Ministry of Higher Education and Scientific Research

Al-Muthanna University

Inorganic Pharmaceutical chemistry

For the 3rd year students of the «faculty of Pharmacy»

Lecture (4)

Electronic Structure of Molecules (Cont…)

+

Coordination compounds and Complexation

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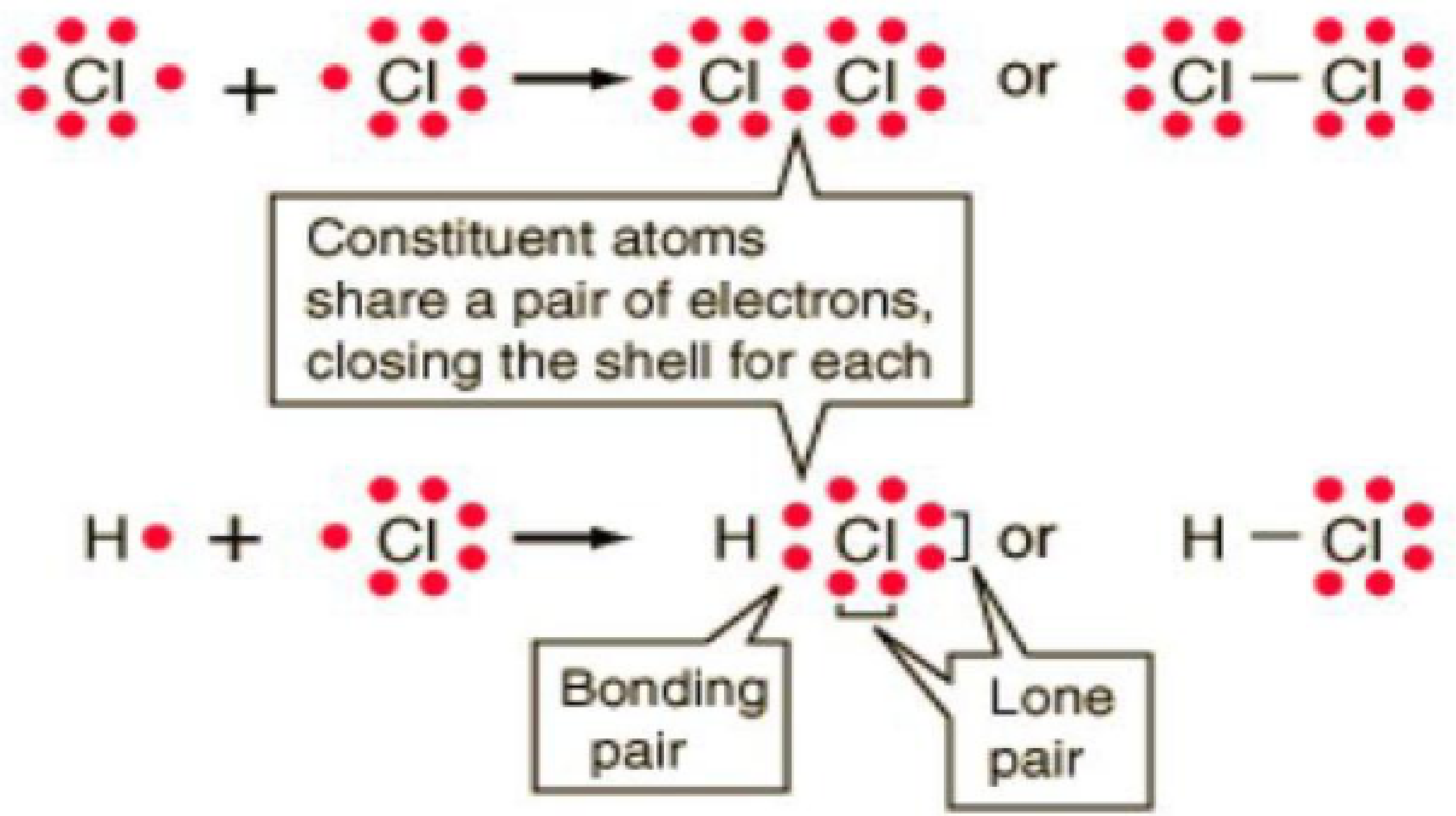
2- Covalent bonding

Is the attractive force that exists between two chemical entities due to their sharing a pair of electrons.

The electronegativity difference between the bonded atoms is small or nonexistent. Bonds within most [organic compound]s are described as covalent although quite common in inorganic compounds.

Occur in homonuclear diatomic molecules such as H_2 , Cl_2 , N_2 , etc. and the electron pair is shared equally by the two bonded atoms.

