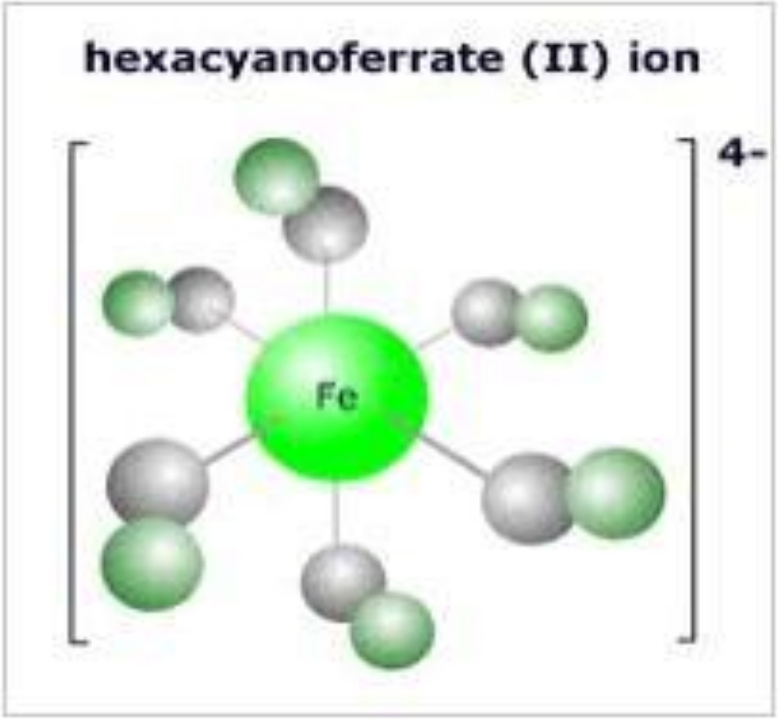


LECTURE 9

Chemistry of Coordination Compounds

30.03.2017

LECTURE OBJECTIVES:

After reading this lesson, the learner will be able to

- state the postulates of Werner’s theory;
- define ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valance bond theory;
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.

Skills to Develop

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:

1) Simple salt: **KOH + HCl → KCl + H2O**

2) Molecular (or) addition compounds:

a) Double salts are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Hence the molecular compounds which dissociate in solution into its constituent ions are known as double salt. Double salts retain their properties only in solid state. They are also called as lattice compounds. **Example** Mohr's salt:

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 6H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 6H_2O$$

b) Coordination (or complex) compounds is 'a compound formed from a Lewis acid and a Lewis base'. The molecular compounds, do not dissociate into its constituent ions in solution are called coordination compounds.

$$Fe(CN)_2 + 4KCl \rightarrow K_4[Fe(CN)_6] \quad or \quad Fe(CN)_2 \cdot 4KCl$$

$$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$$

Ferrous cyanide

One of the important aspects of any chemical research is the preparation of new compounds. This process is called synthesis. In this lecture you will investigate a special kind of compound called a coordination compound.

Transition metals readily react with halogens to form binary compounds of various colors, for example: **green-black ferric chloride ($FeCl_3$)**, **deep blue cobalt chloride ($CoCl_2$)**, and **golden yellow nickel bromide ($NiBr_2$)**.

These compounds dissolve in water to give brightly colored solutions – but of changed colors: **yellow solutions (containing Fe^{3+} ions)**, **red solutions (Co^{2+} ions)**, and **green solutions (Ni^{2+} ions)**.

By evaporating the solutions, crystals of these new compounds can be obtained: **yellow $FeCl_3 \cdot 6H_2O$**, **red $CoCl_2 \cdot 6H_2O$**, and **green $NiBr_2 \cdot 6H_2O$**.

Addition of ammonia to a **green nickel solution** changes its color to **violet, and the compound $NiBr_2 \cdot 6NH_3$** can be crystallized. In all cases these beautiful color changes occur because a new chemical species has formed, and there have been changes in the bonding of the nonmetallic substance to the metal ion.

The Transition Metals

A LARGE GROUP OF METALS IN THE CENTRE OF THE PERIODIC TABLE, THEY ARE LESS REACTIVE THAN THE GROUP 1 & 2 METALS, AND HAVE HIGH MELTING POINTS & DENSITIES

21 **Sc** Scandium	22 **Ti** Titanium	23 **V** Vanadium	24 **Cr** Chromium	25 **Mn** Manganese	26 **Fe** Iron	27 **Co** Cobalt	28 **Ni** Nickel	29 **Cu** Copper	30 **Zn** Zinc
39 **Y** Yttrium	40 **Zr** Zirconium	41 **Nb** Niobium	42 **Mo** Molybdenum	43 **Tc** Technetium	44 **Ru** Ruthenium	45 **Rh** Rhodium	46 **Pd** Palladium	47 **Ag** Silver	48 **Cd** Cadmium
	72 **Hf** Hafnium	73 **Ta** Tantalum	74 **W** Tungsten	75 **Re** Rhenium	76 **Os** Osmium	77 **Ir** Iridium	78 **Pt** Platinum	79 **Au** Gold	80 **Hg** Mercury

