



CHAPTER - 3

*COORDINATION
COMPOUNDS*



CONTENTS

- Coordination Compounds
- Werner's Theory
- Chelating ligands and Chelates
- Nomenclature of Coordination Compounds
- Isomerism in Coordination Compounds
- Effective Atomic Number
- Hybridisation of Atomic Orbitals
- Valence Bond Theory



COORDINATION CHEMISTRY

Coordination chemistry is the study of compounds formed between metal ions and other neutral or negatively charged molecules.

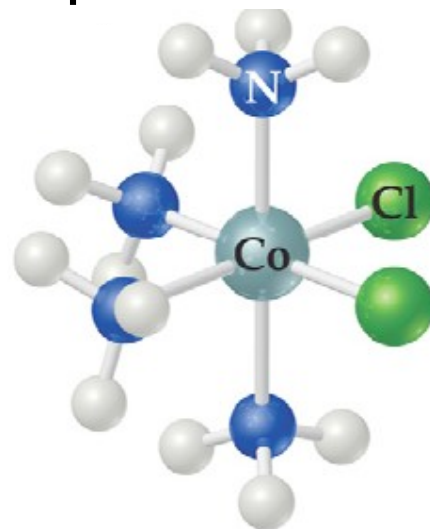


WHAT IS A COORDINATION COMPOUND?

- It is a compound which has one or more co-ordinate bonds
- In a coordination bond there is a species which donates a lone pair of electrons (ligand) and a species which receives the lone pair of electrons
- Most of the time the receiver of the lone pair of electrons is a metal ion (or a metal atom in rare cases) in which case we call it a **metal ligand complex**.

COORDINATION COMPOUNDS

- A central metal atom bonded to a group of molecules or ions is a metal complex.
- If the complex bears a charge, it is a complex ion.
- Compounds containing complexes are coordination compounds.





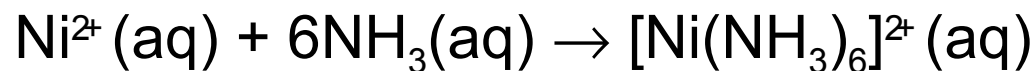
COMPLEX ION

- **A complex ion has a metal ion at its centre with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by co-ordinate (dative covalent) bonds.**



CATIONIC ION

- ***For positively charged complex ions***
- A positively charged complex ion is called a ***cationic complex***. A cation is a positively charged ion.



Lewis acid

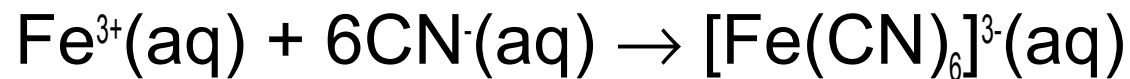
Lewis base

Complex ion



ANIONIC ION

- ***For negatively charged complex ions***
- A negatively charged complex ion is called an ***anionic complex***. An anion is a negatively charged ion.



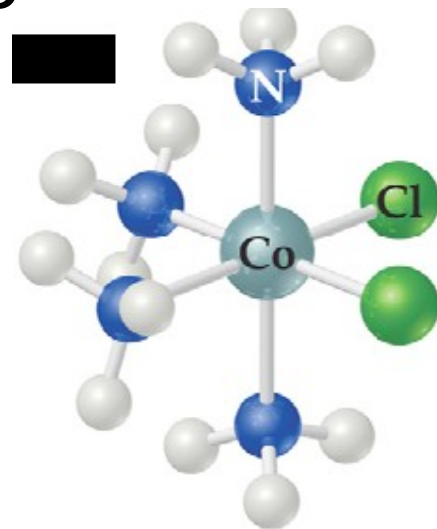
Lewis acid

Lewis base

Complex ion

COORDINATION NUMBER

- • The donor atom is the
- atom directly bound to
- the metal.
- • The coordination
- number is the number
- of atoms directly
- bonded to the central
- atom.





SOME COMMON COORDINATION NUMBER OF METAL IONS

Cu^+ 2, 4

Ag^+ 2

Au^+ 2, 4

Fe^{2+} 6

Co^{2+} 4, 6

Ni^{2+} 4, 6

Cu^{2+} 4, 6

Zn^{2+} 4

Al^{3+} 4, 6

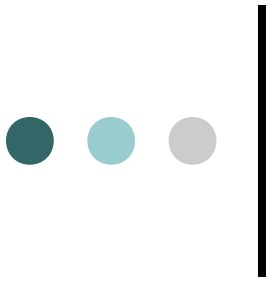
Sc^{3+} 6

Cr^{3+} 6

Fe^{3+} 6

Co^{3+} 6

Au^{3+} 4



- A characteristic feature of the coordination compounds is their ability to retain their identity in solution (which distinguishes them from double salts like carnallite- $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$)
- *Coordination number*- number of ligands bound to the central metal ion (or atom)
- *Coordination sphere*- the group comprising the metal ion and the ligands
- *Polynuclear complex*- complex containing more than one central metal atom



CALCULATION OF CHARGE ON COMPLEX ION

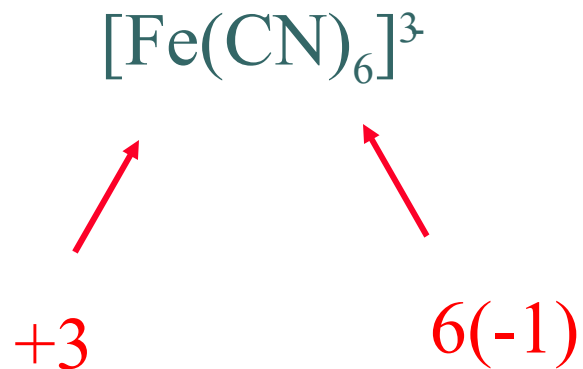
Complex charge = sum of charges
on the metal and the ligands





CALCULATION OF CHARGE ON COMPLEX ION

Complex charge = sum of charges
on the metal and the ligands





CALCULATION OF CHARGE ON COMPLEX ION

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions

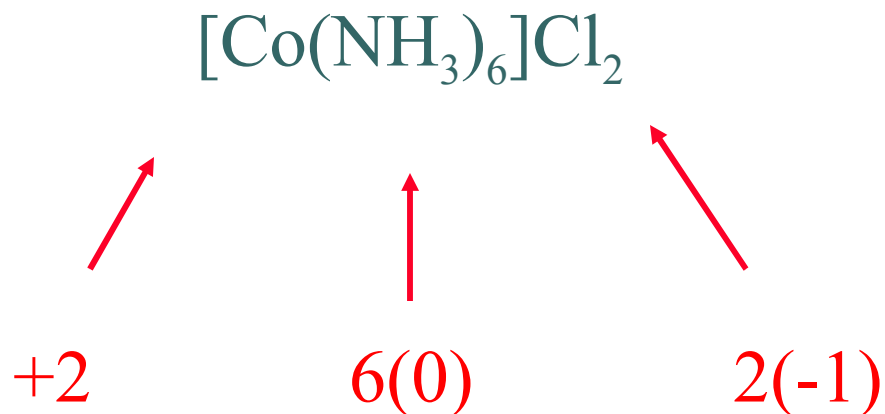


neutral compound



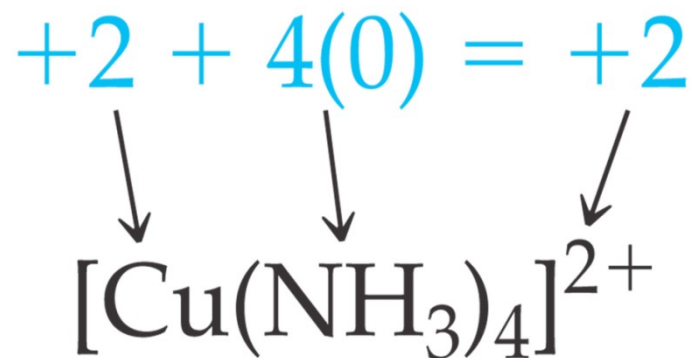
CALCULATION OF CHARGE ON COMPLEX ION

Neutral charge of coordination compound = sum of charges on metal, ligands, and counterbalancing ions





OXIDATION NUMBERS

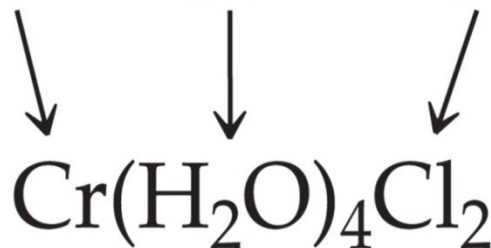


Knowing the charge on a complex ion and the charge on each ligand, one can determine the oxidation number for the metal.



OXIDATION NUMBERS

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



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

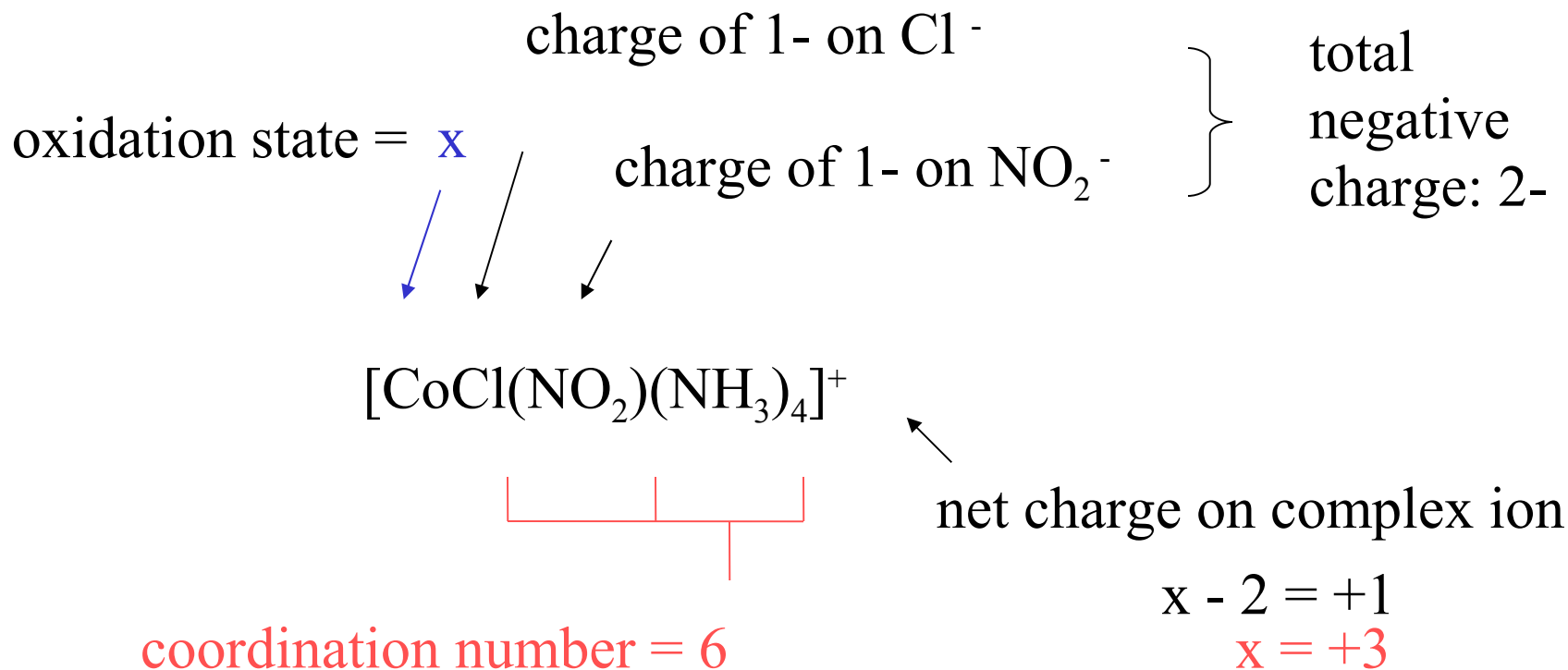


FORMULAS OF COORDINATION COMPOUNDS

- Cation then anion
- Total charges must balance to zero
- Complex ion in brackets



Relating the Formula of a Complex to the Coordination Number and Oxidation State of the Central Metal. What are the coordination number and oxidation state of Co in the complex ion $[\text{CoCl}(\text{NO}_2)(\text{NH}_3)_4]^+$?

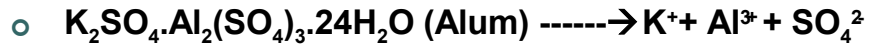




HOW COMPLEXES DIFFER FROM DOUBLE SALTS??