In most covalent molecules the electron density tend to be shifted towards the more electronegative member of the bond.


Cl + Cl → Cl Cl or Cl — Cl
Constituent atoms share a pair of electrons, closing the shell for each
H + Cl → H Cl] or H — Cl
Bonding pair
Lone pair

Types of Covalent Bonds

1. sigma (δ) bond: single covalent bond, formed by end-to-end overlap of orbitals. in which the molecular orbital or electron distribution are symmetrical about the bond axes.

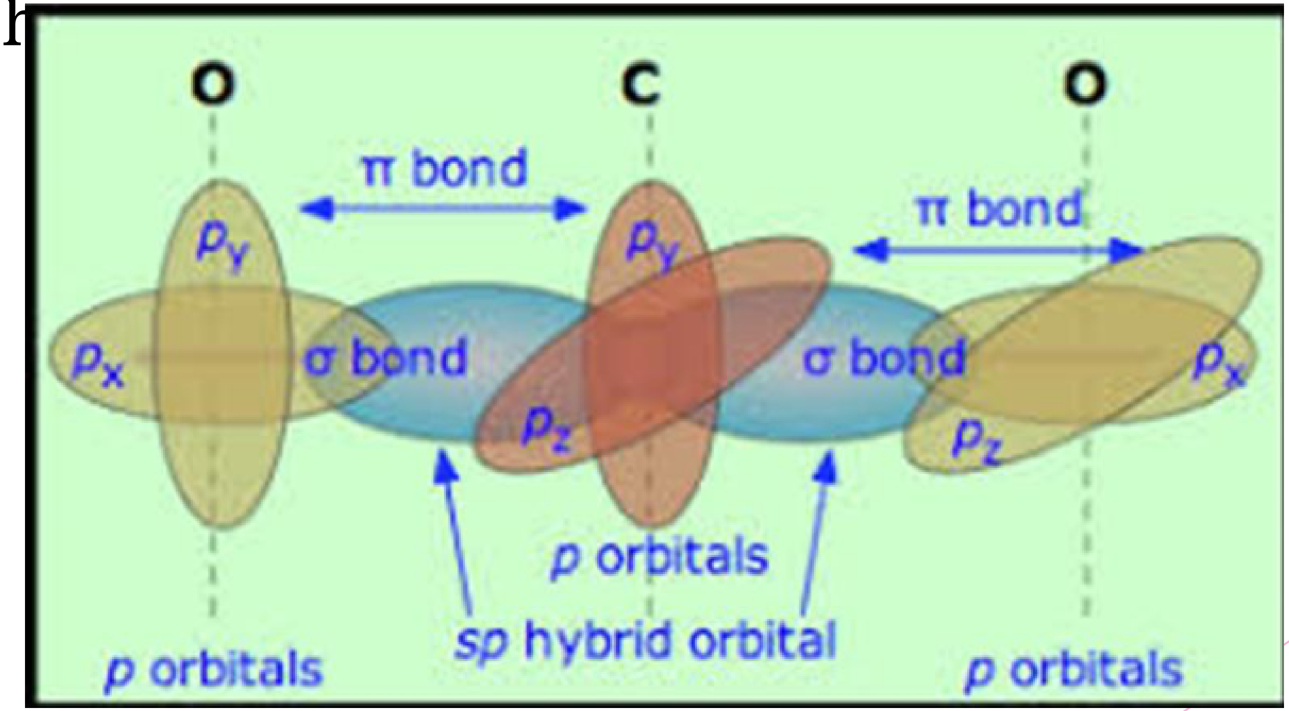
2. Double and triple covalent bond: two and three pairs of electrons are being shared, respectively, between two atoms.

Only one pair of electrons can occupy a single molecular orbital; therefore, atoms bonded in this fashion need to overlap other valence orbitals to form two and three bonding molecular orbitals, respectively.

Only one of the bonds can be a δ bond. The other pairs of electrons will occupy molecular orbitals which are distributed on both sides and perpendicular to a plane passing through a bond axis. This type is called pi bond (π bond).