3422° C

TUNGSTEN HAS **THE HIGHEST MELTING POINT** OF ANY **METALLIC ELEMENT**

TRANSITION METALS FORM

Co^{2+} Cr^{3+} Fe^{3+} Ni^{2+} Fe^{2+} Cu^{2+} Mn^{7+} Mn^{2+}

COLOURED COMPOUNDS

THERE ARE **THREE MAGNETIC METALS**

IRON, COBALT AND NICKEL

MERCURY IS THE ONLY **LIQUID METAL AT ROOM TEMPERATURE** **Hg**

UNLIKE GROUP 1 & 2 METALS TRANSITION METALS CAN FORM **CO-ORDINATION COMPLEXES** WITH OTHER ATOMS & MOLECULES

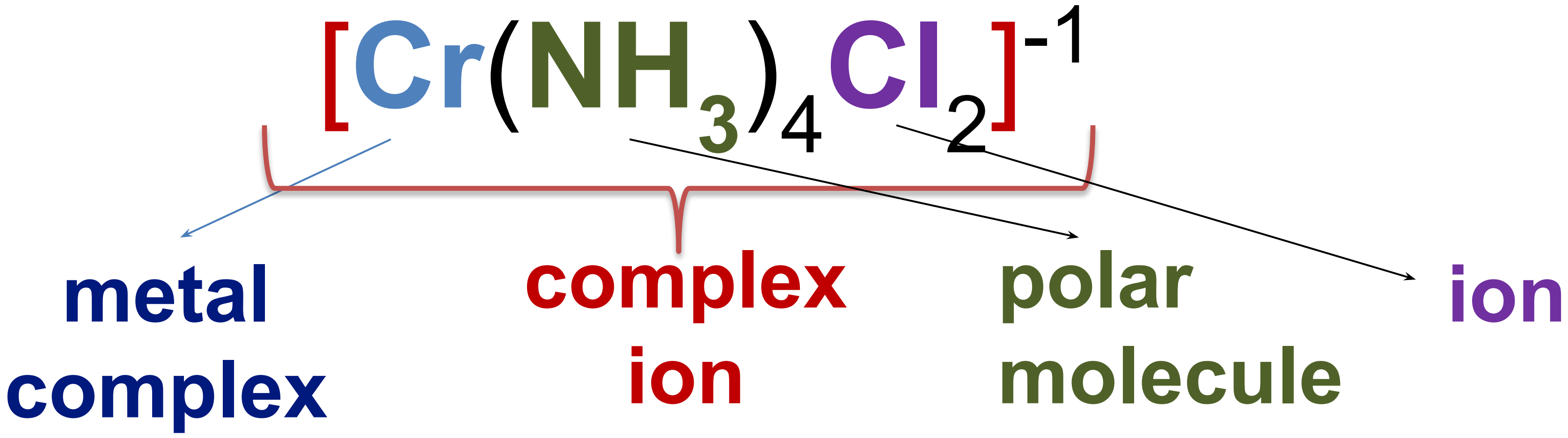
TRANSITION METALS HAVE **VARIOUS OXIDATION STATES**

-3 -2 -1 +1 +2 +3 +4 +5 +6 +7

MANGANESE HAS **TEN POSSIBLE OXIDATION STATES**

COPPER, SILVER & GOLD ARE KNOWN AS THE **COINAGE METALS**

Cu Ag Au



$[Cr(NH_3)_4Cl_2]^{-1}$

metal complex

complex ion

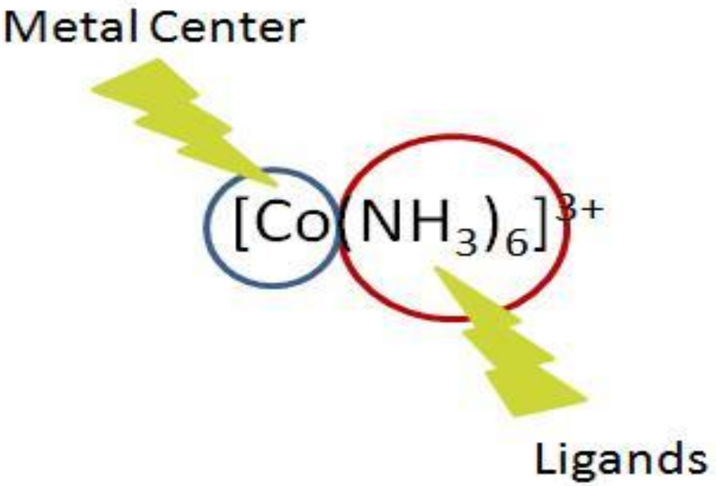
polar molecule

ion

A central metal atom bonded to a group of polar molecules or ions is a **metal complex**.

If the complex bears a charge, it is a **complex ion**.

