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BS-109 Engineering chemistry-I

Chemical Bonding

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CHEMICAL BONDING

Atoms of elements combine to form molecules. For which electrons of the outermost shell of an atom also known as 'valence electrons' takes part in the chemical combinations. This is done to attain a stable electronic configuration which is achieved either by : losing electrons, by gaining electrons, or by sharing electrons.

Types of elements →

1. Electropositive elements : loses one or more electron readily.
2. Electronegative elements : will accept the electrons.
3. Elements which have little tendency to lose or gain electrons.

<p>Electropositive element</p> <p>+ +</p> <p>Electronegative element</p>	<p>? IONIC BOND</p>	<p>Electro negative element</p> <p>+ +</p> <p>Electronegative element</p>	<p>? COVALENT BOND</p>	<p>Electropositive element</p> <p>+ +</p> <p>Electropositive element</p>	<p>? METALLIC BOND</p>
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4) Types of valency based on electronic theory of valency :

1. Electrovalency or Ionic valency:

E.C of Na $\rightarrow 1s^2 2s^2 2p^6 3s^1$ \rightarrow to attain inert gas structure, loss 1 electron

E.C of Cl $\rightarrow 1s^2 2s^2 2p^5 3s^2 3p^5$ \rightarrow to attain inert gas structure, gain 1 electron.

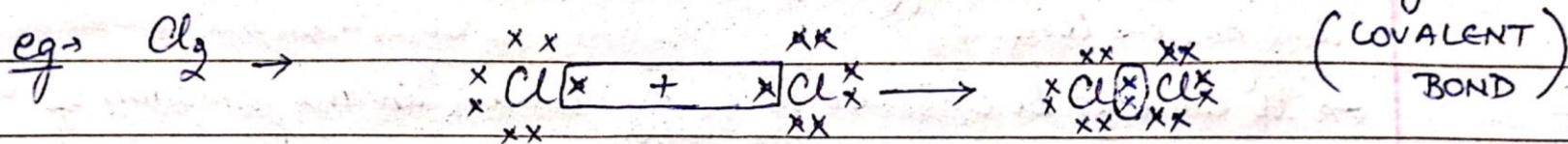
This sort of transfer of electron from 1 atom to other results in formation of Na^+ and Cl^- ions. and remain combined due to "electrostatic force of attraction".

So, this type of combination, where complete transfer of electron from outermost shell of one atom to the other is known as 'electrovalency'.

This bonding of atoms is "IONIC BONDING"



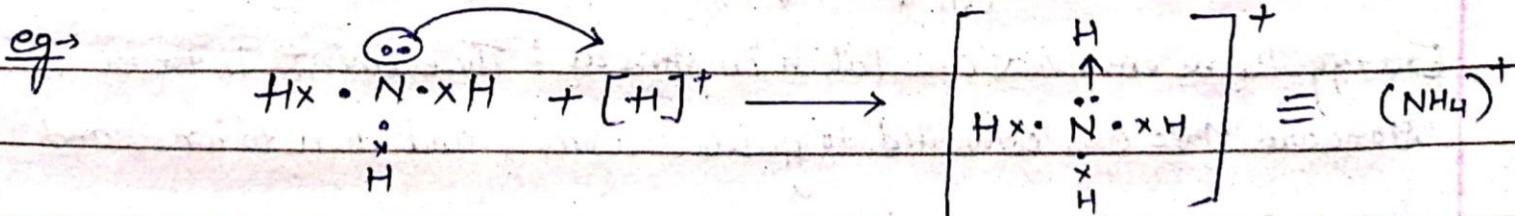
2. Covalency: When atoms, having similar values of electronegativity, combine to form molecules, they share the electrons to fill up their octets in the outermost shells. This combination is called "Covalency".



3. Co-ordinate Covalency:

In this combination, a pair of electron is being contributed by a single atom while other atom contributes no electron. After coordination, the bond formed acts as purely covalent bond. This is called "Co-ordinate covalency" and bond formed is called "co-ordinate bond".

Atom that donates electron pair is called 'donor' atom and atom which accepts the electron pair is called 'acceptor' atom.





