]}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n}$$

$$\alpha_{ML_2} = \frac{\beta_2[L]^2}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n}$$

$$\alpha_{ML_n} = \frac{\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \beta_3[L]^3 + \cdots + \beta_n[L]^n}$$

Complex function $F(L) = \frac{C_M}{[M]}$

$$\alpha(M) = \frac{1}{F(L)} \qquad \alpha(ML_n) = \frac{\beta_n[M][L]^n}{F(L)}$$

$$\bar{n} = \frac{C_L - [L]}{C_M}$$

Average ligand number

$$\bar{n} = \frac{\beta_1[L] + 2\beta_2[L]^2 + \ldots + n\beta_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \ldots + \beta_n[L]^n}$$

3

Ionic strength

$$\beta_n = \beta_n^0 \frac{y_M \cdot y_L^n}{y_{ML_n}}$$

$$\lg \beta_n = \lg \beta_n^o + \Delta\nu z_i^2 A\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0{,}2I\right)$$

$$\Delta\nu z_i^2 = z_{ML_n}^2 - z_M^2 - n z_L^2$$

4

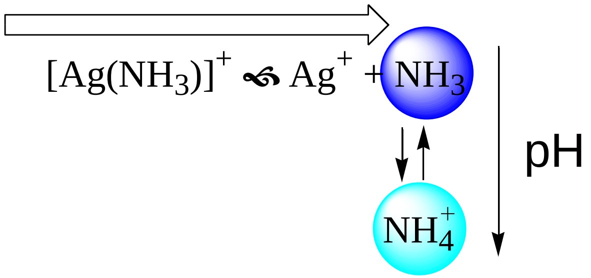
temperature

If ΔH > 0, then with ↑ temperature stability of complexes ↑, if ΔH < 0, with ↑ temperature stability of complexes ↓.

5

pH value

The acidity of a solution may have an influence on the ability of the ligands to complex



$[Ag(NH_3)]^+ \rightleftharpoons Ag^+ + NH_3$

$NH_3 \rightleftharpoons NH_4^+$

pH

A decrease in the pH value decreases the stability of complexes, the ligand of which is the conjugate base of a weak acid.
The more protonated the ligand is (i.e., the lower the pH value), the more the decrease in stability is.

The acidity of a solution may have an influence on the ability of the ligands to complex. Ligands are nucleophilic entities. Very often, but not necessarily, their nucleophilic character parallels their basic character. In this case, they may be protonated according to the pH of the solution, and they hence lose their ability to complex. The following rule summarizes this consideration: “*A decrease in the pH value decreases the stability of complexes, the ligand of which is the conjugate base of a weak acid. The more protonated the ligand is (i.e., the lower the pH value), the more the decrease in stability is.” (Obviously, in this rule, we must understand the word “stability*” as the apparent stability since the complex’s stability is quantified once and for all with its stability constant value.) The rule does not apply to the conjugate bases of strong acids. Then the pH is deprived of any influence on the (apparent) stability of the complexes they form. This is the case with the ligands Cl^-, Br^-, I^-, SCN^-, and so on. Qualitatively speaking, the rule corresponds to a phenomenon of equilibrium displacement. An example is provided by the hydroxide ligand.

Influence various factors on complex compound stability

1. **Stability of complex compounds is more in complexes with high coordination number.**

2. Concentration of complex compounds in solution direct depends to ligand concentration and is inversely proportional to metal ion concentration.

3. Equilibrium in solution of complex compounds depend to pH (concentration of hydrogen ions) and dissociation constant. Increasing the pH value is a cause of complex compounds destroying (hydrolysis).

4. The most complicated is temperature influence on complex compound stability.

Reaction of complex formation may be endothermic or exothermic. Heating can induces
such chemical processes:

– changing acidic-basic equilibrium,
– destroying some ligands,
– oxidation some ligands or metal ions,
– hydrolysis complex ions.

Applications of the Formation of Complexes in Inorganic Analysis

Qualitative Inorganic Analysis

In numerous cases, the formation of complexes permits the identification of inorganic ions after reaction with appropriate ligands. The identification may also be carried out with reagents that are already complexes. From another standpoint, it is possible that some ions disturb the preceding identifications. Hence, they may be masked to the identification reagents by complexing them. In the same connection, the complexation of an ion may allow it to avoid being precipitated in some experimental conditions and may even permit the dissolution of a precipitate to which it gives rise. Finally, it is sometimes possible to extract an ion into a nonpolar phase after complexation.