Example CO_2

Each CO bonds consist of two pairs of electrons, one in the δ bond and one in the π bond.
The δ bonds are formed by overlapping sp orbitals on the carbon with singly occupied p orbitals on the oxygen. This leave two singly occupied p orbitals on carbon and one p orbital on each of the oxygen. The carbon form a π bond with each



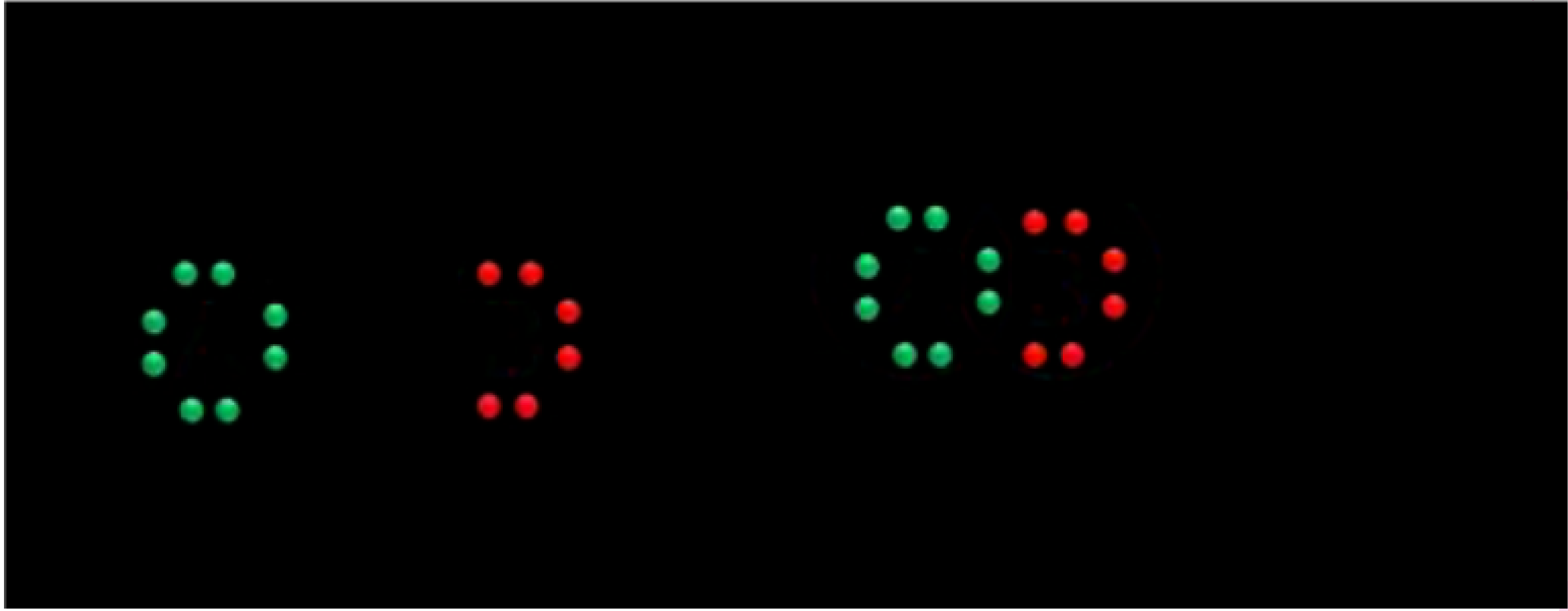
3- Coordinate covalent bond:

A covalent interaction but both electrons in the bond arise from single orbital on one of the atoms forming the bond. It is found most frequently between complex chemical entities.

The entity providing the pair of electrons is referred to as the donor species. The acceptor species is electron deficient and has an empty orbital which can overlap with the orbital from the donor.