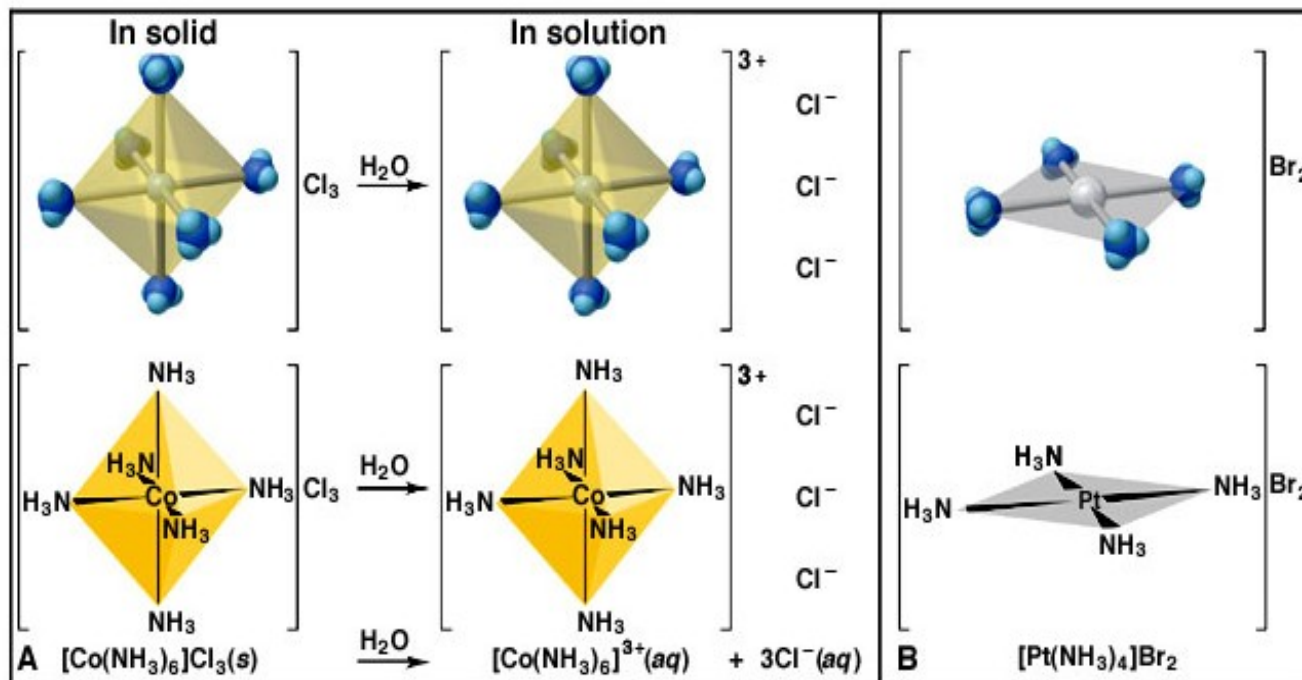
- **Double salts on dissolution in water lose their identity**

Dissolve in water



- **Complex ions don't lose their identity on dissolution**

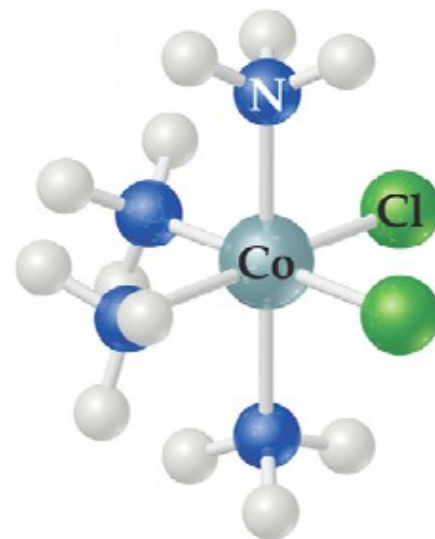
Components of a Coordination Compound



Complex ion remains intact upon dissolution in water

LIGANDS

- • The molecule or ions
- that bond to the metal
- ion are known as
- ligands.
- • The central metal and
- its ligands constitute
- the coordination
- sphere.





LIGANDS

A common feature shared by the ligands in complexes is the ability to donate electrons pairs to central metal atoms or ions act as Lewis bases.



TYPES OF LIGANDS

- A ligand that uses one pair of electrons to form one point of attachment to the central metal atom or ion is called *monodentate* ligand.
- Some ligands are capable of donating more than a single electron pair from different atoms in the ligand and to different sites in the geometry structure of a complex are called *polydentate* ligands.

Ligands in Coordination Compounds

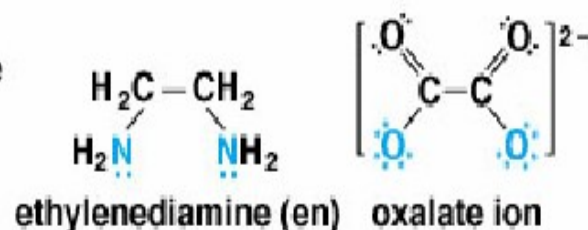
Table 23.7 Some Common Ligands in Coordination Compounds

Ligand

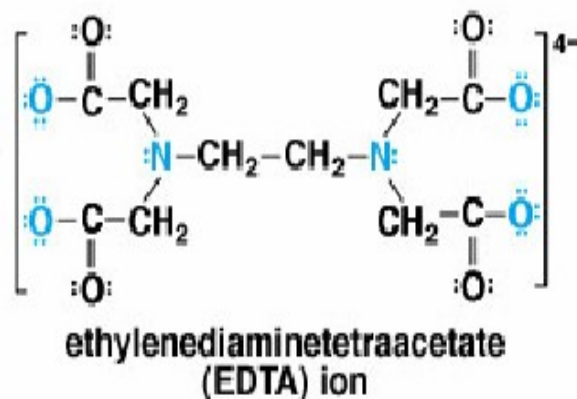
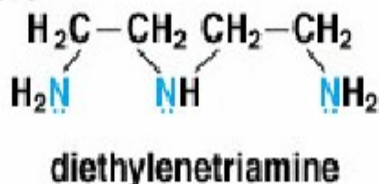
Type Examples

Unidentate	$\text{H}_2\ddot{\text{O}}$ water	$\text{:}\ddot{\text{F}}\text{:}^-$ fluoride ion	$\text{:}\text{C}\equiv\text{N}\text{:}]^-$ cyanide ion	$\text{[:}\ddot{\text{O}}\text{-H]}$ hydroxide ion
	$\text{:}\text{NH}_3$ ammonia	$\text{:}\ddot{\text{Cl}}\text{:}^-$ chloride ion	$\text{[:}\ddot{\text{S}}=\text{C}=\ddot{\text{N}}\text{:}]^-$ thiocyanate ion <small>[or]</small>	$\text{[:}\ddot{\text{O}}-\text{N}=\ddot{\text{O}}\text{:}]$ nitrite ion <small>[or]</small>

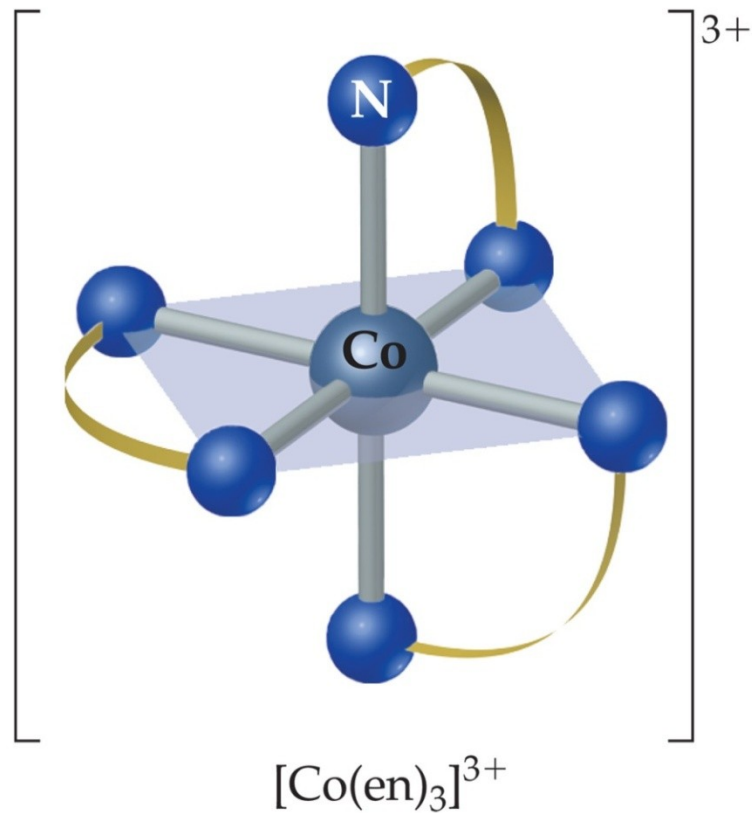
Bidentate



Polydentate

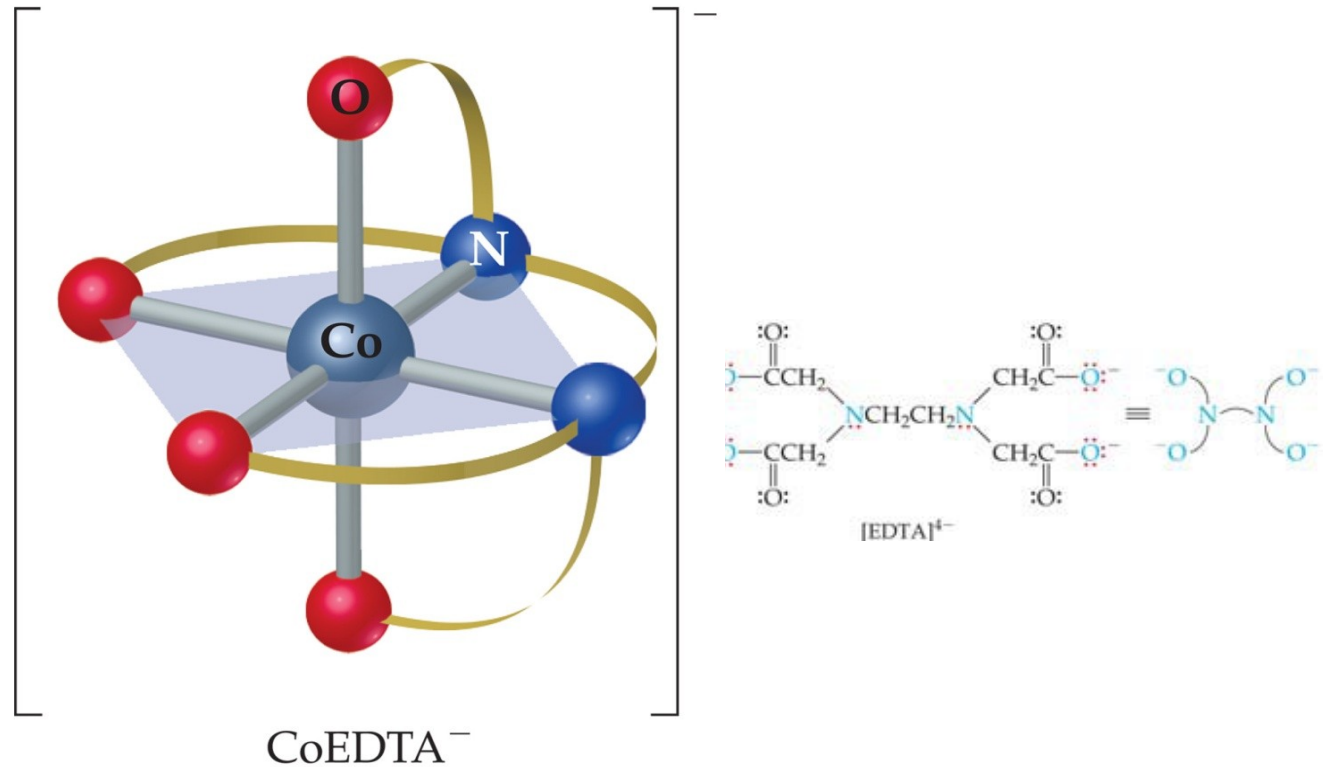


ETHYLENEDIAMINE



Ethylenediamine (en) is a bidentate ligand

ETHYLENEDIAMINE TETRAACETATE ION



EDTA is a polydentate ligand with six donor atoms



WERNER'S COORDINATION THEORY

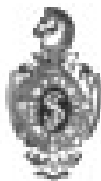
WERNER'S COORDINATION CHEMISTRY

George B. Kauffman

Alfred Werner
Founder of Coordination Chemistry

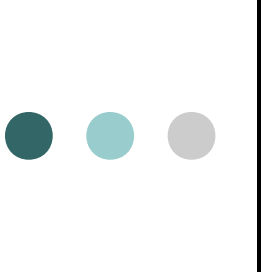


Alfred Werner (1866-1919)



Springer-Verlag Berlin Heidelberg New York 1966

Front cover pages
(merged) from book on
the life of Werner



Alfred Werner received **the Nobel Prize of Chemistry** in 1913 for his coordination theory of transition metal-amine complexes.