Comparison of electrovalent and covalent compounds:

<i>Electrovalent Compounds</i>	<i>Covalent Compounds</i>
<ul style="list-style-type: none">(i) They are Non-directional.(ii) They cannot exhibit isomerism.(iii) m.p. and b.p. are high.(iv) They are conductors of electricity in solution or in their molten state.(v) They are soluble in polar solvents (H_2O) and insoluble in non-polar solvents (C_6H_6, CCl_4).(vi) They are polar in nature.	<ul style="list-style-type: none">(i) They are directional in nature.(ii) They can show isomerism.(iii) m.p. and b.p. are low.(iv) They are nonconductors of electricity in solution or in molten state.(v) They are soluble in organic solvents, generally insoluble in water.(vi) They are non-polar in nature.



+

Calculation of ionic character from electronegativity :

1. If atom A and B, have electronegativity values (χ) as, $\chi_A = \chi_B$,
then Bond is 100% covalent between A-B.

2. When, $\chi_A \neq \chi_B$, there is partial ionic character between A-B &
molecule A-B becomes polar. eg $\rightarrow \text{H-Cl}$.

Greater the difference ($\chi_A - \chi_B$), greater is ionic character of bond.

The relation is represented as :-

Pauling's
relation

$$\% \text{ ionic character} = 100 \left[1 - \exp \left\{ 1 - \frac{1}{4} (\chi_A - \chi_B)^2 \right\} \right]$$

Hansay

$$\% \text{ ionic character} = 16 (\chi_A - \chi_B) + 3.5 (\chi_A - \chi_B)^2$$

- Smith
equation

For HF molecule:

$$\begin{aligned} \% \text{ ionic character for HF} &= 16 (4.0 - 2.1) + 3.5 (4.0 - 2.1)^2 \\ &= 43\% \end{aligned}$$



lattice Energy : it is measure of the strength of bonds in that ionic compound. It is given by symbol 'U'. It is equivalent to the amount of energy required to separate a solid ionic compound into gaseous ions.

→ it can also be considered as energy released in the formation of 1 gm mole of crystal from gaseous ions.

→ Greater the value of lattice energy more is the stability.

→ Eg, $U_{\text{NaCl}} = -774 \text{ KJ/mol}$ (-ve sign shows exothermic process)

* Born-Haber Cycle : (By Born & Haber in 1919)

→ Determination of electron affinity.

→ calculate lattice enthalpy.

→ relates lattice energy of a crystal to other thermochemical data.



Energy terms involved are taken in steps as : The elements in their standard state are converted to gaseous atoms, and then to ions, and finally packed into crystal lattice.

Enthalpies of sublimation, dissociation and ionisation energy are +ve since energy is supplied to system. Whereas, electron affinity and lattice energy are -ve since energy is evolved in these processes.