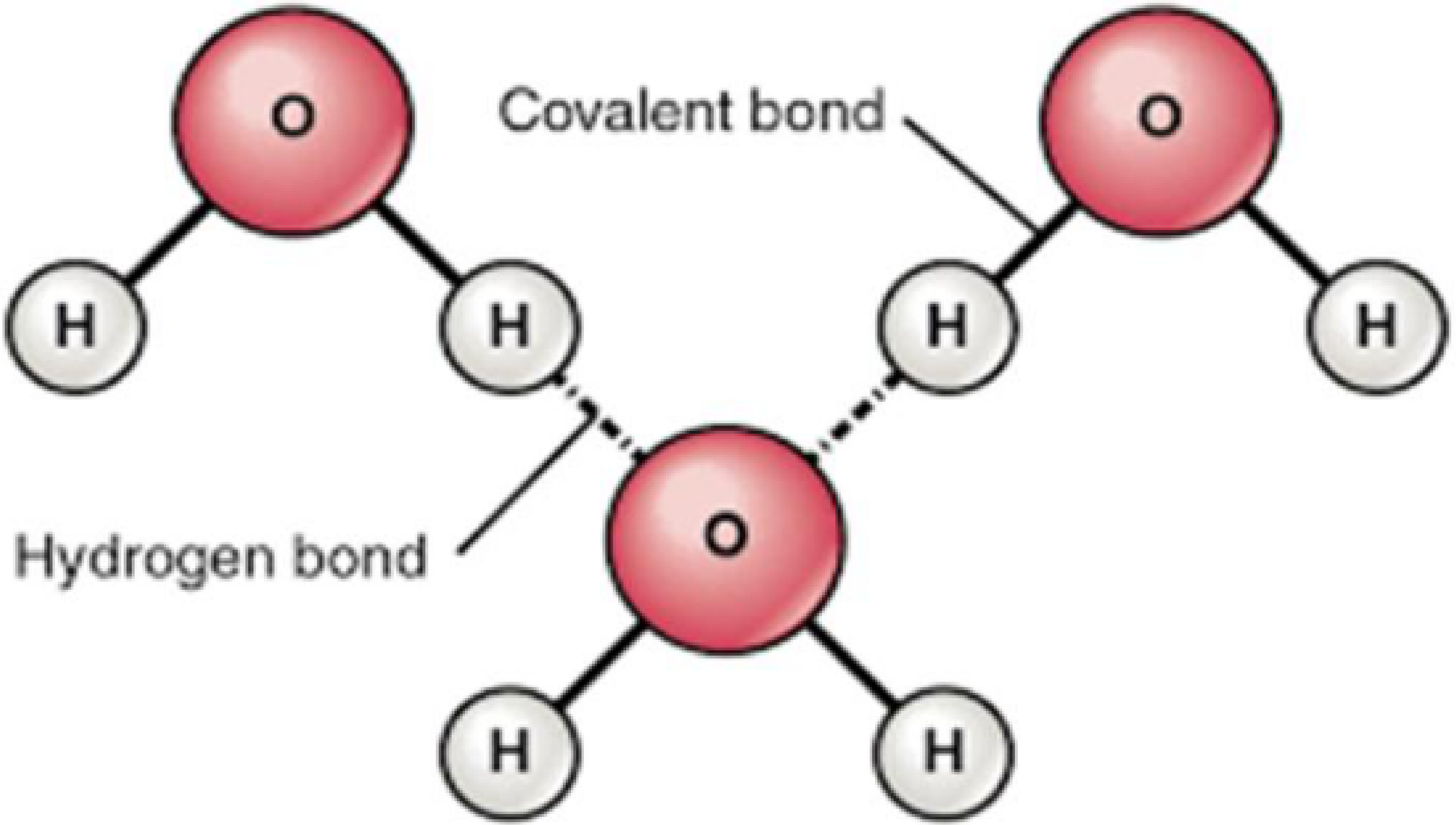
Represented as arrow from the donor atom to the acceptor atom.

Occur in acid –base chemistry between sulfur and oxygen (sulfuric, nitric, phosphoric, and chloric acids).



4-Hydrogen Bonding

- Hydrogen bonding is a force of attraction between a hydrogen atom in one molecule and a small atom of high electronegativity in another molecule.
- When hydrogen is covalently bonded to a more electronegative elements, such as O, F or N, it become electron deficient , taking on a partial positive charge.
- This partially positively charged hydrogen has an increase affinity to the nonbonded electrons on other electronegative atoms in neighbouring molecules. This bond is known as hydrogen bond and not sufficient to cause the original covalent bond to break.
- Its weaker than covalent bond.
- Hydrogen bonding has a very important effect on the physical and chemical properties of water and ice (ex: high boiling point of water). Hydrogen bonding is also very important in complex molecule, secondary structure of proteins and in life processes. It‟s a secondary binding force in drug-receptor interaction.

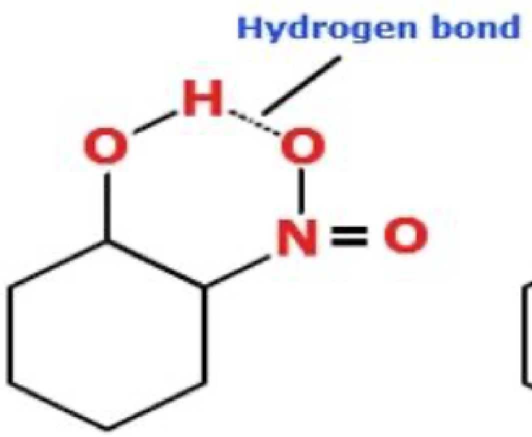

O
Covalent bond
O
H
H
H
H
Hydrogen bond
O
H
H

Types of H-Bonds

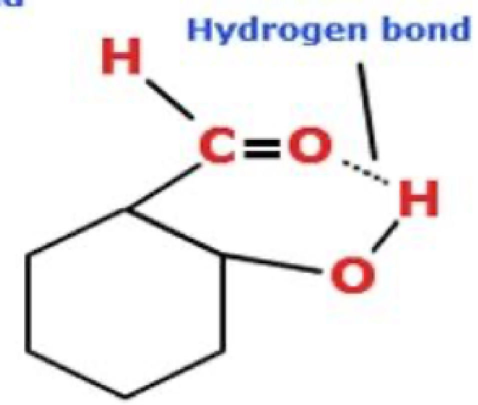
(1) Intermolecular hydrogen bond : It is formed between two different molecules of the same or different compounds. For example, H-bond in case of HF molecule, alcohol or water molecules, etc.