POSTULATES OF WERNER'S THEORY

1. In co-ordination compounds, central metal atoms exhibit primary valency and secondary valency.

The primary valency is ionizable. Secondary valency is not ionizable.

The primary valency corresponds to oxidation state. The secondary valency corresponds to coordination number. (the central metal ion and ligands are not ionizable)

2. Every metal atom has a fixed number of secondary valencies (coordination number(s)).



POSTULATES OF WERNER'S THEORY

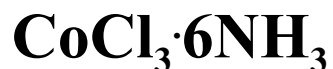
3. The metal atom tends to satisfy both its primary valency as well as its secondary valency. Primary valency is satisfied by negative ions (metal ion has a positive charge) whereas secondary valency (coordination number) is satisfied either by negative ions or by neutral molecules. (In certain case a negative ion may satisfy both types of valencies).

4. The coordination number or secondary valencies are always directed towards the fixed positions in space and this leads to definite geometry of the coordination compound.

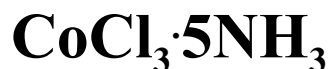


EXPLANATION OF COORDINATE COMPOUNDS ON THE BASIS OF WERNER'S THEORY

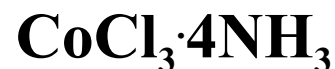
The following formulas describe a series of three coordination compounds:



(a)



(b)



(c)

In 1893, Swiss chemist Alfred Werner proposed that certain metal atoms, primarily those of the transition metals, have two types of valence.

1. The primary valence, is based on the number of electrons the atom loses in forming the metal ion.
2. Secondary or auxiliary, valence is responsible for the bonding of other groups, called *ligands*, to the central metal ion.

EXPLANATION OF COORDINATE COMPOUNDS ON THE BASIS OF WERNER'S THEORY



(a)



(b)



(c)

Ionization of coordination compound (a) can be represented as



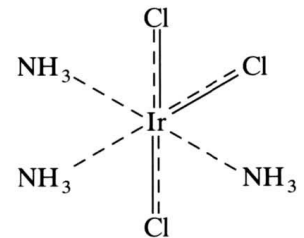
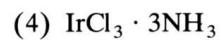
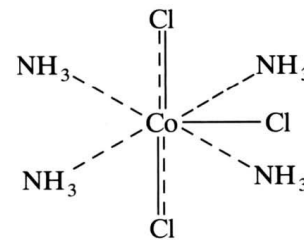
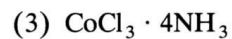
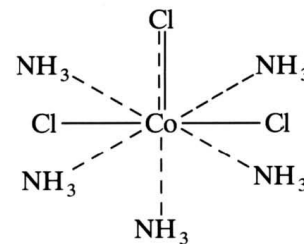
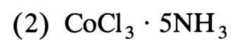
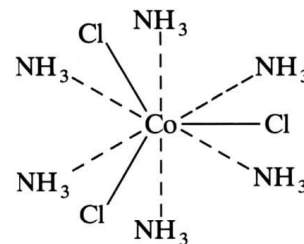
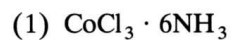
In the presence of an excess of $\text{AgNO}_3(\text{aq})$

(a) yield *three* moles of $\text{AgCl}(\text{s})$ per mole of compound

(b) yield only *two* moles of $\text{AgCl}(\text{s})$ per mole of compound

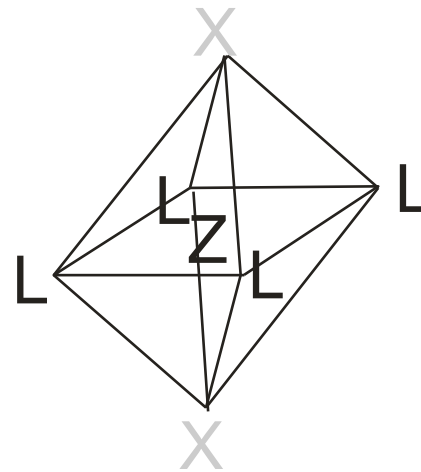
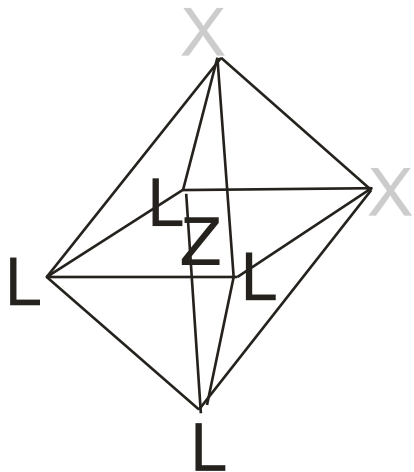
(c) and yield only *one* moles of $\text{AgCl}(\text{s})$ per mole of compound

Some chloride ions must do *double duty* and help satisfy the both of primary valence and secondary valence.



WERNER'S COORDINATION THEORY AND ISOMERISM


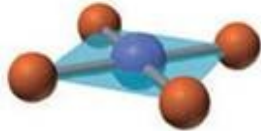
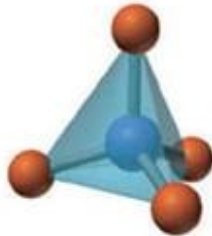
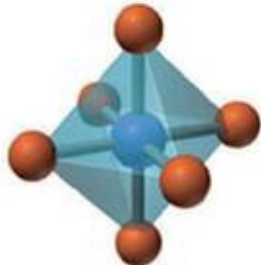
- According to one of the postulates of Werner's coordination theory, the secondary valencies determine the stereochemistry of the complexes.



Possible arrangements of the ligands in an octahedral complex of composition $[ZL_4X_2]$

Werner also assigned two arrangements for this complex

Table 23.6 Coordination Numbers and Shapes of Some Complex Ions

Coordination Number	Shape		Examples
2	Linear		$[\text{CuCl}_2]^-$, $[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{AuCl}_2]^-$
4	Square planar		$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$
4	Tetrahedral		$[\text{Cu}(\text{CN})_4]^{3-}$, $[\text{Zn}(\text{NH}_3)_4]^{2+}$, $[\text{CdCl}_4]^{2-}$, $[\text{MnCl}_4]^{2-}$
6	Octahedral		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{CN})_6]^{4-}$, $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{FeCl}_6]^{3-}$, $[\text{Co}(\text{en})_3]^{3+}$

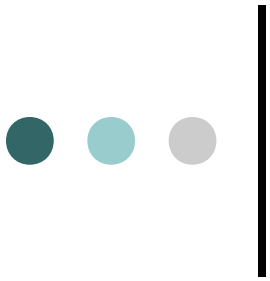
EXPERIMENTAL VERIFICATION FOR WERNER'S COORDINATION THEORY

Conductivities of $\text{CoCl}_3 \cdot 6\text{NH}_3$ were measured when the compounds were dissolved in water.

Formula	Conductivity	No. of Cl^- ions precipitated
$\text{CoCl}_3 \cdot 6\text{NH}_3$	High	3
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Medium	2
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Low	1
$\text{IrCl}_3 \cdot 3\text{NH}_3$	Zero	0



The no. of Cl^- ions precipitated supported the Werner's theory



CHELATING LIGANDS AND CHELATES

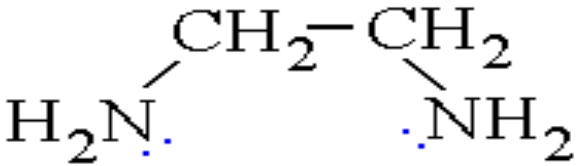
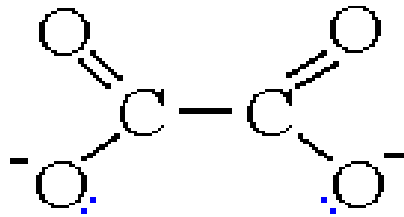
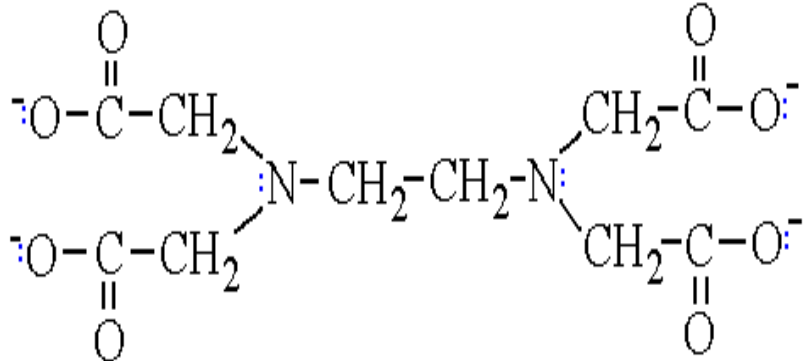


CHELATING LIGANDS AND CHELATES

When a bidentate or a polydentate ligand is attached by two or more donor atoms to the same central ion forming a ring structure, the ligand is called **chelating ligand**. The complex is called **Chelate** and the process is called **Chelation**.

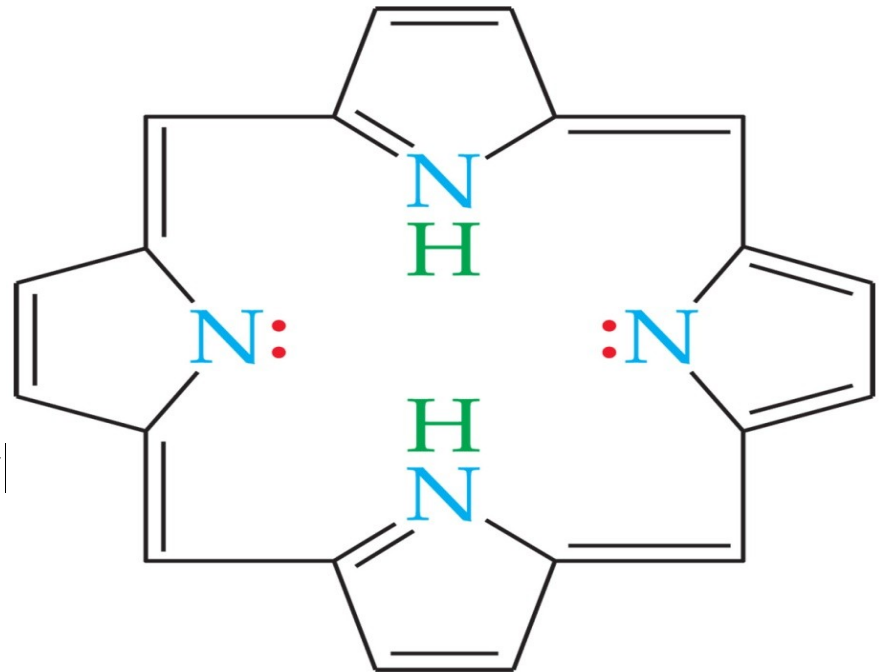
Chelating agent is a polydentate ligand. It simultaneously attaches to two or , more position in the coordination sphere of the central atom of a complex ion.

Table 25.3 Some Common Polydentate Ligands (Chelating Agents)

Abbreviation	Name	Formula
en	ethylenediamine	
ox	oxalato	
EDTA	ethylenediaminetetraacetato	

CHELATING AGENTS

- Porphyrins are complexes containing a form of the porphine molecule shown at the right.
- Important biomolecules like heme and chlorophyll are porphyrins.





FACTORS AFFECTING STABILITY OF CHELATES

- Chelating ligands form stable complexes than ordinary ligands. This is also called chelate effect.
- The stability of chelate depends upon the number of atoms in the ring. Generally, chelating ligands which do not contain double bonds form stable complexes with five membered rings. On the other hand, the chelating ligands which contain double bonds form stable complexes with six membered rings.
- Chelating ligands with smaller groups form stable complexes, than with larger and bulky groups. This is because of steric reasons.



NOMENCLATURE OF COORDINATION COMPLEXES



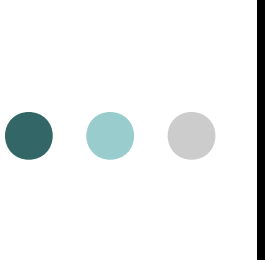
NAMING COORDINATION COMPOUNDS

1. In naming salts, the name of the cation is given before the name of the anion.

For example, in $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, we name $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ before Cl^- .