Compounds containing complexes are **coordination compounds**.



Complexes or coordination compounds are molecules that posess a metal center that is bound to ligands (atoms, ions, or polar molecules that donate electrons to the metal).

Coordination complexes (a complex ion) is comprised of two important parts:

- **the central atom**
- **and its surrounding ligands.**

THE CENTRAL ATOM

It is can be:

- **any metallic ion (usually a transition d- or f-metal);**
- **nonmetals (B, Si);**
- **p-element (Al).**

The overall it charge can be positive, negative, or neutral.

Thus, in the complex ion an acceptor accepts a pair of electrons from the donor atoms. The acceptor is usually a metal / metal ion to which one (or) more of neutral molecules (or) anions are attached. The acceptor metal cation is referred to as central metal cation. Hence, central metal cation in a complex serves as a lewis acid.

Coordination compounds are complex or contain complex ions, for example:

- **Complex Cation**: $[Co(NH_3)_6]^{3+}$

$$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$$

- **Complex Anion**: $[CoCl_4(NH_3)_2]^{-1}$

$$K_3[Cr(CN)_3Cl_3] \rightarrow 3K^+ + [Cr(CN)_3Cl_3]^{3-}$$

- **Neutral Complex**: $[CoCl_3(NH_3)_3]^{\circ}$

- Coordination Compound: $K_4[Fe(CN)_6]$

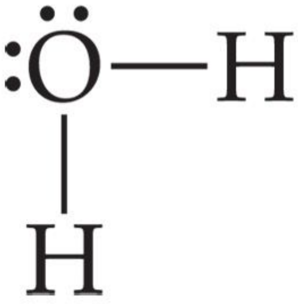
The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913).

Werner proposed putting all molecules and ions within the sphere in brackets and those “free” anions (that dissociate from the complex ion when dissolved in water) outside the brackets.

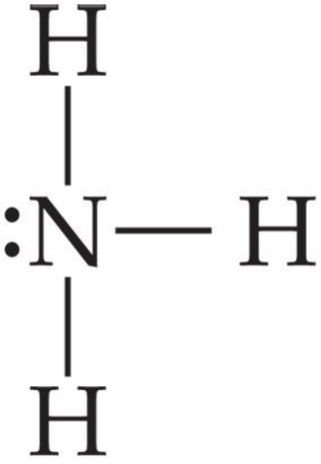
STRUCTURE OF COMPLEXES:

Central Metal Ion: It is an acceptor atom containing vacant orbitals to which a fixed number of ligands are attached via co-ordinate bonds in definite geometrical arrangement.

The molecules or ions coordinating to the metal are **the ligands**. They are usually anions or polar molecules.



aqua-



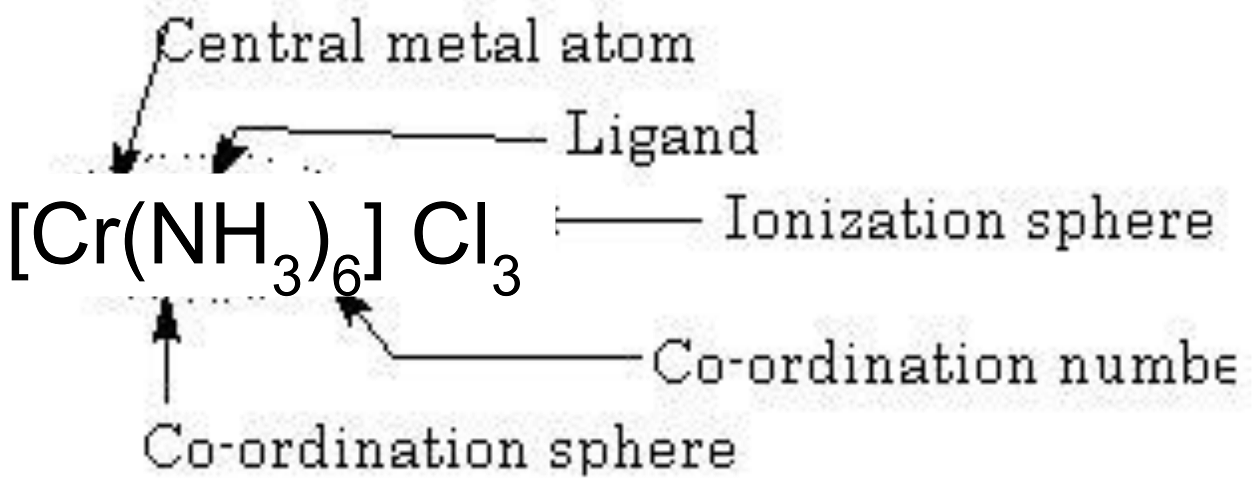
ammino-

chlorido-

ciano-

Coordination Sphere: Central atom and ligands comprise the *inner coordination sphere*; complex ion enclosed in square bracket, it behaves as a single unit.