(2) Intramolecular hydrogen bond : It is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present within the same molecule. For example, in o-nitropheno

two oxygen atoms.



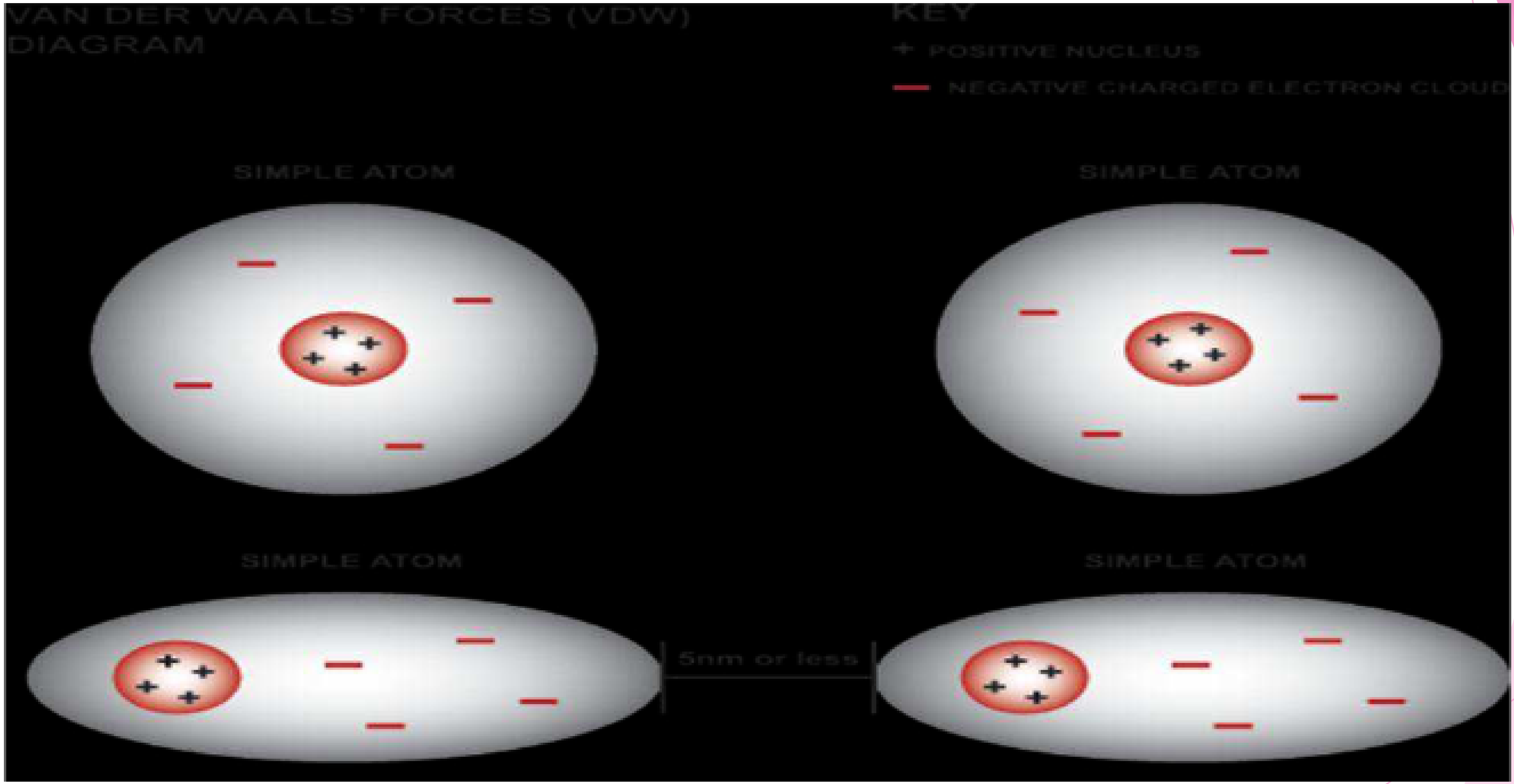
Ortho-Nitro phenol



Salicilaldehyde

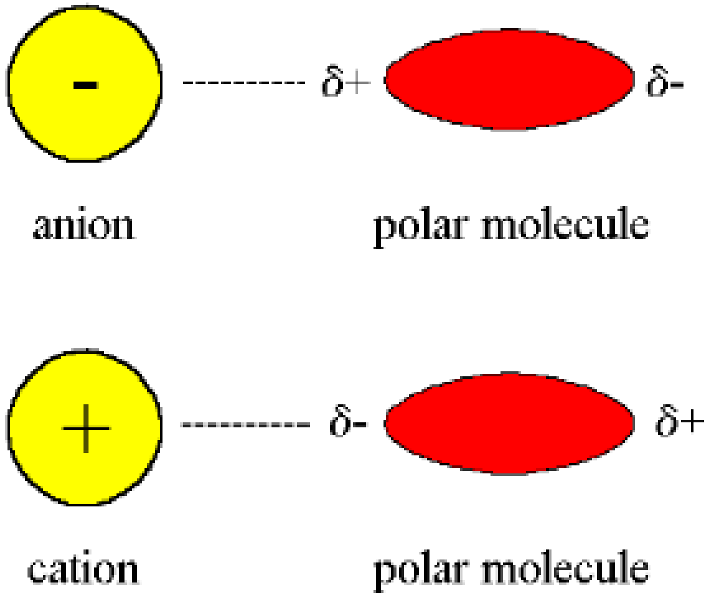
5- Van der Waals (London) forces:

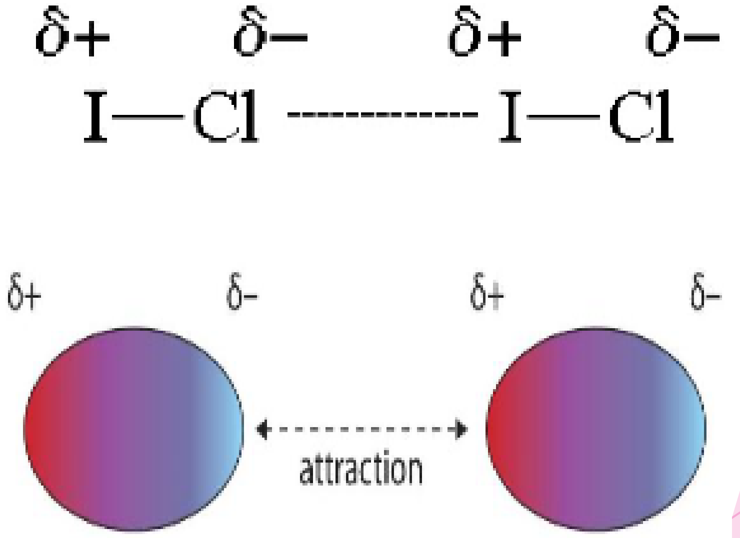
- Relatively weak electrical forces. The electrons in one atomic or molecular species inducing a repulsive distortion in the electron cloud of a neighbouring species. The result is weak induced dipole.
- The positive end of the dipole, which is produced by protons in the nuclei, then has an attraction for the oppositely charged electron in the same or in a neighbouring species.
- This force is active over a very short range, the strength depend upon the polarize-abilities of the interacting entities.
- It‟s the only attractive forces between nonpolar molecules.
- The association between aromatic hydrocarbon molecules, such as benzene, are due to van der Waals forces.


VAN DER WAALS' FORCES (VDW) DIAGRAM
KEY
+ POSITIVE NUCLEUS
— NEGATIVE CHARGED ELECTRON CLOUD
SIMPLE ATOM
SIMPLE ATOM
SIMPLE ATOM
SIMPLE ATOM
5nm or less

6- Ion-dipole and dipole-dipole interactions

- Take place between polar molecules and ions or other polar species. They are dependent on phenomenon known as polarization.





COORDINATION COMPOUNDS

Coordination compounds and Complexation

Metal complexes play a variety of important roles in biological systems. Many enzymes (metalloenzymes), hemoglobin, Vit. B 12 and chlorophyll are examples of naturally occurring coordination compounds. In addition, novel therapeutic and diagnostic metal complexes are now having an impact on medical practice.

Coordination chemistry = Transition metal chemistry

The metallic cation appears to be able to bind with additional anions or molecules after the normal valence requirements have been satisfied.

The central atom of coordinated compound are most often cation (positive ion).