2. Within a complex ion or molecule, the ligands are named before the metal. Ligands are listed in alphabetical order, regardless of charge on the ligand. Prefixes (see Rule #4 below) that give the number of ligands are **NOT** considered part of the ligand name in determining alphabetical order.

Consider once again the $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ ion. Name the ammonia ligand first, then the chloride, followed by the metal: **pentaamminechlorocobalt(III)**.



3. The names of the anionic ligands end in the letter “o”, whereas neutral ones ordinarily bear the name of the molecules. Special names are given for H₂O (**aqua**), NH₃ (**ammine**), CO (**carbonyl**), and NO (**nitrosyl**).

For example, [Fe(CN)₂(NH₃)₂(H₂O)₂]⁺ would be named **diamminediaquacyanoiron(III) ion**.

4. Greek prefixes (di, tri, tetra, penta, and hexa) are used to indicate the number of each kind of ligand when more than one is present as shown in the examples above. If the ligand already contains a Greek prefix (as in ethylenediamine) or if it is polydentate (i.e. able to attach at more than one binding site), then the following prefixes are used instead:

2: bis-

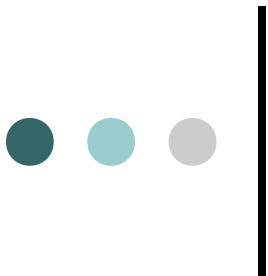
3: tris-

4: tetrakis-

Names of Some Ligands

Table 23.8 Names of Some Neutral and Anionic Ligands

Name	Formula
A. Neutral	
Aqua	H_2O
Ammine	NH_3
Carbonyl	CO
Nitrosyl	NO
B. Anionic	
Fluoro	F^-
Chloro	Cl^-
Bromo	Br^-
Iodo	I^-
Hydroxo	OH^-
Cyano	CN^-



5. If the complex is an anion, its name ends in **-ate**. If the symbol of the metal originates from a Latin name, then the Latin stem is used instead

For example, the compound $K_4[Fe(CN)_6]$ is named **potassium hexacyanoferrate(II)**.

Common Latin stem listings (in parentheses):

Copper (**cuprate**);

iron (**ferrate**);

tin (**stannate**);

lead (**plumbate**).

6. The oxidation number of the metal is given in parentheses in Roman numerals directly following the name of the metal.

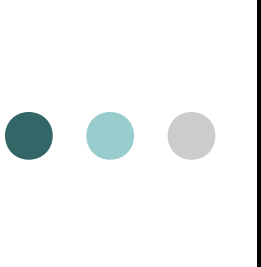
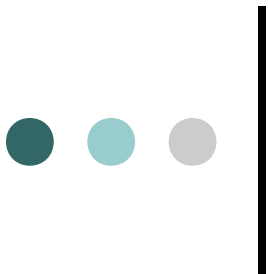


TABLE 20.15 Latin Names Used for Some Metal Ions in Anionic Complex Ions

Metal	Anionic Complex Base Name
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argentate
Gold	Aurate
Tin	Stannate

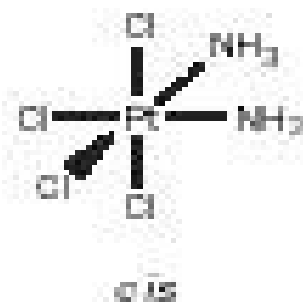
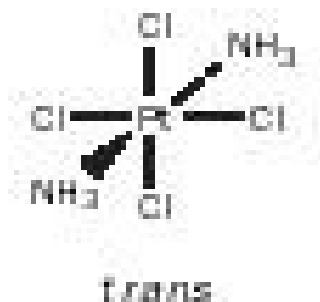
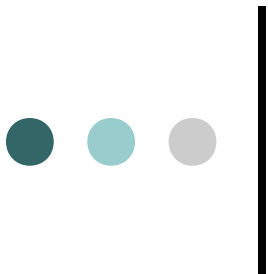


7. The coordination number of ligands attached to more than one metal (bridging ligands) is indicated by a subscript to the Greek symbol μ placed before the ligand name. This can be illustrated by the following example



μ -hydroxobis [pentaamminechromium(III)] chloride

8. Geometrical isomers are named by the use of the terms **cis** to designate adjacent positions and **trans** to designate opposite positions. For example, in square planar complexes the positions 1,4 ; 1,2 ; 2,3 and 3,4 are **cis** while 1,3 and 2,4 are **trans** with respect to each other



9. Optically active compounds are designated by the symbols (+) or d- for dextro rotatory and (-) or l- for laevo rotatory.

For example ,

d-K₃[Ir(C₂O₄)₂]
potassium (+) trioxalatoiridate(III)



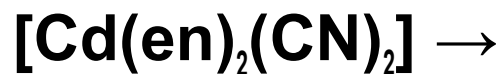
EXAMPLES:



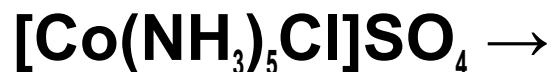
Tetrachloronickelate(II) ion



Amminepentachlorocuprate(II) ion



Dicyanobis(ethylenediamine)cadmium(II)



Pentaamminechlorocobalt(III) sulphate



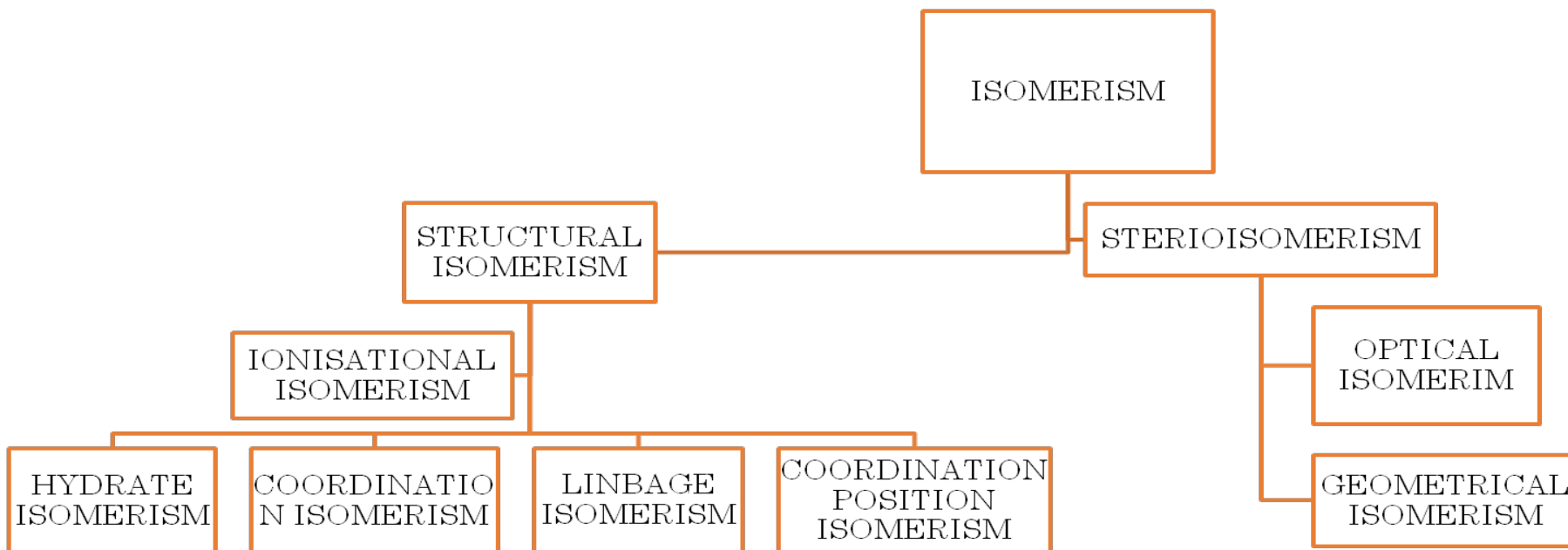
ISOMERISM IN COORDINATION COMPOUNDS



ISOMERISM IN COORDINATION COMPOUNDS

Compounds having the same molecular formula, but differing in physical and chemical properties are known as isomers. This phenomenon is known as isomerism. The isomers can be identified and distinguished from one another because of difference in their physical and chemical properties

TYPES OF ISOMERISM

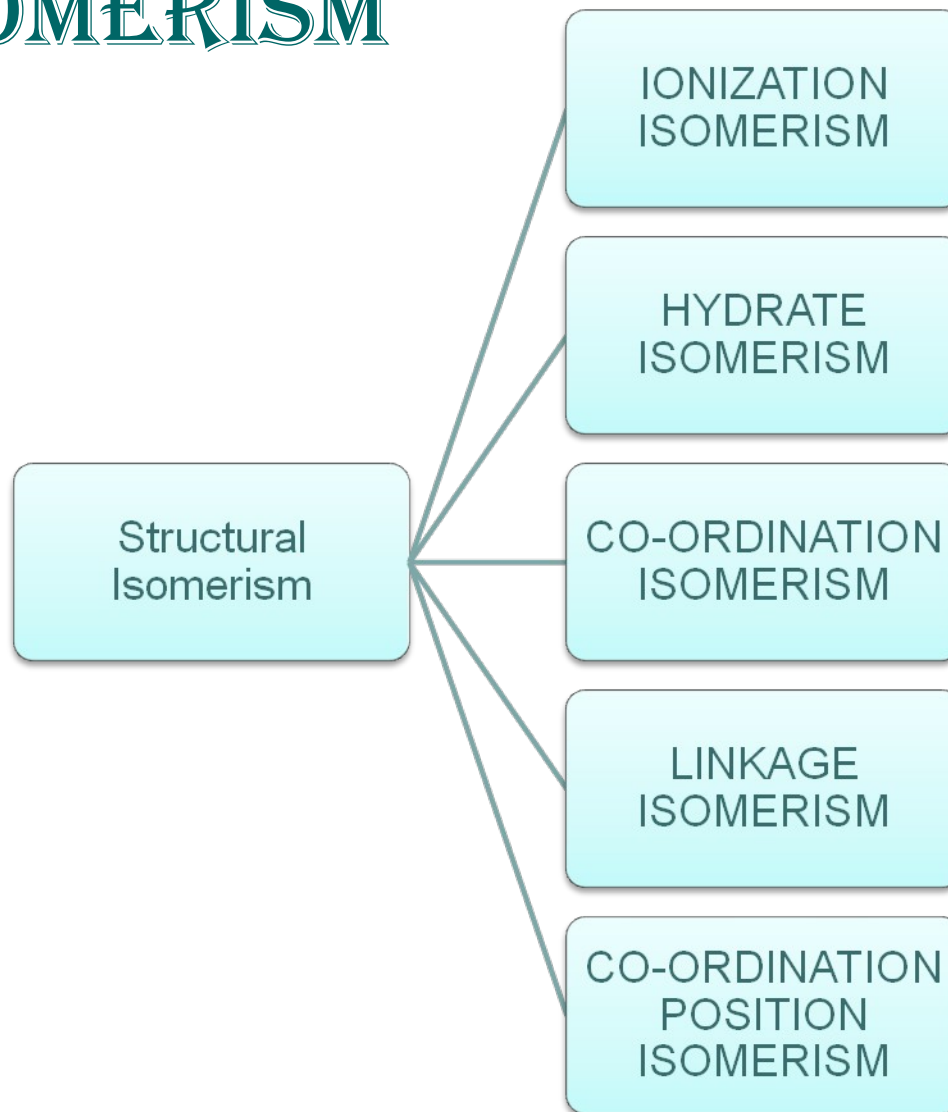




STRUCTURAL ISOMERISM

- It is displayed by compounds that have different ligands within their coordination spheres.
- These isomers have the same molecular formula but different structural arrangement of atoms (or groups of atoms) around the central metal ion

TYPES OF STRUCTURAL ISOMERISM



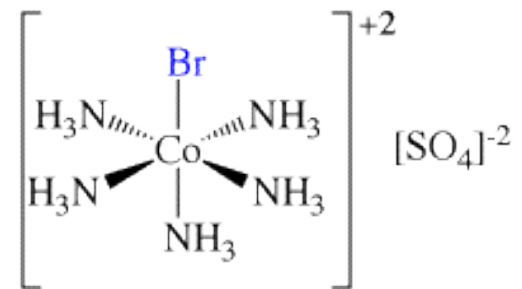
IONIZATION ISOMERISM

- It arises due to the exchange of anion within and outside the co-ordination sphere. As a result, these isomers give different ions in solution.