Ionization Sphere: Part of compound present outside coordination sphere, *an outer coordination sphere* constitute a positive or negatively charged ions that are on more distance from the central ion or associated therewith:



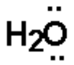
LIGANDS

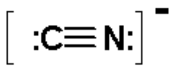
It is an ion or polar molecule capable of donating a pair of electrons to the central atom via a donor atom.

Types of ligands:

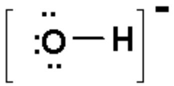
- ***Unidentate ligands:*** Ligands with only one donor atom, e.g. NH_3, Cl^-, F^- etc.
- ***Bidentate ligands:*** Ligands with two donor atoms, e.g. ethylenediamine, $C_2O_4^{2-}$(oxalate ion) etc.
- ***Tridentate ligands:*** Ligands which have three donor atoms per ligand, e.g. (dien) diethyl triamine.
- ***Hexadentate ligands:*** Ligands which have six donor atoms per ligand, e.g. EDTA.
- ***Chelating Ligands:*** Multidentate ligand simultaneously co-ordinating to a metal ion through more than one site is called chelating ligand. These ligands produce a ring like structure called chelate. Chelation increases the stability of complex. This effect is called chelation effect.

Unidentate

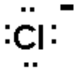


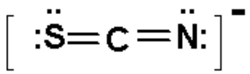


cyanide ion

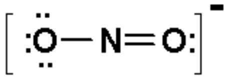


hydroxide ion



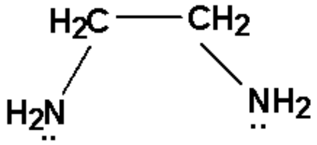


thiocyanate ion

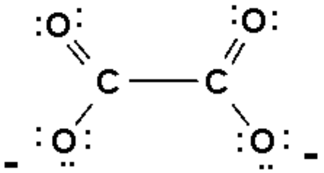


nitrite ion

Bidentate

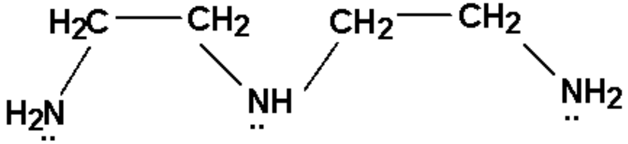


ethylenediamine (en)

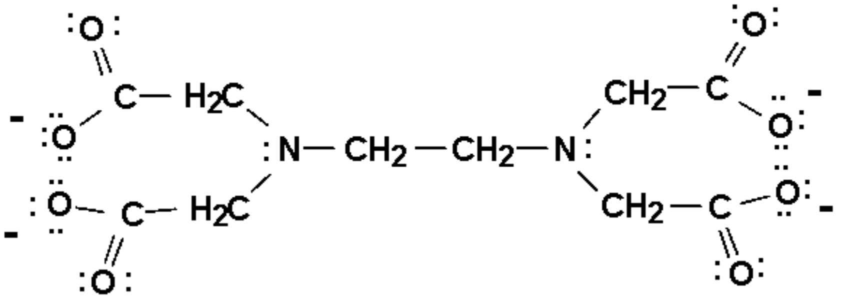


oxalate ion

Polydentate



diethylenetriamine



ethylenediaminetetracetate (EDTA) ion

Coordination Number:

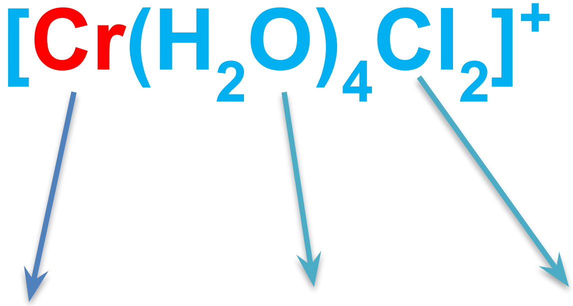
It is the total number of ligands attached to the central metal atom through coordinate bonds or the number of atoms of a ligand attached to the same central atom, e.g. hexadentate ligand should be counted as forming six co-ordinate bonds.

Charge of central atom	Coordination number
Ag +1	2
Cu +2	4, 6
Bi +3	6, 4
Zr +4	8, 6

Oxidation number:

It is the charge which the central atom appears to have if all the ligands are removed along with the electron pairs that are shared with the central atom.

$$[Cr(H_2O)_4Cl_2]NO_3 \;\Rightarrow\; \underbrace{[Cr(H_2O)_4Cl_2]^+}_{\text{Coordination sphere}} + \underbrace{NO_3^-}_{\text{Ionization sphere}}$$