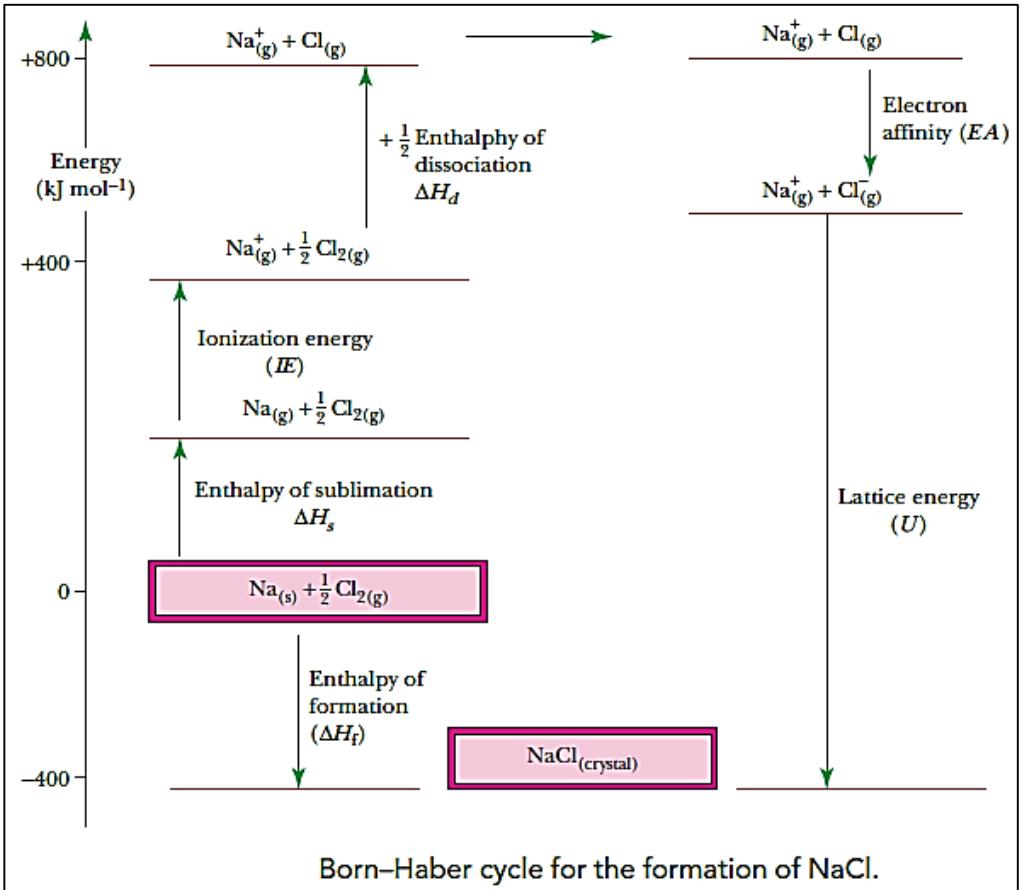
According to HESS'S LAW : the overall energy change in a process depends only upon energy of initial and final states and not on the route taken.

To make gaseous ions from elements, necessary is to atomise the elements and then ionise the atoms.

If the element is normally a molecule than we have to consider its bond dissociation energy as well.

The energy involved in removing e^- to make ion is called 'IONISATION ENERGY'.

The energy or enthalpy of adding e^- to atom is called "Electron Affinity".



Born-Haber cycle of NaCl :

- Step-1: Sublimation energy (ΔH_s) of metal. $\text{Na}(s) \rightarrow \text{Na}(g)$
- Step-2: Ionisation enthalpy (IE) of metal $\text{Na}(g) \rightarrow \text{Na}^+(g) + e^-$
- Step-3: Dissociation energy (ΔH_d) of NON metal $\frac{1}{2} \text{Cl}_2(g) \rightarrow \text{Cl}(g)$
- Step-4: Electron Affinity (EA) of NON metal $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$
- Step-5: lattice Enthalpy (U) of NaCl $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s)$.

Hence, Enthalpy of formation (ΔH_f) = $\Delta H_s + IE + \frac{1}{2} \Delta H_d + EA + U$

As, except EA & U, all can be measured. Originally cycle was used to calculate electron affinity. By using known crystal structure, it was possible to calculate the lattice energy (U) & hence electron affinity (EA) was calculated.

Higher lattice energy then,

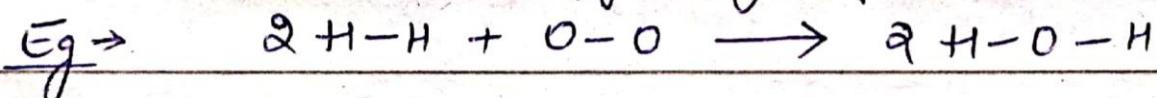
1. higher is stability of ionic solids.
2. higher melting & boiling points.
2. lesser is the solubility.



→ Covalent Bond - Energy changes:

- Bond energies can be used to estimate the energy change of a chemical reaction.
- When a bond is broken in the reactant, process is endothermic. ($\Delta H = +ve$)
- When a bond is formed in the products, process is exothermic. ($\Delta H = -ve$)

So, we combine the positive energy change with the negative energy change to estimate the overall energy change of the reaction.