- Example:

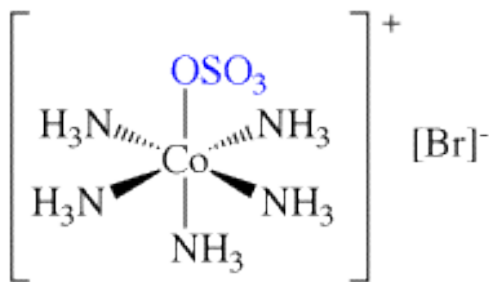


violet



- $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br} \rightarrow \text{Br}^-$ anion in solution

red

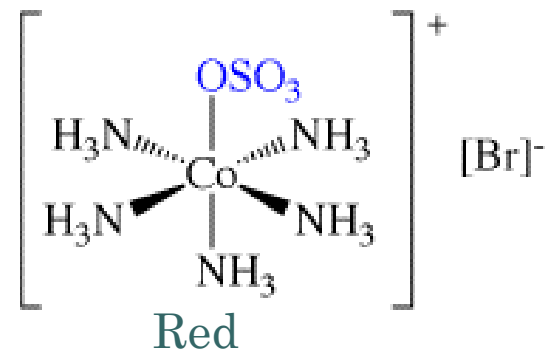
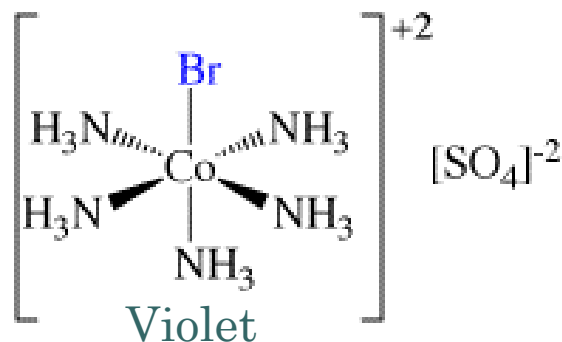


IONIZATION ISOMERISM

Both the compounds have different physical and chemical properties

Red isomer forms an off white precipitate of AgBr with Ag⁺ ions but gives no precipitate with Ba⁺⁺ ions

Violet isomer gives precipitate with Ba⁺⁺ ions and no precipitate with Ag⁺ ions





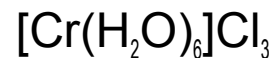
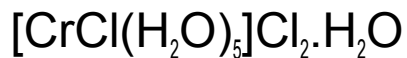
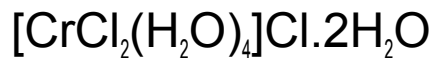
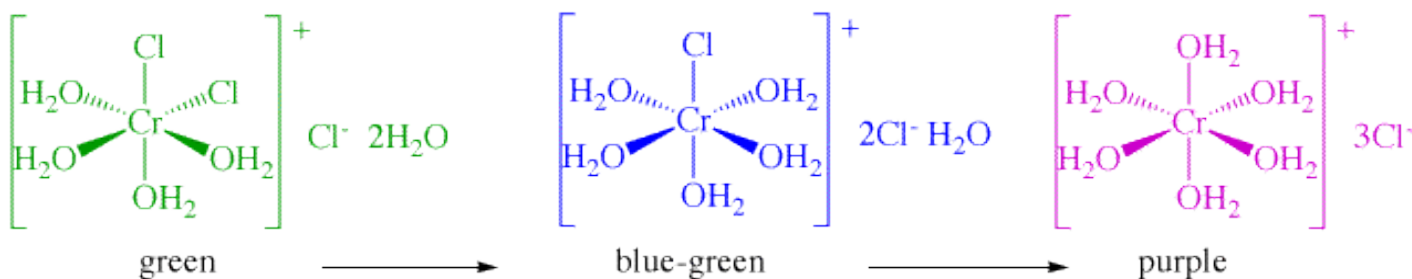
IONIZATION ISOMERISM

Other Examples:

- $[\text{PtBr}(\text{NH}_3)_3]\text{NO}_2 \rightarrow \text{NO}_2^-$ anions in solution
- $[\text{Pt}(\text{NH}_3)_3(\text{NO}_2)]\text{Br} \rightarrow \text{Br}^-$ anions in solution

HYDRATE ISOMERISM

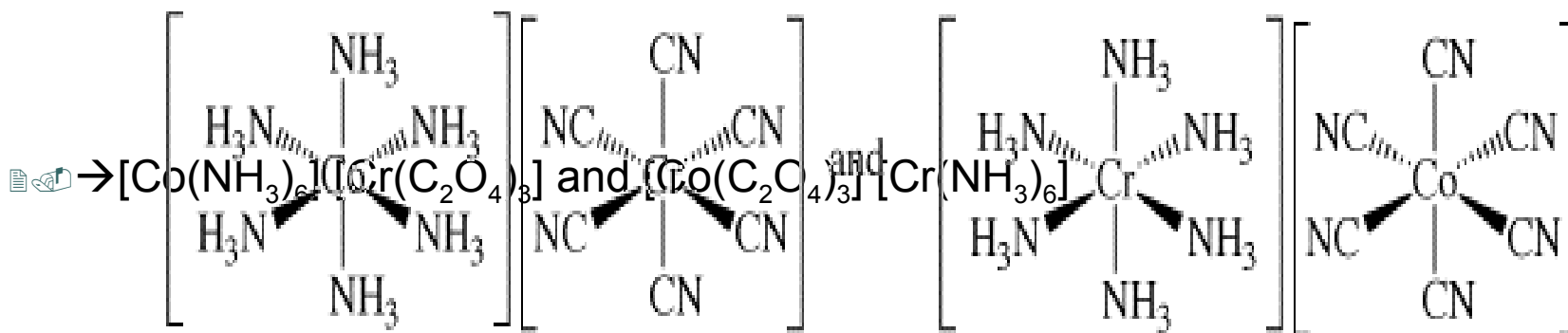
- It arises when different number of water molecules are present inside and outside the co-ordination sphere. This isomerism is illustrated by the 3 isomers that have the formula $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$



- These isomers have very different chemical properties and on reaction with AgNO_3 to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.
- These isomers can lose two, one and no water molecules on dehydration with conc. sulphuric acid respectively

COORDINATION ISOMERISM

- It is observed in the co-ordination compounds having both cationic and anionic complex ions. The ligands are interchanged in both the cationic and anionic ions to form isomers.
- For examples





LINKAGE ISOMERISM

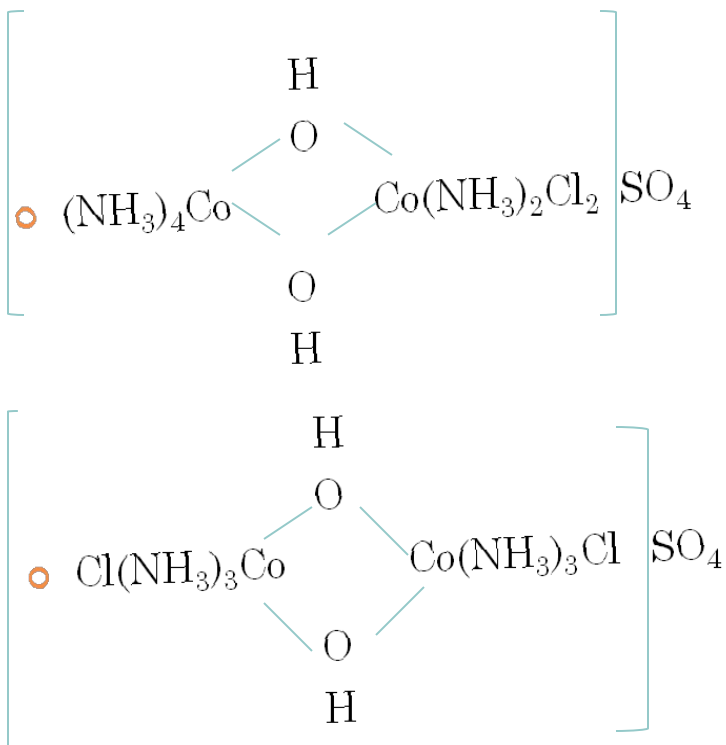
- Occurs in co-ordination compounds with ambidentate ligands. These ligands are capable of coordinating in more than one way. The best known cases involve the monodentate ligands $\text{SCN}^- / \text{NCS}^-$ and $\text{NO}_2^- / \text{ONO}^-$.
- Examples:
- $[\text{Co}(\text{NH}_3)_5(\text{ONO})]\text{Cl}_2$ the nitrito isomer -O attached
 $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ the nitro isomer - N attached.
- $[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$ Co-NCS isothiocyanate and
 $[\text{Co}(\text{NH}_3)_5(\text{SCN})]\text{Cl}_2$ Co-SCN thiocyanate



COORDINATION POSITION ISOMERISM

- This type of isomerism occur in polynuclear bridged complexes i.e., complexes having more than one metal atoms.
- It arises due to interchange of ligands between the different metal centres

COORDINATION POSITION ISOMERISM



In the above isomers ligands NH_3 and Cl are interchanged between two cobalt atoms

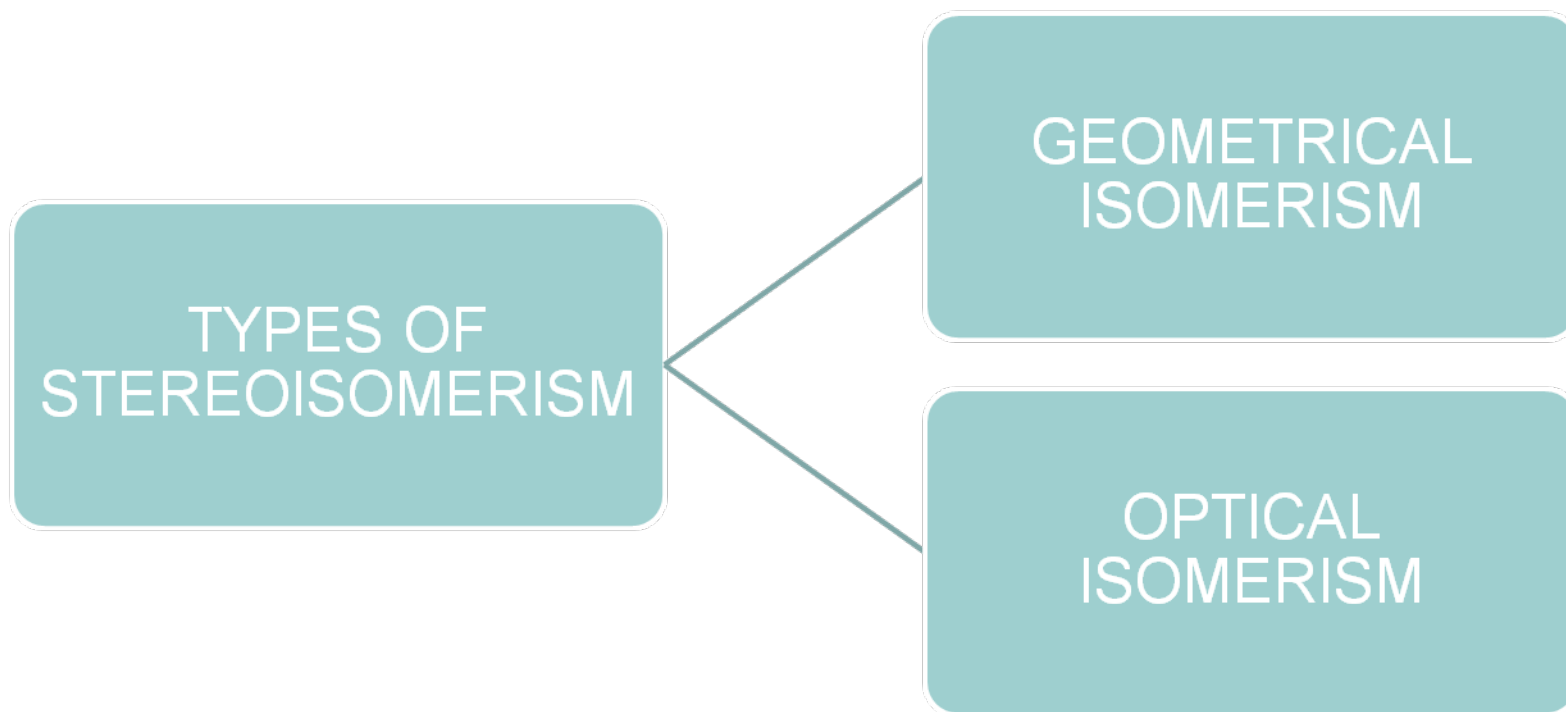


STEREISOMERISM

- Compounds are stereoisomer when they contain the same ligands in their coordination spheres but differ in the way that these ligands are arranged in space
- They have the same atom to atom bonding sequence but the atoms differ in their arrangement in space
- They have the same atoms, same sets of bonds but differ in the relative orientation of these bonds



STEREOMERISM



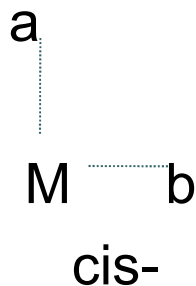


GEOMETRICAL ISOMERISM

- It is due to ligands occupying different positions around the central metal atom or ion
- Also known as cis-trans isomerism .
- Common in **square planar** and **octahedral** complexes but **not** in **tetrahedral** complexes because all tetrahedral complexes [such as Ma_4 , Ma_2b_2 , $Mabcd$, where a,b,c,d represents ligands]exist in only one geometric form in which all positions are adjacent to each other.
- Existence of two different compounds having the molecular formula $[Pt(NH_3)_2Cl_2]$ was used by the father of co-ordination chemistry Alfred Werner to prove that transition metals often have square planar geometries.

GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

cis- and *trans-* refer to the position of 2 groups relative to each other. In the *cis-* isomer they are "next to each other" i.e. at 90 degrees in relation to the central metal ion, whereas in the *trans-* isomer they are "opposite each other", i.e. at 180 degrees relative to the central metal ion.





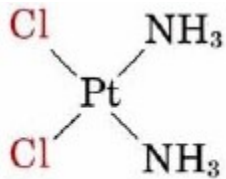
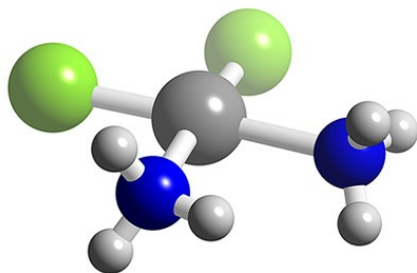
GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

- Compound type No. of isomers
Ma₂b₂ 2 (cis- and trans-)
Ma₂bc 2 (cis- and trans-)
Mabcd 3 (use cis- and trans- relations)
here a, b, c, and d refer to monodentate ligands.
M(ab)₂ 2(cis- and trans-)
ab refer to unsymmetrical bidentate ligand.
- A number of examples of these types have been isolated and characterised and they show very different chemical and biological properties.

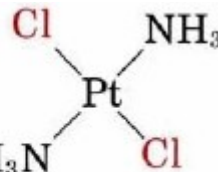
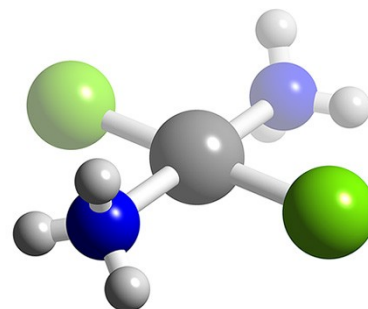
GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

Example of Ma_2b_2 type compound

○ *cis*- and *trans*- isomers of $[PtCl_2(NH_3)_2]$



pale *Cis isomer* *N*

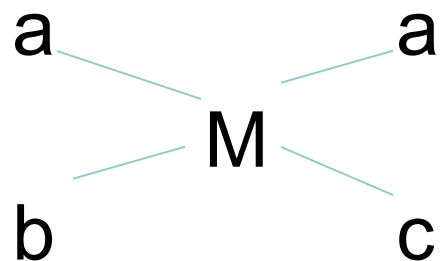


de *Trans isomer*

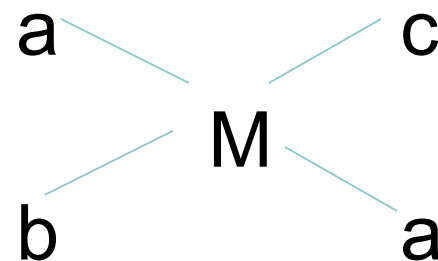
cis-[PtCl₂(NH₃)₂] is an anti-cancer agent (it is toxic), and so not useful in Chemotherapy. *trans*-[PtCl₂(NH₃)₂] is inactive against cancer (it is toxic), and so not useful in Chemotherapy.

GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

○ Isomers of Ma_2bc



cis

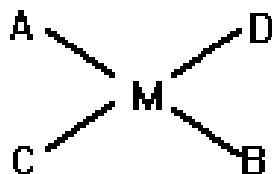
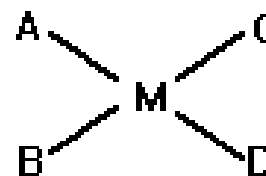
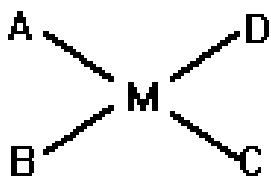


trans

Example $[Pt(NH_3)_2ClNO_2]$

GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

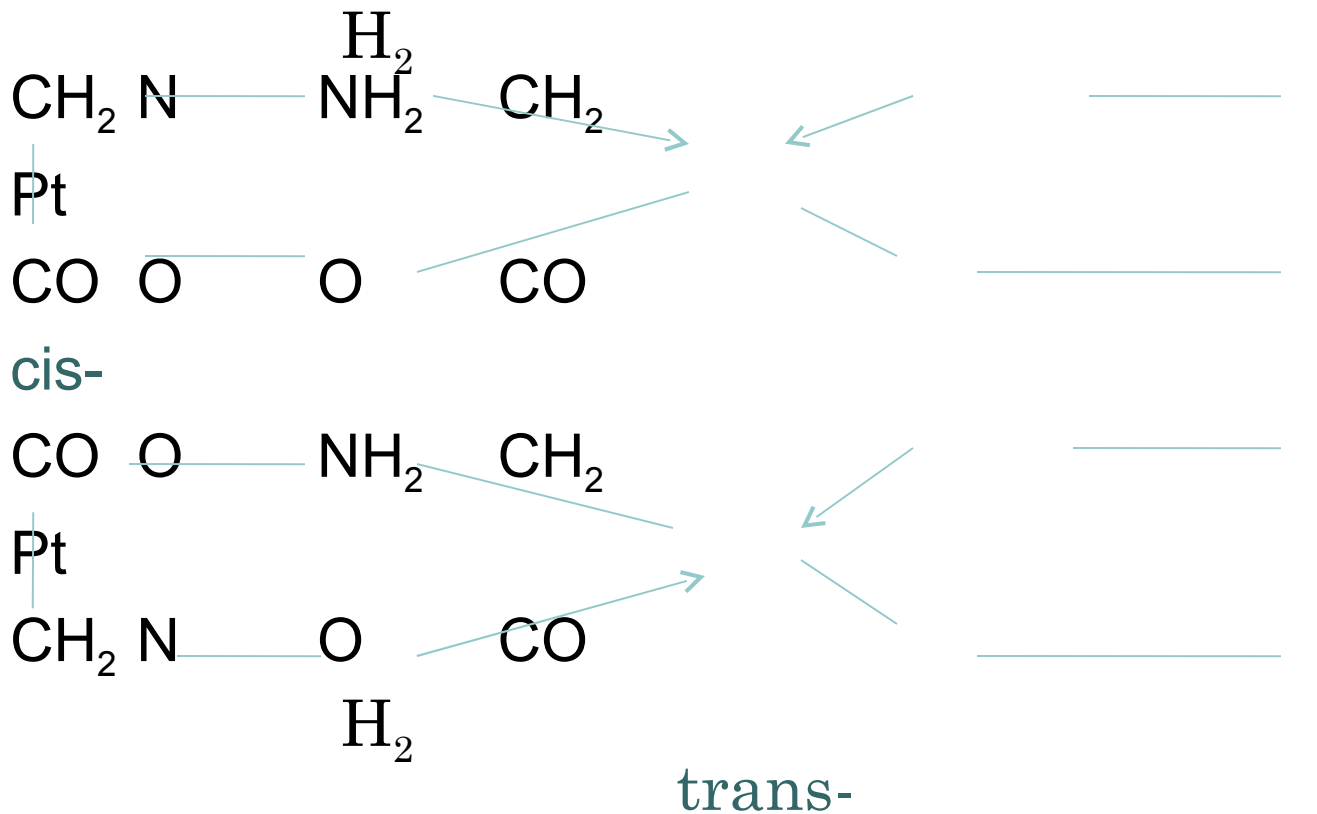
○ Isomers of $Mabcd$



○ Example $[Pt(NH_3)(NH_2OH)(NO_2)(py)]NO_2$

GEOMETRICAL ISOMERISM IN SQUARE PLANER COMPOUNDS

- Isomers of $M(ab)_2$
- Example : $[Pt(gly)_2]$ where gly is glycine



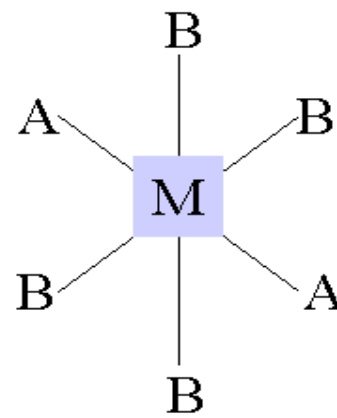
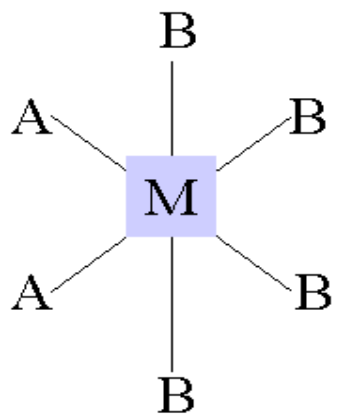
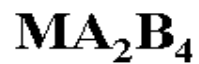


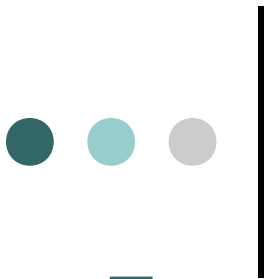
GEOMETRICAL ISOMERISM IN OCTAHEDRAL COMPLEXES

Compound type	No. of isomers
Ma_2b_4	2 (cis- and trans-)
Ma_3b_3	2 (fac- and mer-)
$\text{M}(\text{aa})_2\text{b}_2$	3 (2cis- and trans-)
Mabcdef	15

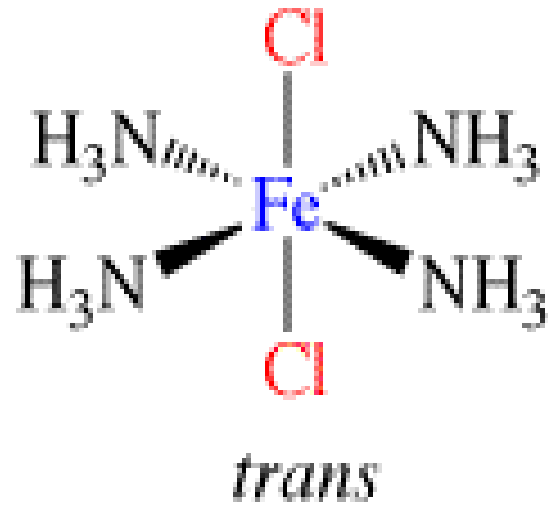
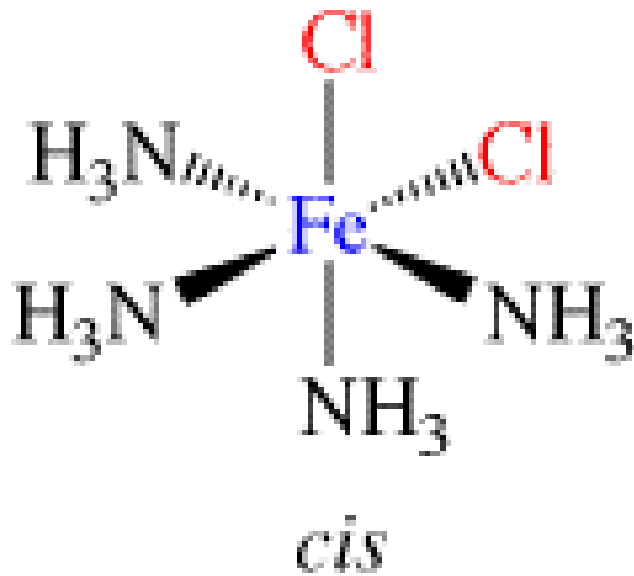
Here a,b,c,d,e,f represents monodentate ligand and aa represents bidentate ligand.