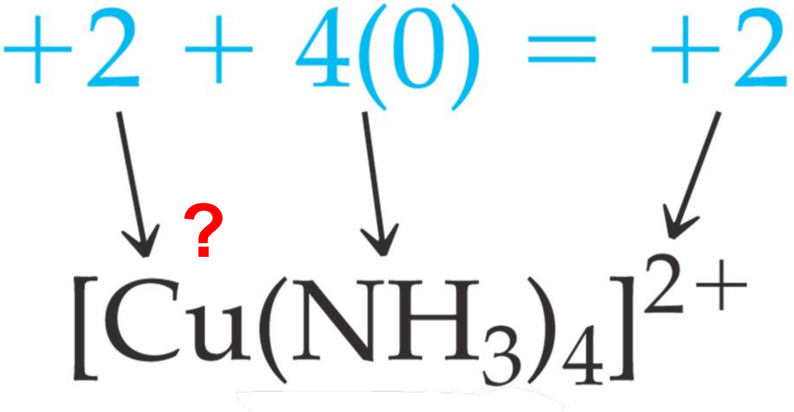


$[Cr(H_2O)_4Cl_2]^+$

x + (4 × 0) + (-1 × 2) = +1 [because the ligand H_2O is neutral and $2Cl^-$ carries - 2 charge]

x + 0 - 2 = +1

x = + 3 (Cr^{3+})

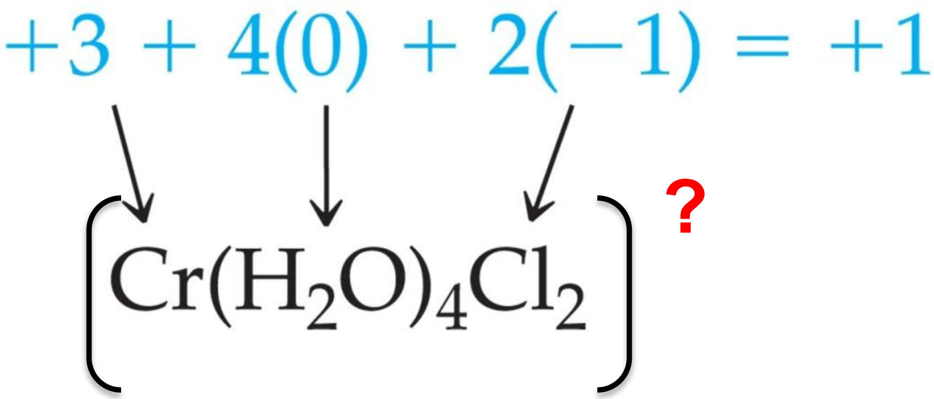


$$+2 + 4(0) = +2$$

?

$$[Cu(NH_3)_4]^{2+}$$

Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the central metal ion.



$$+3 + 4(0) + 2(-1) = +1$$

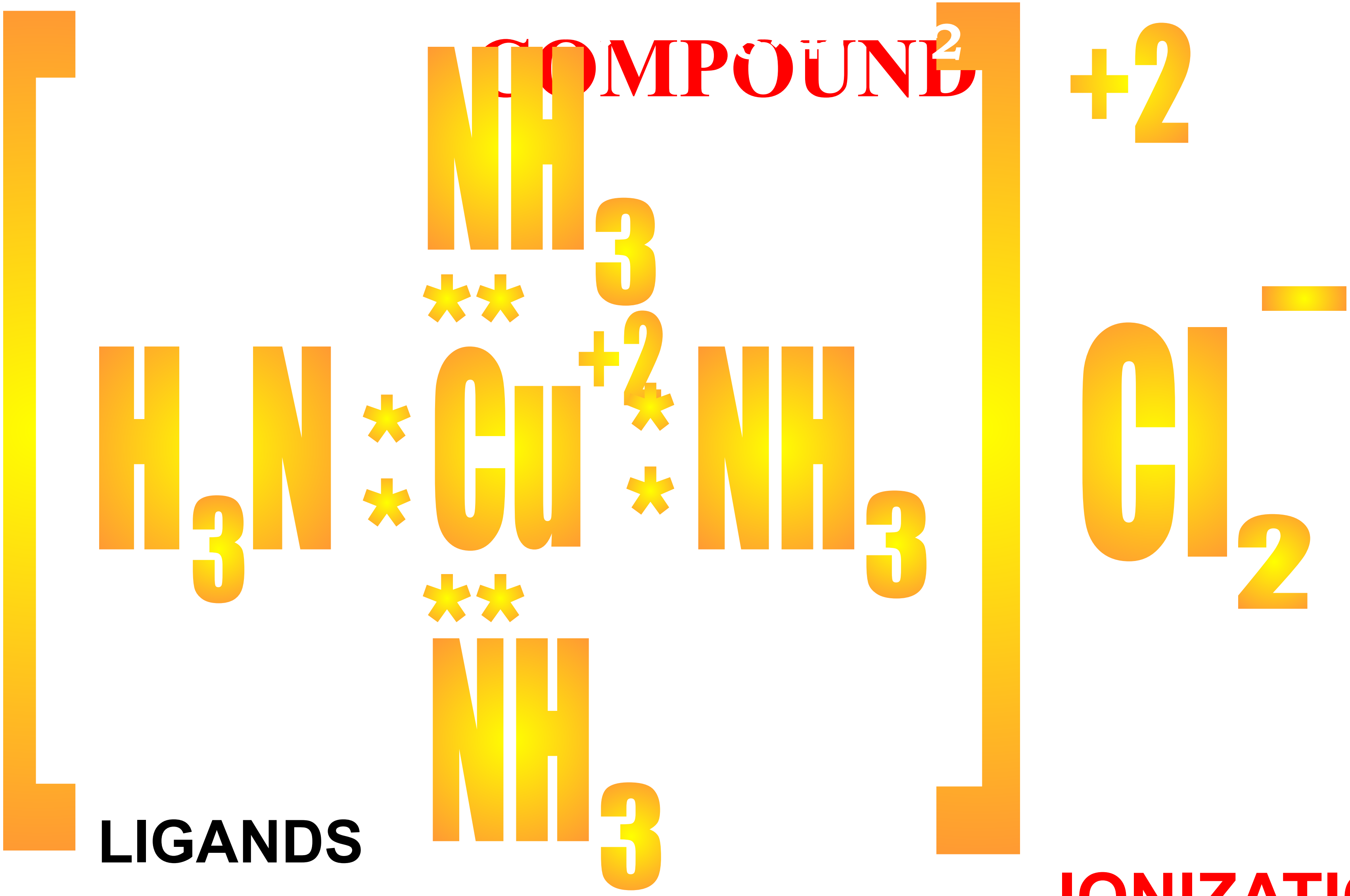
?