Energy required to break.

$$2 \text{H-H} = 2(+436 \text{ KJ/mol})$$

$$1 \text{O-O} = (+498 \text{ KJ/mol})$$

$$\hline$$
$$\text{Total} = +1,370 \text{ KJ/mol}$$

Energy required to form 4 O-H bonds.

$$4(\text{O-H}) = 4(-463 \text{ KJ/mol})$$

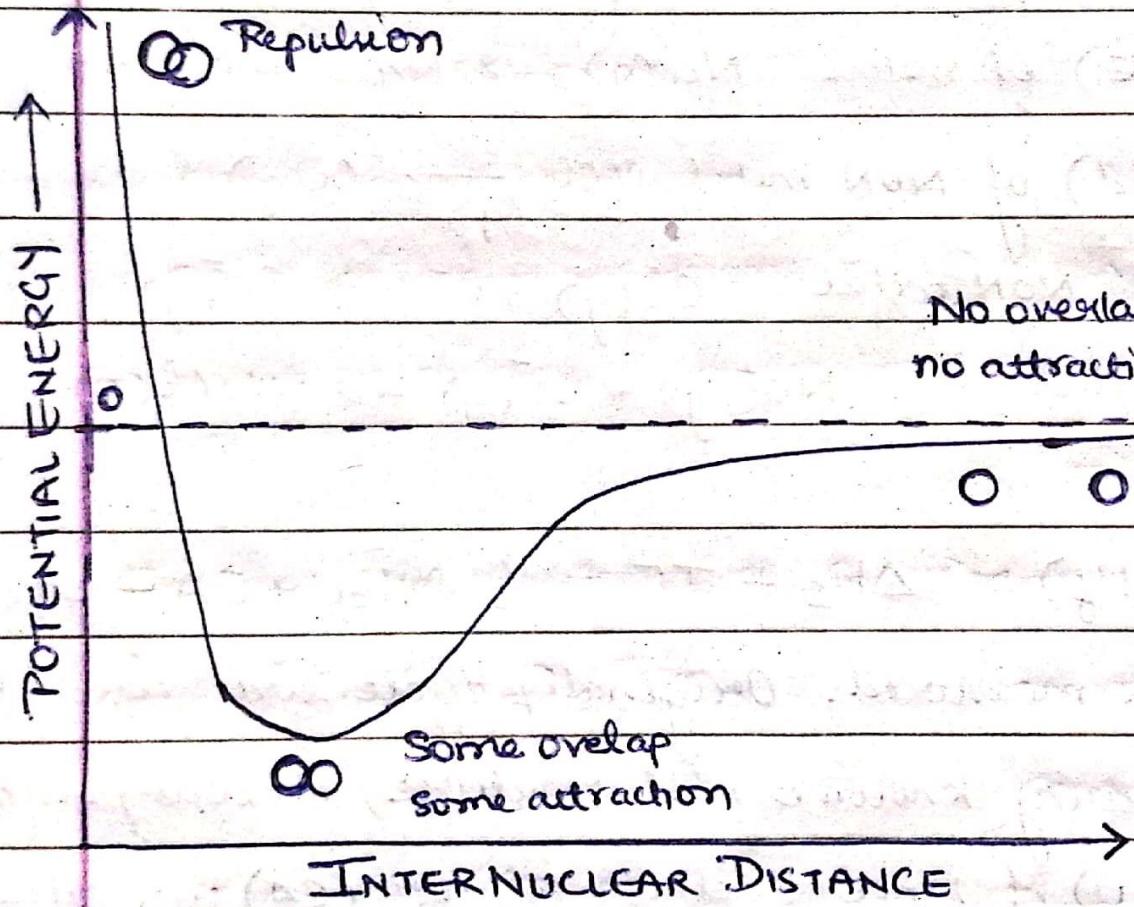
$$\hline$$
$$\text{Total} = -1,852 \text{ KJ/mol}$$

$$\text{Net energy change} \Rightarrow (+1,370) + (-1,852) = -482 \text{ KJ/mol}$$



Energy curve of H_2 molecule:

- most atoms attain lower potential energy when they are bonded to other atoms.