ISOMERS OF MA_2B_4

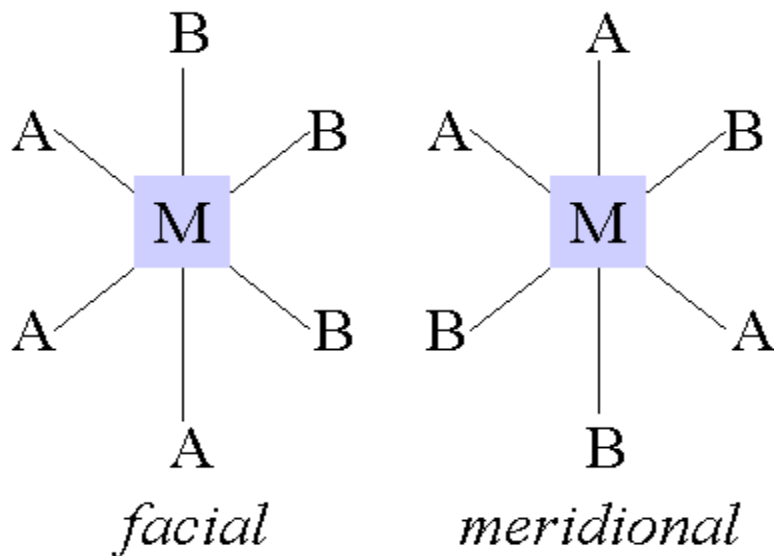




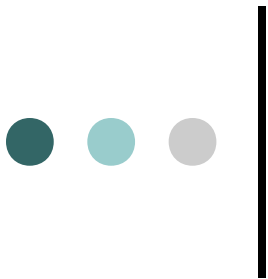
Example : $[\text{FeCl}_2(\text{NH}_3)_4]$



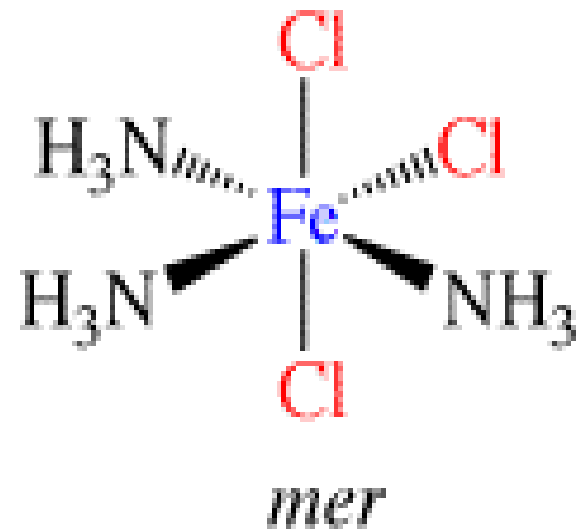
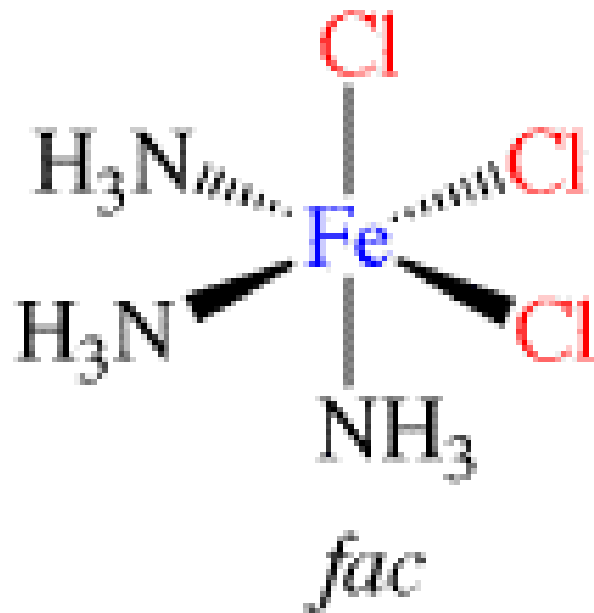
ISOMERS OF MA_3B_3



New labels are introduced to reflect the relative positions of the ligands around the octahedral structure. Thus; placing the 3 groups on one face of the octahedron gives rise to the *facial* isomer and placing the 3 groups around the centre gives rise to the *meridional* isomer.



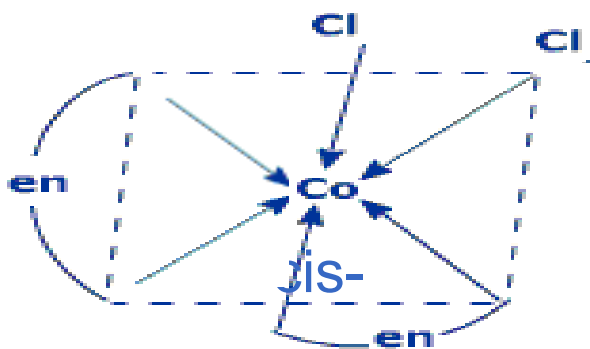
Example : $[\text{Fe}(\text{NH}_3)_3\text{Cl}_3]$



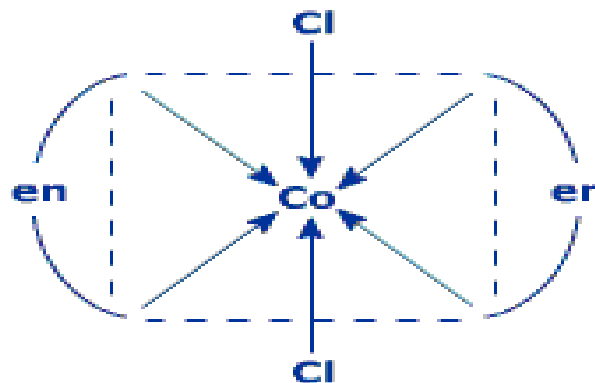
ISOMERS OF MAA_2B_2

○ Example: $[Co(en)_2Cl_2]$

where en is ethylene diamine bidentate ligand which exists in cis- and trans- form.



trans-





NOTE :

- Geometrical isomerism is not observed in
 1. complexes of co-ordination number 2 and 3 .
 2. Complexes of tetrahedral geometry.
 3. Complexes Ma_3b or Mab_3 or Ma_4 of square planar geometry.
 4. Complexes Ma_6 and Ma_5b of octahedral geometry.



OPTICAL ISOMERISM

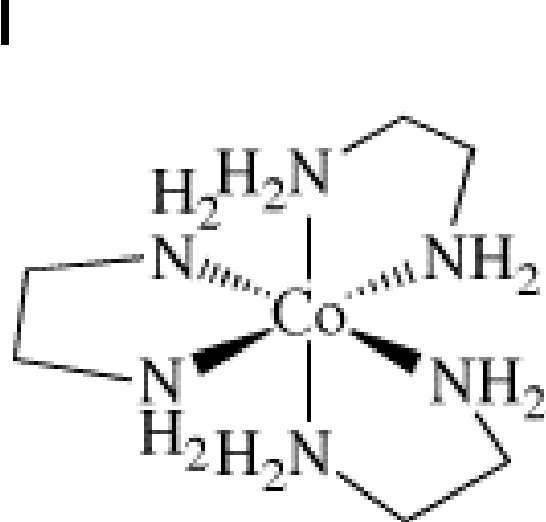
- Optical isomers are related as non-superimposable mirror images and differ in the direction with which they rotate plane-polarised light. These isomers are referred to as enantiomers or enantiomorphs of each other and their non-superimposable structures are described as being asymmetric.
- Common in tetrahedral and octahedral complexes but not in square planar because of the presence of axis of symmetry.
- Very common in octahedral complexes.



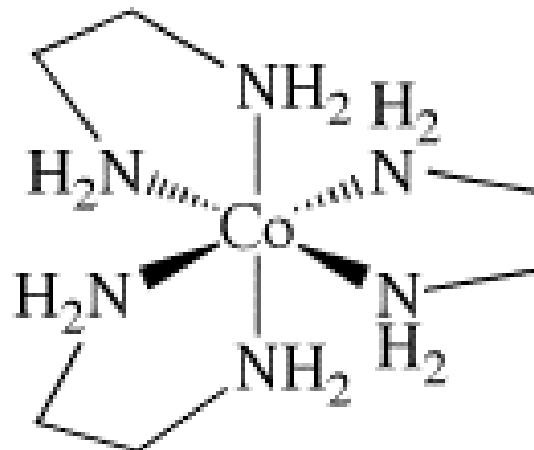
OPTICAL ISOMERISM IN OCTAHEDRAL COMPLEXES

- Octahedral complexes of the type $[M(aa)_3]$, $[M(aa)_2b_2]$, $[M(aa)b_2x_2]$ and $[M(ab)_3]$ show optical isomerism.
- Where;
 - aa is symmetrical bidentate ligand (e.g. en)
 - ab is unsymmetrical bidentate ligand (e.g. gly)
 - b,x is monodentate ligand

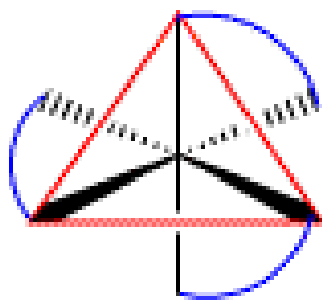
- Isomer of $M(aa)_3$
- Example: $[Co(en)_3]Cl_3$



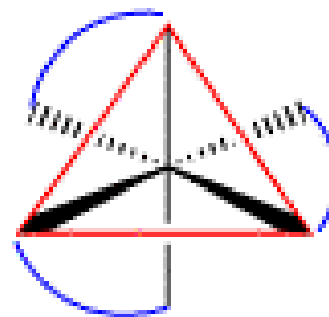
d form



l form

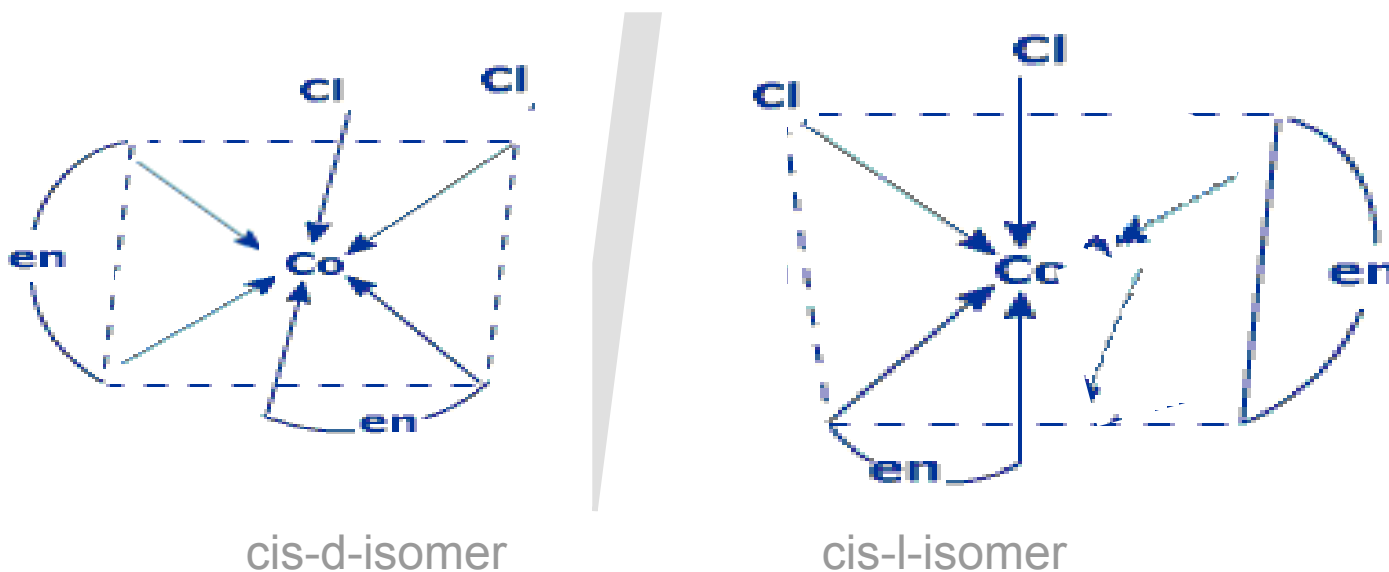


Δ

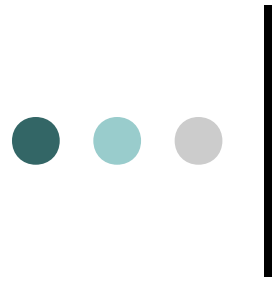


Λ

- Isomers of $M(aa)_2b_2$
- Example $[Co(en)_2Cl_2]^+$



Trans-form of the above compound does not show optical isomerism because it has plane of symmetry