$$\left(Cr(H_2O)_4Cl_2\right)$$

Or, knowing the oxidation number on the metal and the charges on the ligands, one can calculate the charge on the complex ion.

STRUCTURE OF COORDINATION COMPOUND

COMPLEX ION



$$[Cu(NH_3)_4]^{+2}Cl_2^{-}$$

LIGANDS

COORDINATION NUMBER-4

COORDINATION SPHERE

IONIZATION SPHERE

Classification of complex compounds:

By the charge of the complex ion

Cationic

$[Cr(H_2O)_4]^{3+}Cl_3$

Cationic and anionic

$[Cu(NH_3)_4]^{2+}[PtCl_4]^{2-}$

Anionic

$K_2[PtCl_6]^{2-}$

Neutral

$[PtCl_4(NH_3)_2]^0$

By composition of ionization sphere

ACIDS

$H_2[PtCl_6]$

SALTS

$Na_3[AlF_6]$

BASIS

$[Ag(NH_3)_2]OH$

NONELECTROLYTES

$[Pt(NH_3)_2Cl_2]$

By the nature of the ligand:

Aqua complex

(ligand is water)

$[Fe(H_2O)_6]SO_4$

Acidocomplexes

(ligand is an anion)

$K[Au(CN)_4]$

Mixed ligands

$[CoCl(NH_3)_3(H_2O)_2](NO_3)_2$

Ammines

(ligand is ammonium)

$[Zn(NH_3)_4]Cl_2$

Nomenclature of Coordination Compounds

Ligand	Name in Complexes	Ligand	Name in Complexes
Azide, N_3^-	Azido	Oxalate, $C_2O_4^{2-}$	Oxalato
Bromide, Br^-	Bromo	Oxide, O^{2-}	Oxo
Chloride, Cl^-	Chloro	Ammonia, NH_3	Ammine
Cyanide, CN^-	Cyano	Carbon monoxide, CO	Carbonyl
Fluoride, F^-	Fluoro	Ethylenediamine, en	Ethylenediamine
Hydroxide, OH^-	Hydroxo	Pyridine, C_5H_5N	Pyridine
Carbonate, CO_3^{2-}	Carbonato	Water, H_2O	Aqua

- **The basic protocol in coordination nomenclature is to name the ligands attached to the metal as prefixes before the metal name.**
- **Some common ligands and their names are listed above.**

Name of Central atom (Transition Metal)	Latin
Iron	Ferrate
Copper	Cuprate
Tin	Stannate
Silver	Argentate
Lead	Plumbate
Gold	Aurate