The most important complex compounds with inorganic ligands, used in analysis

1. Ammonia:

– selection (colourless complex): $[Ag(NH_3)_2]^+$, $[Zn(NH_3)_4]^{2+}$, $[Cd(NH_3)_4]^{2+}$;

– detection (coloured complex): $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Ni(NH_3)_4]^{2+}$.

2. Halogen and rhodanide:

– selection with extraction in inorganic solvents;

– detection (coloured complex): $[Fe(SCN)_3]^{3-}$, $[BiI_4]^-$, $[CoCl_4]^{2-}$.

3. Fluor – separation and masking (colourless complex): $[FeF_6]^{3-}$

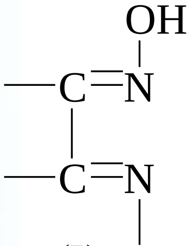
4. Cyanide – determination (coloured complex): $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{2-}$.

Qualitative inorganic analysis carried out through the formation of complexes frequently involves other physicochemical phenomena in addition to that of complexation.

Thus, there often exists a superimposition of several processes, among which complexation is present. The latter may indeed be followed, for example, by a precipitation. This is often the case with organic reagents such as oximes, dimethylglyoxime, cupferron, and so forth. As a result, gravimetric measurements might also be considered. The formed complexes may also be extracted in organic solvents that are very poorly miscible with water. Once extracted, and because of their characteristic UV spectra, these complexes can often be quantitatively analyzed by absorption measurements.

Organic Reagents in Analysis

Organic reagents are more selective than inorganic precipitants or complex ions. Possibility of interaction ions with reagent depends to specific atoms group in structure of organic compound. These specific atoms groups called *functional or analytic-active groups*. Organic reagent bond cation through the active analytical group.



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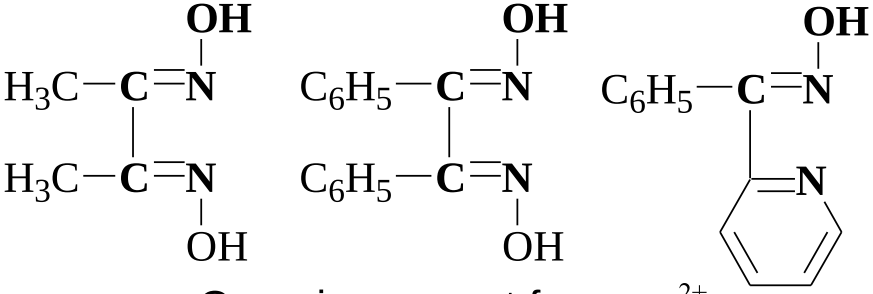


Organic reagent for Ni^{2+}

Organic reagents take part in reaction formation of:

1) insoluble compounds;

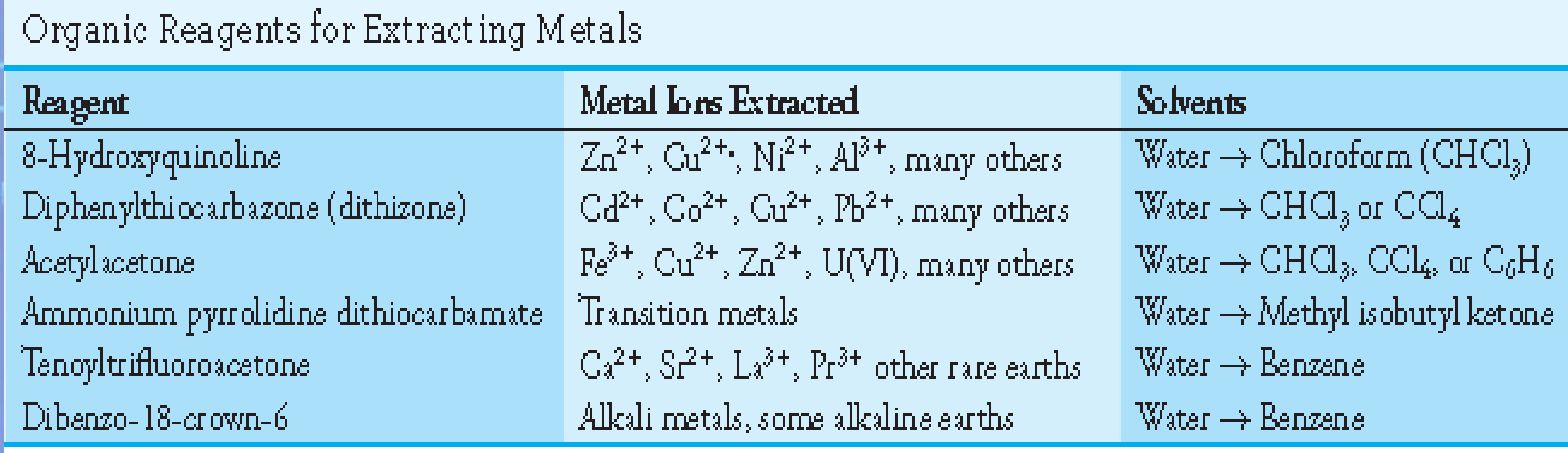
2) traditional complex compounds, which are soluble in water or organic solvents;