Ligands The species that bind directly to the metal cation in accordance with maximum coordination numbers. They may be displaced by other ligands, but they do not normally dissociate from the metal.

Werner’s explanation of coordination complexes

- Metal ions exhibit two kinds of valence: primary and secondary valences
- The primary valence is the oxidation number (positive charge) of the metal (usually 2+ or 3+)
- The secondary valence is the number of atoms that are directly bonded (coordinated) to the metal is satisfied that by negative ions or by neutral molecules.
- The secondary valence is also termed the “coordination number” metal in a coordination complex

Conventions in writing the structure of coordination compounds:

- A coordination compounds is a neutral species consisting of a coordinate complex and uncoordinated ions required to maintain the charge balance

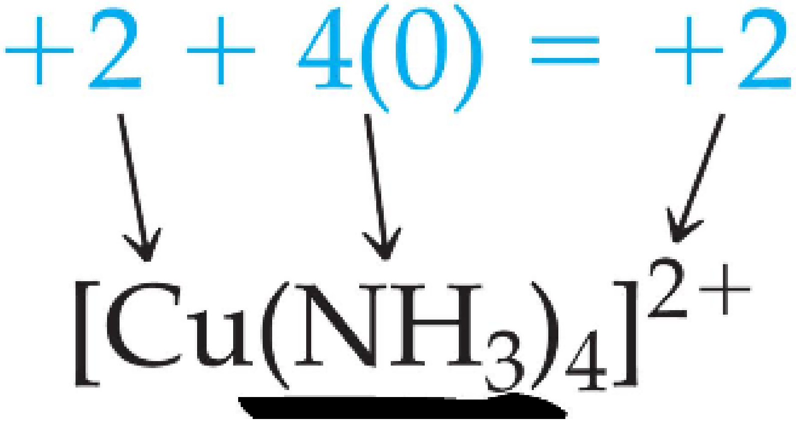
Brackets [] are used to indicate all of the composition of the coordinate complex

- The symbol for the central atom metal of the complex is first within the brackets
- Species outside of the [ ] are not coordinated to the metal but are require to maintain a charge balance

Table of Common Ligands

Type	Charge	Ligand	Formula	Name in Complexes
monodentate	neutral	ammonia	NH_3	ammine
		water	H_2O	aqua
		carbon monoxide	CO	carbonyl
		pyridine	pyr	pyridine
	-1	azide	N_3^-	azido
		bromide	Br^-	bromido
		chloride	Cl^-	chlorido
		cyanide	CN^-	cyanido
		fluoride	F^-	fluorido
		hydroxide	OH^-	hydroxido
		nitrite	NO_2^-	nitrito
		thiocyanate	SCN^- or NCS^-	thiocyanato
bidentate	neutral	bipyridine	bipy	bipyridine
		ethylenediamine	en	ethylenediamine
	-2	carbonate	CO_3^{2-}	carbonato
		oxide	O^{2-}	oxo
		oxalate	$C_2O_4^{2-}$	oxolato
		sulfate	SO_4^{2-}	sulfato

Oxidation Numbers



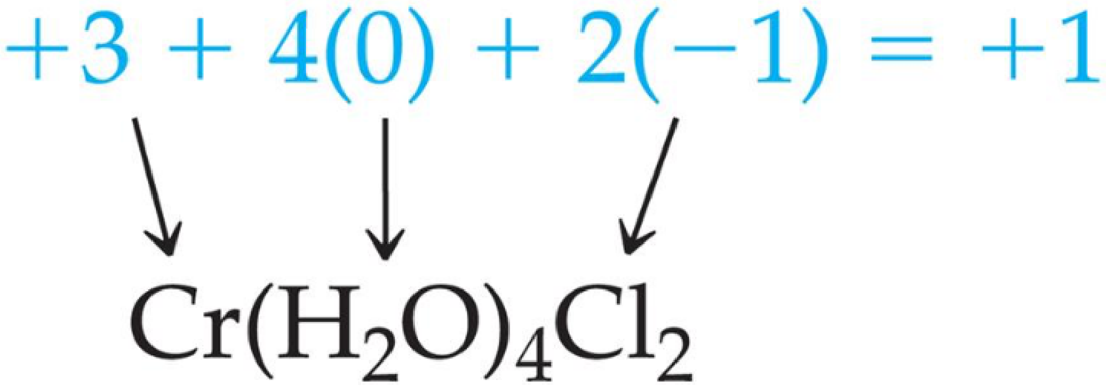
$$+2 + 4(0) = +2$$

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

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

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

- Example: $Cr(III)(H_2O)_4Cl_2$



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

$$Cr(H_2O)_4Cl_2$$

Coordination sphere The space about the metal occupied by the ligands. The coordination sphere is usually enclosed in brackets [ ] when written in formula.