ANIONIC MONODENTATE LIGANDS

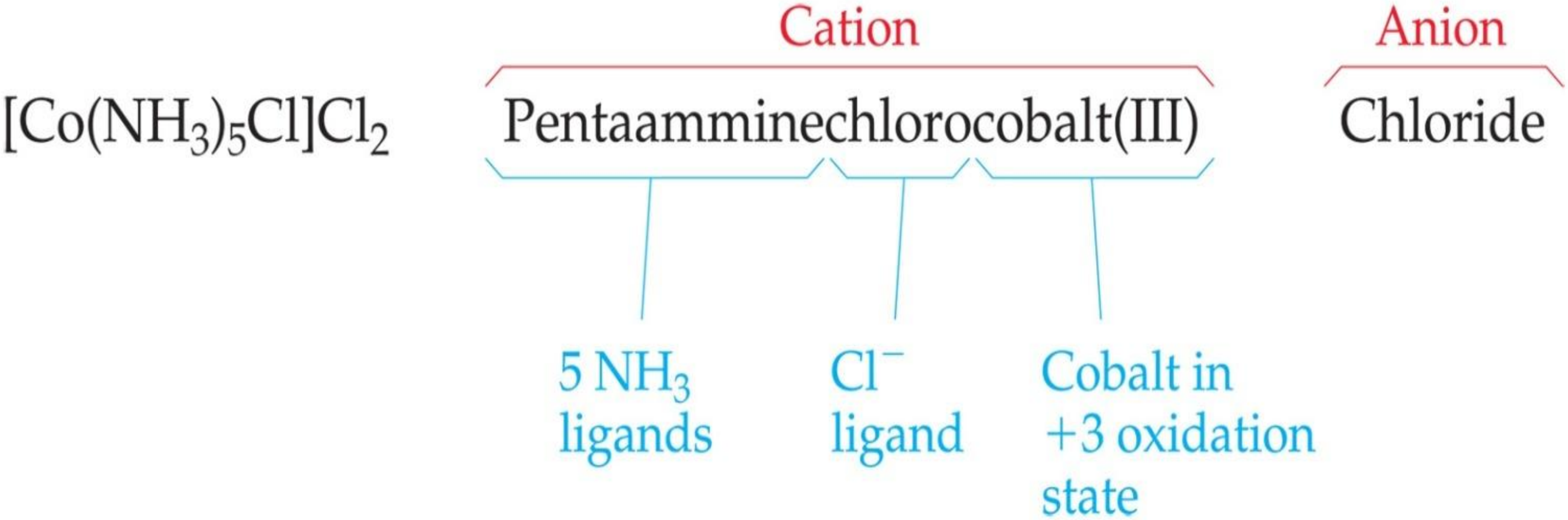
F^-	Fluoro	OH^-	Hydroxo
Cl^-	Chloro	SO_4^{2-}	Sulfato
Br^-	Bromo	$S_2O_3^{2-}$	Thiosulfato
I^-	Iodo	NO_2^-	Nitrito-N-; Nitro
O^{2-}	Oxo	ONO^-	Nitrito-O-; Nitrito
CN^-	Cyano	SCN^-	Thiocyanato-S-; Thiocyanato
NC-	Isocyano	NCS^-	Thiocyanato-N-; Isothiocyanato

Neutral Monodentate Ligands

NH_3	Ammine
H_2O	Aqua
CO	Carbonyl
NO	Nitrosyl
CH_3NH_2	Methylamine
C_5H_5N	Pyridine

Nomenclature of Coordination Compounds

- As is the case with ionic compounds, the name of the cation appears first; the anion is named last.
- Ligands are listed alphabetically before the metal. Prefixes denoting the number of a particular ligand are ignored when alphabetizing.



Cation

Anion

$[Co(NH_3)_5Cl]Cl_2$ Pentaamminechlorocobalt(III) Chloride

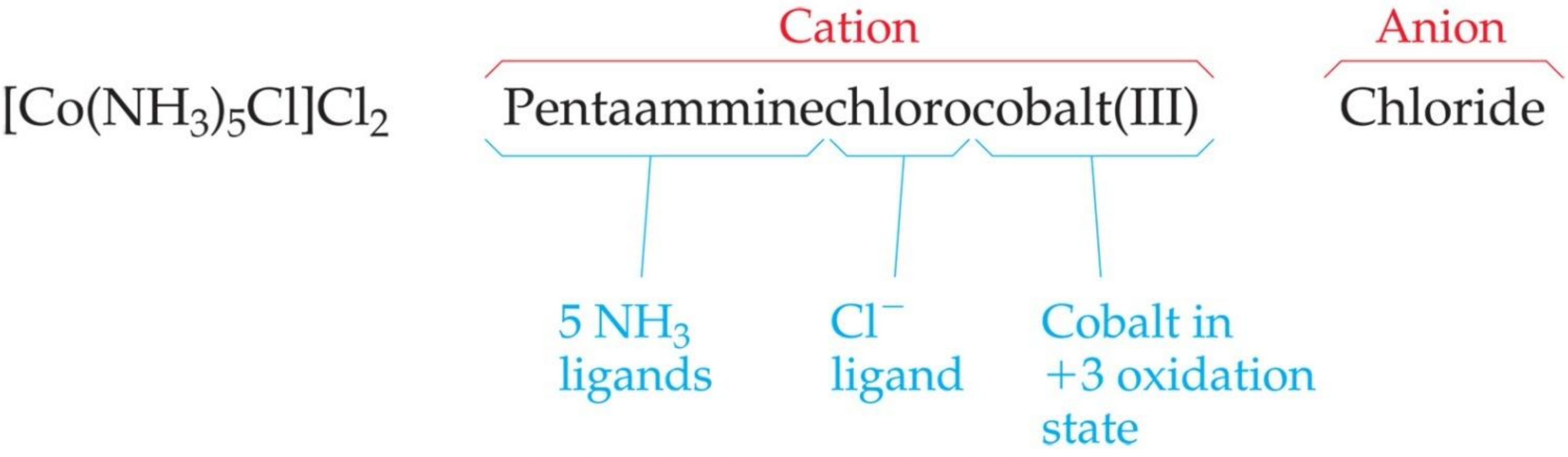
$5\ NH_3$ ligands

Cl^- ligand

Cobalt in +3 oxidation state

Nomenclature of Coordination Compounds

- The names of anionic ligands end in “o”; the endings of the names of neutral ligands are not changed.
- Prefixes tell the number of a type of ligand in the complex. If the name of the ligand itself has such a prefix, alternatives like *bis*-, *tris*-, etc., are used.