3) chelates.

Examples of organic reagents application:

1. Formation of organic dyes – detection of NO_2^- ion with aromatic amines.
2. Formation of coloured complex compound – identification of Ni^{2+} with dimetylglioxime.
3. Formation of coloured precipitate – detection of Ba^{2+} with sodium rhodizonate.
4. Formation of compound which change colour depending to red-ox potential – diphenilamine.
5. As specific reagents for definite cations (anions).
6. in extracting metals from one solvent to another,
7. in forming complexes that absorb light for spectrophotometric determinations.
8. As masking agents (EDTA)
9. In electrochemical determinations and in molecular fluorescence spectrometry . In this instance, the metal-ligand complex is either colored or absorbs ultraviolet radiation.

The most useful organic reagents form chelate complexes with metal ions.



Organic Reagents for Extracting Metals

Reagent	Metal Ions Extracted	Solvents
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Water → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Water → $CHCl_3$ or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Water → $CHCl_3$, CCl_4, or C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Water → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+} other rare earths	Water → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Water → Benzene

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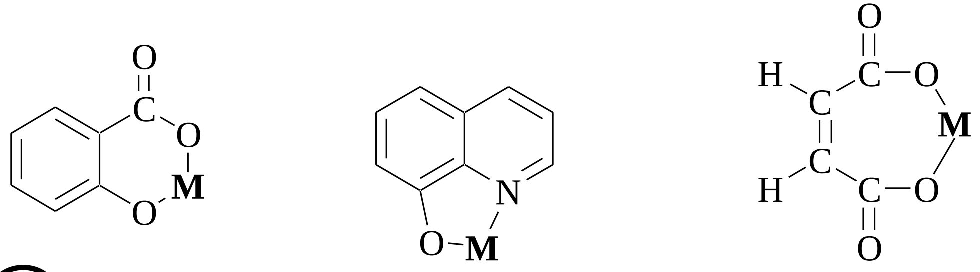

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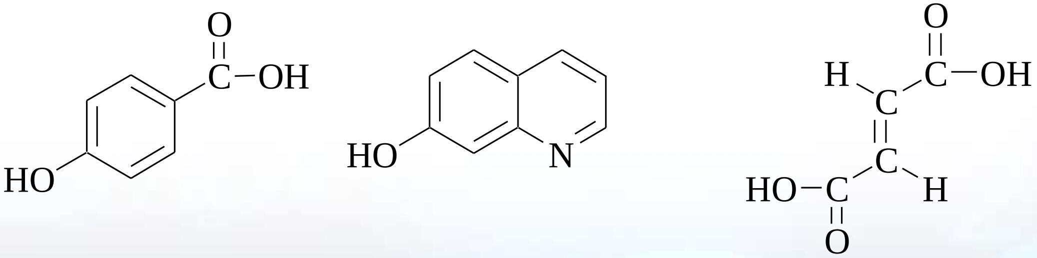

$$\beta_n^0 = \frac{a_{ML_n}}{a_M\, a_L^n}$$

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

$$\beta'_n = \frac{[ML_n]}{C_M C_L^n}$$

thermodynamic formation constant

conditional formation constant, or effective formation constant

$$\beta_n = \beta_n^0 \frac{y_M \cdot y_L^n}{y_{ML_n}}$$

$$\beta'_n = \beta_n \cdot \alpha_M \cdot \alpha_L^n$$

$$\alpha_M = \frac{[M]}{c_M}; \quad \alpha_{ML} = \frac{[ML]}{c_M};$$

$$\alpha_{ML_2} = \frac{[ML_2]}{c_M}; \quad \alpha_{ML_n} = \frac{[ML_n]}{c_M}$$

alpha value of Me is the fraction of the total metal concentration in that form. Thus, α_M is the fraction of the total metal present at equilibrium in the free metal form, α_{ML} is the fraction in the ML form.