No overlap
no attraction

- consider two H atoms, separated by distance large enough to prevent any interaction between them.

At this distance potential energy of system is said to be equal to zero.



- as atoms first begin to interact, attractive force is stronger than the repulsive force, so potential energy of system decreases. Lower the energy, more is the stability.
- as 2 H atoms move closer and closer together, potential energy continues to decrease. And point comes where energy is lowest. (ideal distance H-H)
- Further, moving closer results in domination of repulsive force between two positively charged nuclei. This repulsive force is very strong as can be seen by the sharp rise in energy at far left of diagram.

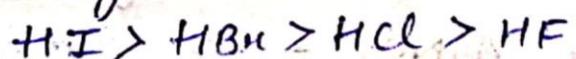


Properties of covalent compound:

1. are generally gases or liquid at room temperature
2. low melting and boiling point except for diamond, silica.
3. soluble in non-polar solvents like benzene & chloroform etc.
4. no mobile electron, so do not conduct electricity.
5. are soft and waxy.
6. bonds are directional and strong.

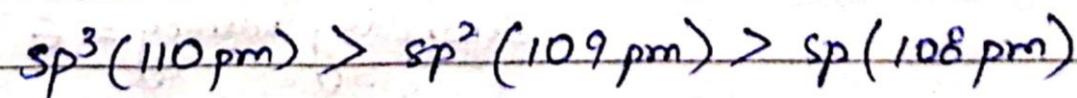
BOND LENGTH : average distance b/w covalent bonded atoms is expressed in Å or picometre.

↳ for given atom bond length increases with increase in size of other bonded atom



↳ Bond length $\propto \frac{1}{\text{Bond order}}$.

↳ bond length decreases with increase in s-character.





BOND ENERGY :

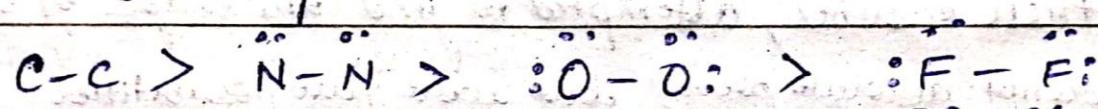
↳ Energy increases with increase in electronegativity difference b/w atoms.



↳ Energy increases with increase in s-character. $\text{sp}^3 < \text{sp}^2 < \text{sp}$

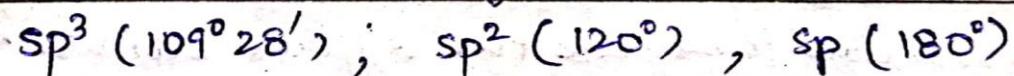
↳ Bond order more, more is energy. $\text{C-C} < \text{C=C} < \text{C}\equiv\text{C}$

↳ Energy decreases with increase in number of lone pair on bonded atoms.
due to electrostatic repulsion.



BOND ANGLE :

↳ increase in s-character, bond angle increases. (but varies due to lp repulsion)
 $\text{H}_2\text{O}(104.5^\circ)$.



↳ bond angle decreases with decrease in electronegativity : (less repulsion in bond pairs.)





WERNER'S THEORY

- ↳ In 1893, explained bonding in coordination complexes.
- ↳ Central atom exhibits two types of valency:

(1) PRIMARY VALENCY

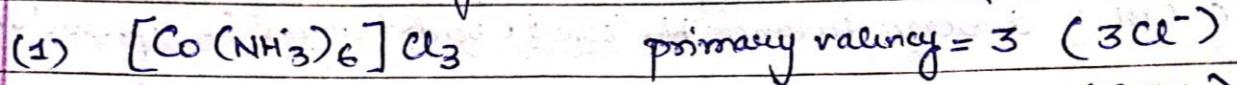
- ↳ equal to charge of ion.
- ↳ satisfied by negative ions.
- ↳ written outside of coordination sphere.