$[Co(NH_3)_5Cl]Cl_2$

Cation

Anion

Pentaamminechlorocobalt(III)

Chloride

$5\ NH_3$ ligands

Cl^- ligand

Cobalt in +3 oxidation state

Examples of Naming Coordination Compounds

Some examples of IUPAC names are:

$[Pt(NH_3)_2Cl_2]$

diamminedichloroplatinum (II)

$[Co(NH_3)_5Cl]Cl_2$

pentaamminecobalt (III) chloride

$K_4[Fe(CN)_6]$

potassium hexacyanoferrate (II)

$K_3[Fe(CN)_6]$

potassium hexacyanoferrite (III)

Preparation of complex compounds

Complex compounds prepared by such reactions:

1) Connection reactions:

$$HgI_2 + 2KI \rightarrow K_2[HgI_4]$$

2) Substitution reactions:

$$[Cu(H_2O)_4]SO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$$

3) Exchange reactions:

$$2\,ZnCl_2 + K_4\,[Fe(CN)_6] \rightarrow Zn_2[Fe(CN)_6] + 4KCl$$

4) Redox reactions:

$$2Al + 6KOH + 6H_2O \rightarrow K_3[Al(OH)_6] + 3H_2\uparrow$$

Nature of chemical bonding in complex compounds

Structure physico-chemical and biological properties of complex compounds depend on the nature of chemical bonds in them. Currently, the nature of chemical bonds in complex compounds such theories explain:

1) the method of valence bonds ;
2) the crystal field theory ;
3) the method of molecular orbitals .

A coordination compound consists of a central metal ion which is chemically bonded to one or more atoms or groups of atoms by coordinate covalent bonds. The metal ion contains one or more empty orbitals which can receive pair(s) of electrons and the atom or group of atoms bonded to the metal ion (ligands) contain one or more pairs of electrons which can be donated to the metal ion. When a covalent bond (a bond formed by sharing of one or more pairs of electrons) contains a pair of electrons which comes from only one atom in the bond it is called a coordinate covalent bond.

PROPERTIES OF COMPLEX COMPOUNDS

1) *Dissociation* of complex compounds.

Complex compounds are strong electrolytes. In aqueous solution, they readily dissociate to a complex ion and the outer sphere. This is called the *primary dissociation*.

$$[Ag(NH_3)_2]Cl \leftrightarrow [Ag(NH_3)_2]^+ + Cl^-$$

The formed complex ion may also dissociate, albeit weaker. This *secondary* dissociation, which is stepwise:

$$[Ag(NH_3)_2]^+ \leftrightarrow Ag^+ + 2NH_3$$

2) *Stability* of complex compounds.

This *formation constant* (K_f), describes the formation of a complex ion from its central ion and attached ligands. This constant may be called a **stability constant** or **association constant**; the units depend on the specific reaction it is describing.

At its most basic level, *Kf* can be explained as the following, where *M* is a metal ion, *L* is a ligand, and *x* and *y* are coefficients:

$$K[Ag(CN)_2] = K^+ + [Ag(CN)_2]^-$$

$$[Ag(CN)_2]^- = Ag^+ + 2CN^-$$

$$K_f = \frac{[M_xL_y]}{x[M^{+n}]\cdot y[L]}$$

$$K_f = \frac{[Ag(CN)_2]^-}{[Ag^+]\cdot[CN^-]^2} = 5{,}6\cdot 10^{18}$$

The larger the *Kf* value of a complex ion, the more stable it is.

Applications of Coordination Compounds

- **Extraction of metals from ores**
  - Silver and gold as cyanide complexes
  - Nickel as $Ni(CO)_4$ (*g*)
- **Use of chelating agents in heavy metal poisoning**
  - EDTA for Pb poisoning
- **Chemical analysis:**
  - Qualitative analysis for metal ions:

  Blue = $[CoSCN]^+$

  Red = $[FeSCN]^{2+}$

  Ni^{2+} and Pd^{2+} form insoluble colored precipitates with dimethylglyoxime.
- **Commercial coloring agents:**

  Prussian blue = mixture of hexacyanoFe(II) and Fe(III)

  Inks, blueprinting, cosmetics, paints.
- **Hardness of water** is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to difference in the stability constants of calcium and magnesium complexes