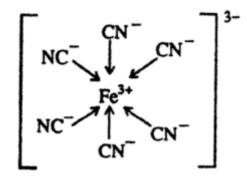
### **COORDINATION CHEMISTRY**

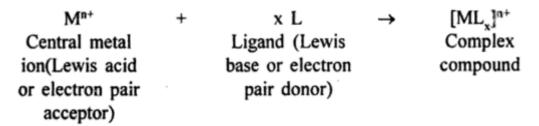
### COORDINATION CHEMISTRY CONSEPT

Coordination chemistry is the study of compounds that contain a central atom or ion (usually a metal) which is chemically bonded to various groups is called the acceptor and the attached groups are known as donor groups or ligands. For example, in the complex ion  $[Fe(CN)_6]^{3-}$ ,  $Fe^{3+}$  ion is the central metal ion or acceptor while the  $CN^-$  ions are ligands. The ligands are attached to the central atom by dative bonds, also known as coordinate bonds, in which both electrons in the bond are supplied by the same atom on the ligand.



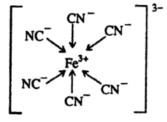
### COORDINATION COMPOUNDS (Coordination complexes, complexes)

They are compounds consisting of a cation in the center and a different number of charged or uncharged groups bound to it according to the properties of this cation. This definition includes organometallic compounds containing metal-carbon bonds. The name of the coordination compound comes from the coordinate covalent bond. Since the coordination compounds are usually formed by introducing an electron pair into the metal from the ligand, it is considered appropriate to give this name. The coordination compound is also an acidbase addition compound and is also referred to as the complex. If there is a load, it is called the complex ion.



## LIGANDS

Neutral molecules or ions (usually anions) which are attached to the central ion in coordination compounds are called ligands or coordinating groups. For example in complex ion,  $[Fe(CN)_6]^{3-}$  the six  $CN^-$  ions which are attached with the central  $Fe^{3+}$  ion act as ligands.



Negative ligands	
$F^{-}$	Fluoro
Cŀ	Chloro
Br	Bromo
Γ	Iodo
$O^{2-}$	Oxo
$O_2^{2-}$	Peroxo
S <sup>2-</sup>	Thio
SH <sup>-</sup>	Mercapto
H <sup>-</sup>	Hydrido
OH <sup>-</sup>	Hydroxo
$CH_3COO^2$	Acetato
$NH_2^-$	Amido
NH <sup>2-</sup>	İmido
$N^{3-}$	Azido
$NO_3^-$	Nitrato
$NO_2^-$	Nitro
ONO	Nitrito
$SO_4^{2-}$	Sulfato
$ClO_3^-$	Chlorato
$ClO_2^-$	Chlorito
$H_2NCH_2COO^-$	Glisinato
$SO_{3}^{2}$	Sulfito
$S_2O_3^{2-}$	Thiyosulfato
$CN^{-}$	Cyano
NC-	İsocyano
SCN <sup>-</sup>	İsothiocyanato
$CO_{3}^{2-}$	Carbonato
$C_2 O_4^{2-}$	Oxalato
NHOH <sup>-</sup>	Hydroksilamido

 $(CH_3)_2N^2$  $S_2CNR_2^2$ 

CH<sub>3</sub>COCHCOCH<sub>3</sub><sup>-</sup>

Dimethylamido Dialkyldithiocarbamato (dtc)

Acetylacetonato (acac)

 $(^{-}OOCCH_2)_2NCH_2CH_2N(CH_2COO^{-})_2$ 

Ethylenediaminetetraacetato (EDTA)

-o-g-ch , CH2 Č

Neutral ligands H<sub>2</sub>O CO CS NO O<sub>2</sub> PR<sub>3</sub> H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>

 $H_{2}NCH_{2}CH_{2}NHCH_{2}NH$ 

C5H5N C5H4N-C5H4N

 $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ 

- chi-CHi P Phr

NH3 N2 H2 CH3NH2 Aqua Carbonyl Thiocarbonyl Nitrocyl Dioxygene Trialkylphosphine Ethylenediamine (en) Diethylenediamine (dien)

Triethylenediamine (trien)

*Pyridine (py)* 2,2'-Bipyridine (bipy)

1,2-Bis(diphenylphosphino)ethane (dppe)

Ammine Dinitrojen Dihidrojen Methylamine

 $C_{12}H_8N_2$ HONC(CH<sub>3</sub>)-C(CH<sub>3</sub>)NOH cH HO  $N(C_2H_5NH_2)_3$ 1NH  $C_5H_4N$ -  $C_5H_3N$ - $C_5H_4N$ **Positive ligands**  $NO^+$  $NH_2NH_3^+$ 

*1,10-Phenanthroline (phen)* 

Dimethylglyioxime (DMG)

 $\beta,\beta',\beta''$ -Triaminotriethylamine (tren)

*Terpyridine (terpy)* 

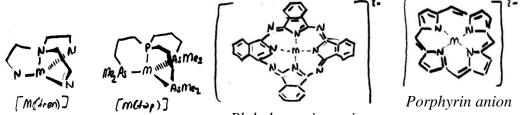
Pirazolilborat

 $O_2^+$ 

Nitronium Hydrazinium Dioxygenyl

Another criterion used in the classification of ligands is the number of donor atoms.