(2) SECONDARY VALENCY

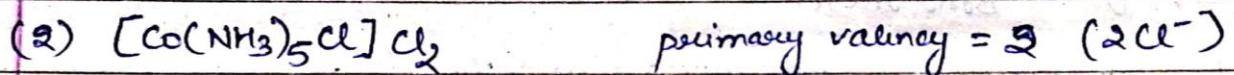
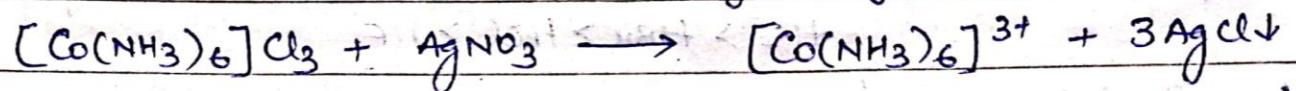
- ↳ equal to ligands coordinated to metal.
- ↳ called coordination number.
- ↳ written inside the coordination sphere.
- ↳ are directional.



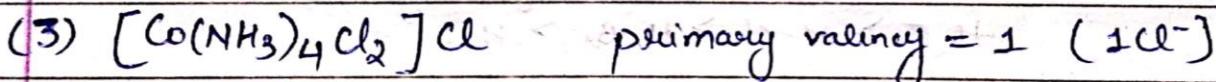
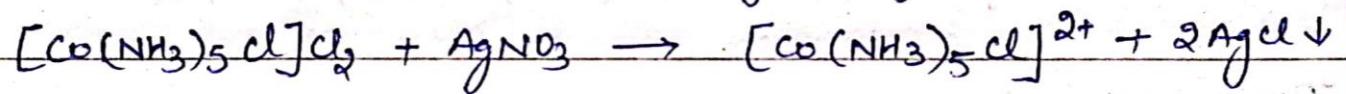
Explain the structure of Co(III) ammines on basis of Werner's theory:-



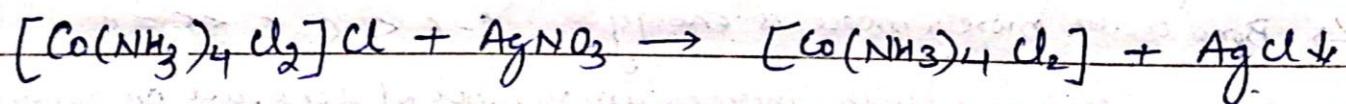
secondary valency = 6 (6NH_3)



secondary valency = 6 ($5\text{NH}_3 + 1\text{Cl}^-$)

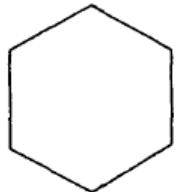


secondary valency = 5 ($4\text{NH}_3 + 2\text{Cl}^-$)

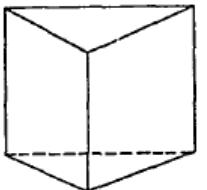


Based on these results, attempted to find the shapes of complexes.

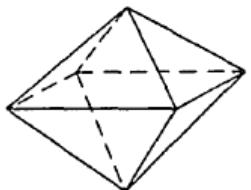
Results were not absolute proof but were just possibilities.



Planar hexagon

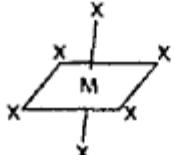


Trigonal prism



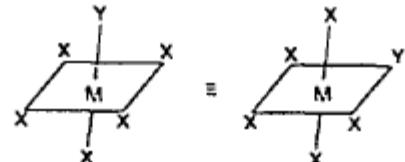
Octahedron

MX_6
 eg
 $[Co^{III}(NH_3)_6]^{3+}$
 $[Fe^{III}(CN)_6]^{3-}$



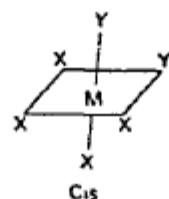
Only one form

MX_5Y
 eg
 $[Pt^{IV}(NH_3)_5Cl]^{3+}$
 $[Co^{III}(NH_3)_5Cl]^{2+}$

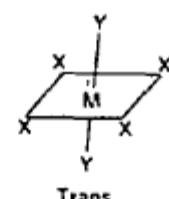


Only one form
 as all six corners
 are equivalent

MX_4Y_2
 eg
 $[Pt^V(NH_3)_4Cl_2]^{2+}$
 $[Co^{III}(NH_3)_4Cl_2]^+$
 $[Pt^V(NH_3)_2Cl_4]$