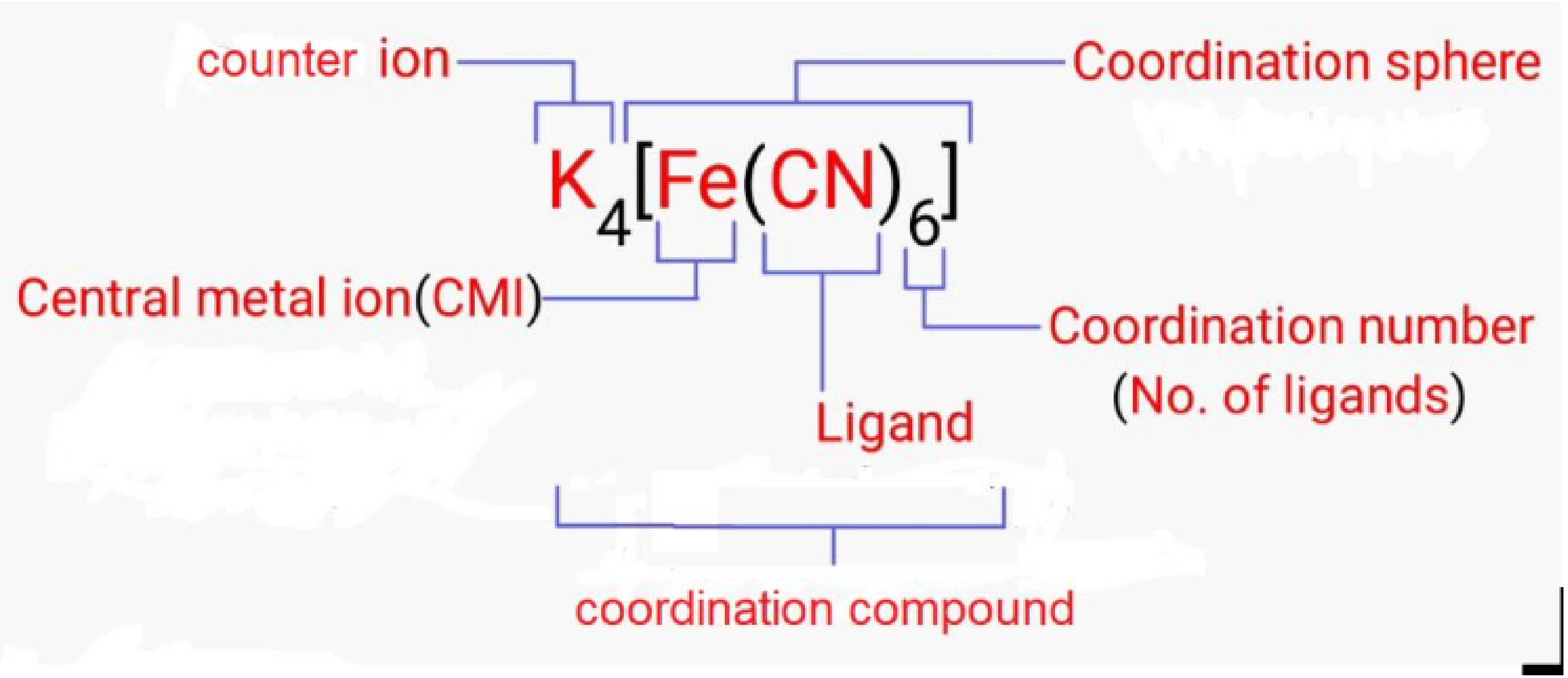
The metal and associated ligands constitute what is known as a **complex** or **complex ion** (if charged).

$[Pt(NH_3)_2Cl_2]$	complex (neutral)
$[Pt(NH_3)_4]^{+2}$	complex ion

Counter ions: The ions present outside the coordination sphere

$[Pt(NH_3)_4]Cl_2$

The coordination compound the neutral complex or complex ion with its counter ions.



Example of a coordination complex: $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$

What is the atomic composition of the complex?	$[\mathrm{Co(NH_3)_6}]$
What is the net charge of the complex?	$[\mathrm{Co(NH_3)_6}]^{3+}$
How do we know the charge is 3+ on the metal?	3+ is required to balance the three $\mathrm{Cl^-}$ ions

The primary valence of $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ is 3 (charge on Co)
The secondary valence of $[\mathrm{Co(NH_3)_6}]\mathrm{Cl_3}$ is 6 (ligands)

Best Regards!

Thank you!