- a) Monodentate ligands
- b) Polydentate ligands bidentate ligand tridentate ligand tetradentate ligand kinkidentate ligand seksedentate ligand



Phthalocyanine anion

### DEVELOPMENTS IN COORDINATION CHEMISTRY

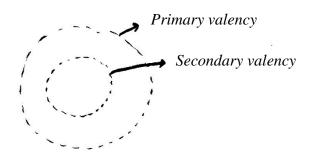
Although the explanation of the reactions of the coordination compounds and the bond theories were assumed to have begun with Alfred Werner (Father of coordination chemistry, 1866-1919, Nobel Prize in Chemistry in 1913), these compounds were already known. Examples of coordination compounds has used as a dyestuff since ancient times are Prussian blue (found in the 18th century by Diesbach) [KFe(Fe(CN)<sub>6</sub>], aurolin {K<sub>3</sub>[Co(NO<sub>2</sub>)<sub>6</sub>.6H<sub>2</sub>O, yellow} and alizarin red {calcium and aluminum salts of 1,2-dihydroxy-9,10-anthraquinone}. The structure of the blue colored dye known as tetramine(II) ion {[Cu(NH<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup>, its structure in solution} is known in prehistoric times. In ancient times, however, chemistry was dominated by the valence bond theory, and according to this theory, the cations could only bind as much as their valence. This thought prevented the development of coordination chemistry. Coordination compounds obtained during the rule of valence theory were generally used in the production of painter's paint. Some of them are:

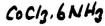
CoCl<sub>3</sub>.6H<sub>2</sub>O (yellow) CoCl<sub>3</sub>.5H<sub>2</sub>O (purple) CoCl<sub>3</sub>.4H<sub>2</sub>O (violet) CoCl<sub>3</sub>.4H<sub>2</sub>O (green) CoCl<sub>3</sub>.5NH<sub>3</sub>.H<sub>2</sub>O (pink) CoCl<sub>3</sub>.3NH<sub>3</sub> (blue-green) CoCl<sub>3</sub>.6NH<sub>3</sub> (yellow) CoCl<sub>3</sub>.5NH<sub>3</sub> (purple) CoCl<sub>3</sub>.4NH<sub>3</sub> (green) CoCl<sub>3</sub>.4NH<sub>3</sub> (violet)

For the illumination of the complex structure, the first theory was chain theory proposed by C.W. Blomstrand (1826-1894) and developed further by S.M Jørgensen (1837-1914).

Cociz 6 NHz	-NH3-CI Co - NH3-NH3-NH3-NH3-CI NH3-CI	precipitated 3 moles AgCl with AgNO <sub>3</sub>
Coclg. SNH3	Co - NHJ-NHJ-NHJ-NHJ-CI	precipitated 2 moles AgCl with AgNO3
Co CIg. 4 N Hg	Co NHg-NHJ-NHJ-NHJ-CI	precipitated 1 mole AgCl with AgNO <sub>3</sub>

 $\begin{array}{l} \hline \left[ c_{0}(NH_{3})_{6} \right] Cl_{2} + 3A_{f}NO_{2} \xrightarrow{H_{1}O} \left[ c_{0}(NH_{3})_{6} \right]^{2+} 3NO_{2}^{-} + 3A_{f}Cl_{4} \\ \hline \left[ c_{0}(NH_{3})_{5}Cl \right] Cl_{2} + 2A_{f}NO_{2} \xrightarrow{H_{3}O} \left[ c_{0}(NH_{2})_{5}Cl \right]^{2+} 2NO_{2}^{-} + 2A_{f}Cl_{4} \\ \hline \left[ c_{0}(NH_{3})_{4}Cl_{2} \right] Cl_{4} + A_{f}NO_{2} \xrightarrow{H_{3}O} \left[ c_{0}(NH_{3})_{4}Cl_{2} \right]^{2+} NO_{2}^{-} + A_{f}Cl_{4} \\ \hline \left[ c_{0}(NH_{3})_{4}Cl_{2} \right] Cl_{4} + A_{f}NO_{2} \xrightarrow{H_{3}O} \left[ c_{0}(NH_{3})_{4}Cl_{2} \right]^{2+} NO_{2}^{-} + A_{f}Cl_{4} \\ \hline \end{array}$ ( CO (NH3), Cl3) + ApNO3 H12 X

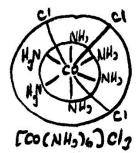


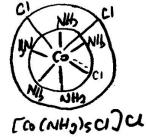


Co CI3 5NH3

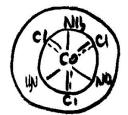
Coc134NH3

Co Clo. JNI Ho









[Co(NH5)4C12]CI [Co(NH2)2C12]