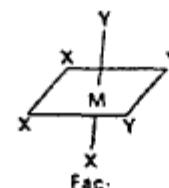
Cis



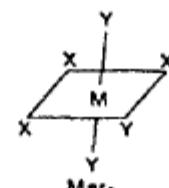
Trans

Two isomers
 cis and trans

MX_3Y_3
 eg
 $[Pt^V(NH_3)_3Cl_3]^+$
 $[Co(NH_3)_3Cl_3]$



Fac.



Mer.

Two isomers
 and facial Fac-
 meridional Mer

Table 7.2 Number of isomers predicted and actually found

Complex	Observed	Predicted		
		Octahedral	Planar hexagon	Trigonal prism
$[MX_6]$	1	1	1	1
$[MX_5Y]$	1	1	1	1
$[MX_4Y_2]$	2	2	3	3
$[MX_3Y_3]$	2	2	3	3



Also, studied complexes having coordination number 4. e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

- ↳ There are two possible structures tetrahedral or square planar.
- ↳ Werner was able to prepare two different isomers of this complex.
- ↳ But, Tetrahedral exist in one form whereas, Square planar can exist in two forms.

This proved complex is square planar.

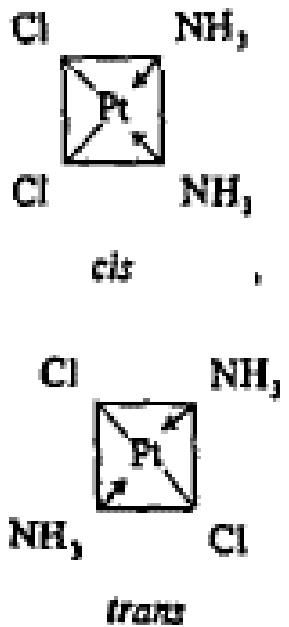


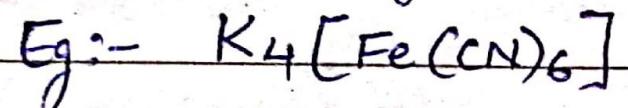
Figure 7.5 Isomerism in square planar complexes



EFFECTIVE ATOMIC NUMBER → (SIDGWICK)

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→ Electron pairs from ligands were added until the central metal was surrounded by same number of electrons as the next noble gas.



e⁻ count: $Fe^{2+} \Rightarrow 24$ electrons.

CN^- (gives $2e^-$) $\Rightarrow 6 \times 2 = 12$ electrons.

$$24 + 12 = 36 \quad Fe^{2+} \text{ have EAN} = 36.$$

EAN predicted correctly the number of ligands in many complexes, but exceptions were for those complexes where EAN is not quite that of a noble gas.

[metal having odd no. of electrons, adding e⁻ pairs will not give noble gas forms]



Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN
Cr	24	[Cr(CO) ₆] ⁰	0	12	36
Fe	26	[Fe(CN) ₆] ⁴⁻	2	12	36
Fe	26	[Fe(CO) ₅] ⁰	0	10	36
Co	27	[Co(NH ₃) ₆] ³⁺	3	12	36
Ni	28	[Ni(CO) ₄] ⁰	0	8	36
Cu	29	[Cu(CN) ₄] ³⁻	1	8	36
Pd	46	[Pd(NH ₃) ₆] ⁴⁺	4	12	54
Pt	78	[PtCl ₆] ²⁻	4	12	86 (Rn)
Fe	26	[Fe(CN) ₆] ³⁻	3	12	35
Ni	28	[Ni(NH ₃) ₆] ²⁺	2	12	38
Pd	46	[PdCl ₄] ²⁻	2	8	52
Pt	78	[Pt(NH ₃) ₄] ²⁺	2	8	84