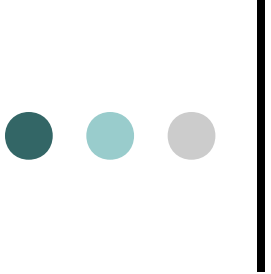


EFFECTIVE ATOMIC NUMBER



SIDGWICK THEORY

- Sidgwick in 1927 extended the Lewis theory of electron pair bond formation to explain the bonding in coordination compounds.
- He suggested that metal ion accepts electron pairs from the ligands until it achieves the next noble gas configuration.
- This is called **EFFECTIVE ATOMIC NUMBER RULE**. The total number of electrons possessed by the central metal ion and the electrons gained by it from ligands is called the **EFFECTIVE ATOMIC NUMBER (EAN)**



The EAN rule is helpful for organometallic compounds and carbonyl complexes, which obey in most cases this rule:



$$\begin{array}{r} \text{Cr} \quad 24 \text{ e}^- \\ 6\text{CO} \quad \underline{12 \text{ e}^-} \\ \quad \quad 36 \text{ e}^- \end{array}$$



$$\begin{array}{r} \text{Fe} \quad 26 \text{ e}^- \\ 5\text{CO} \quad \underline{10 \text{ e}^-} \\ \quad \quad 36 \text{ e}^- \end{array}$$



$$\begin{array}{r} \text{Ni} \quad 28 \text{ e}^- \\ 4\text{CO} \quad \underline{8 \text{ e}^-} \\ \quad \quad 36 \text{ e}^- \end{array}$$

Similarly the formation of olefin complexes and metallocenes may be explained by the EAN rule:

olefines donate 2 electrons /double bond

ethylene 2

butadiene 4

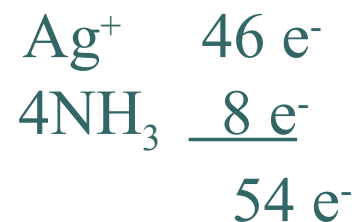
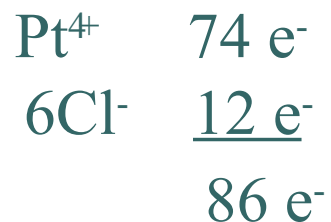
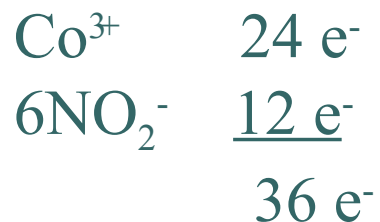
benzene 6

cyclopentadienyl radical 5

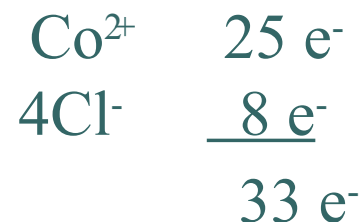
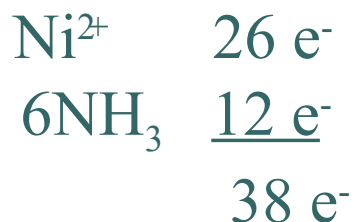
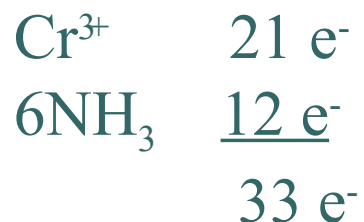




Examples:



but

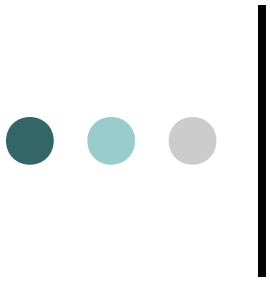


Many elements form complexes which do not obey the



LIMITATIONS OF SIDGWICK THEORY

- Many complexes are stable but do not follow EAN rule.
- Theory doesn't predict the geometry of the complexes
- Theory doesn't predict the magnetic behavior of the complexes



HYBRIDISATION OF ATOMIC ORBITALS



HYBRIDIZATION

- The phenomenon of intermixing of the atomic orbitals of slightly different energies so as to redistribute their energies and to give new set of orbitals of equivalent energy and shape



HYBRID ORBITALS

The number of hybrid orbitals obtained equals the number of atomic orbitals mixed.

The type of hybrid orbitals obtained varies with the types of atomic orbitals mixed.

Types of Hybrid Orbitals

sp





sp^2

sp^3

sp^3d

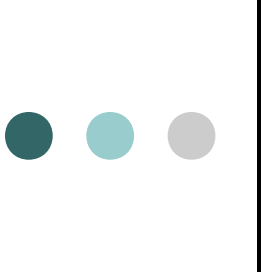
sp^3d^2



Geometry	Hybridization	Orbitals
Linear	sp	
Tetrahedral	sp^3	
Square planar	dsp^2	
Octahedral	d^2sp^3	



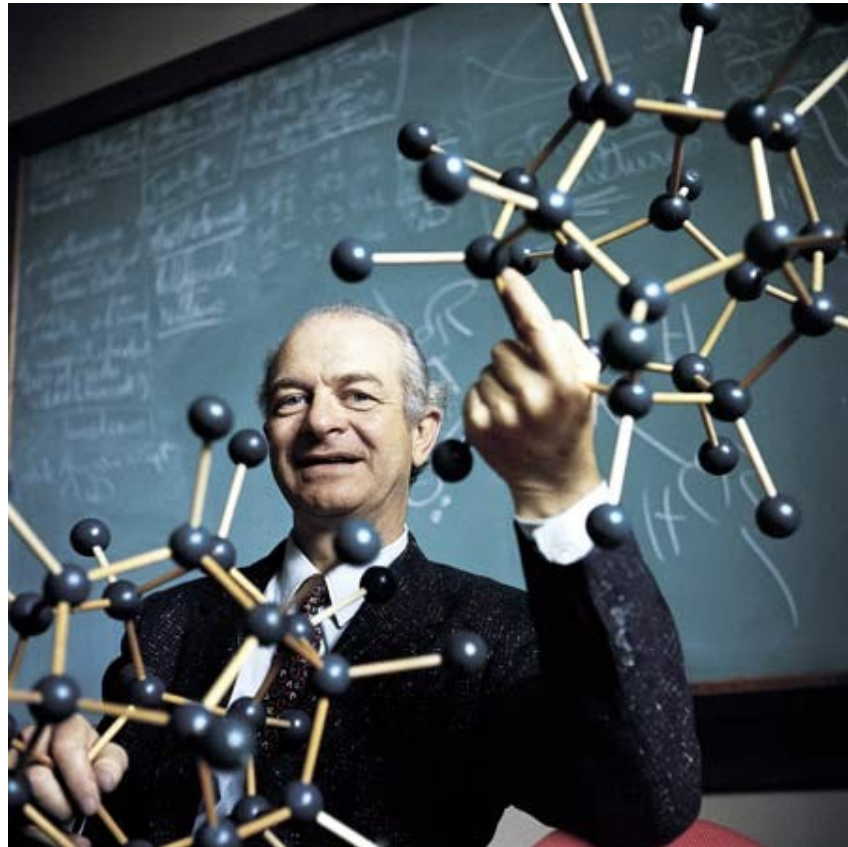
VALENCE BOND THEORY



THEORIES OF BONDING IN COORDINATION COMPOUNDS

- Valence bond theory
- Crystal field theory
- Molecular orbital theory

LINUS PAULING



**He developed
valence bond theory.**

Notable awards Nobel Prize in Chemistry (1954)
Nobel Peace Prize (1962)
Lenin Peace Prize (1968-1969)



POSTULATES OF V.B.THEORY

- According to this theory
- The central metal atom or ion in the complex makes available a number of empty orbitals for the formation of coordinate bonds with suitable ligands.
- The appropriate atomic orbitals (s,p and d) of the metal hybridise to give a set of new orbitals of equivalent energy, called hybrid orbitals.
- The d-orbitals involved in the hybridisation may be either inner (n-1) d-orbitals or outer (nd) orbitals.
- Each ligand has at least one orbital (of donor atom) containing a lone pair of electrons.
- The empty hybrid orbitals of metal ion overlap with the filled orbitals of the ligand to form a covalent sigma bond (L \longrightarrow M). The bond is also called a coordinate bond

APPLICATIONS OF VALENCE BOND THEORY

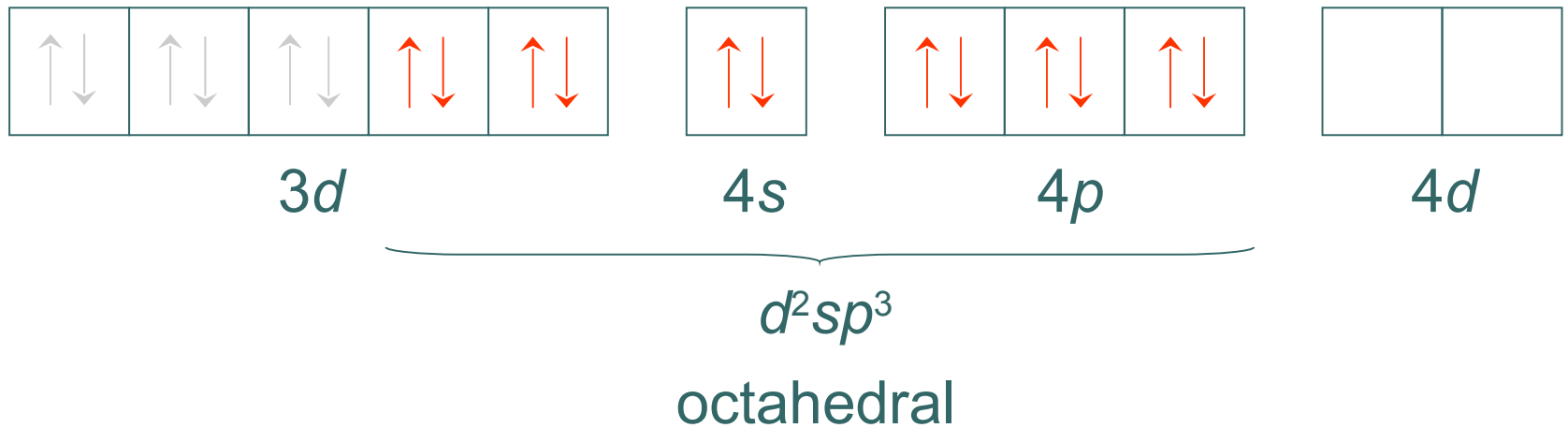
Valence Bond Theory

..

Example 1: $[\text{Co}(\text{NH}_3)_6]^{3+}$

Co [Ar] $3d^7 4s^2$

Co³⁺ [Ar] $3d^6$



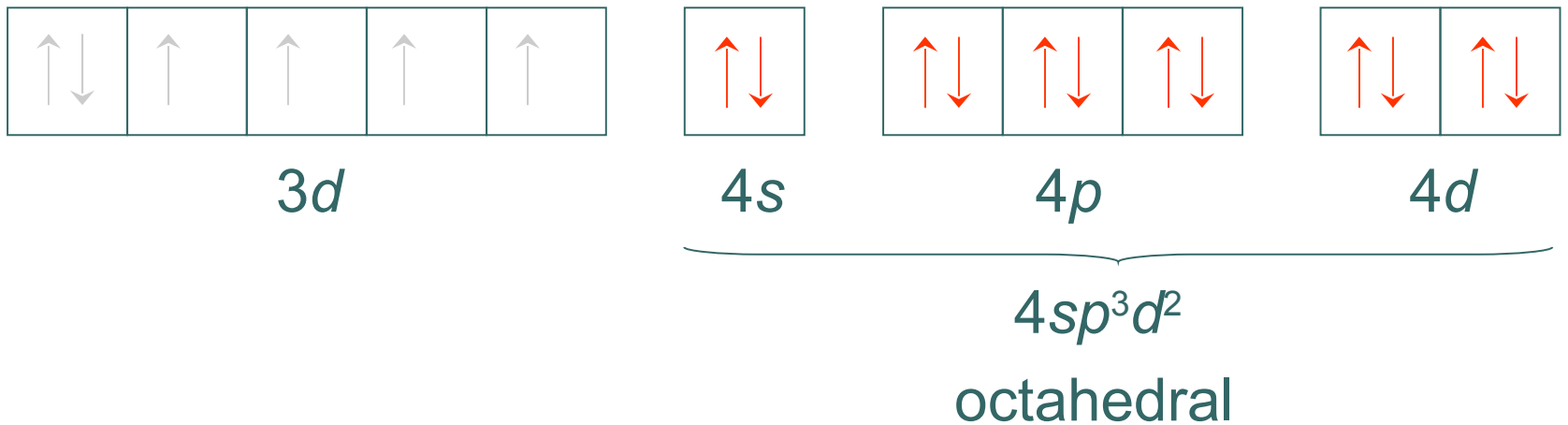
if complex is diamagnetic

Valence Bond Theory

Example 2: $[\text{CoF}_6]^{3-}$

Co $[\text{Ar}] 3d^7 4s^2$

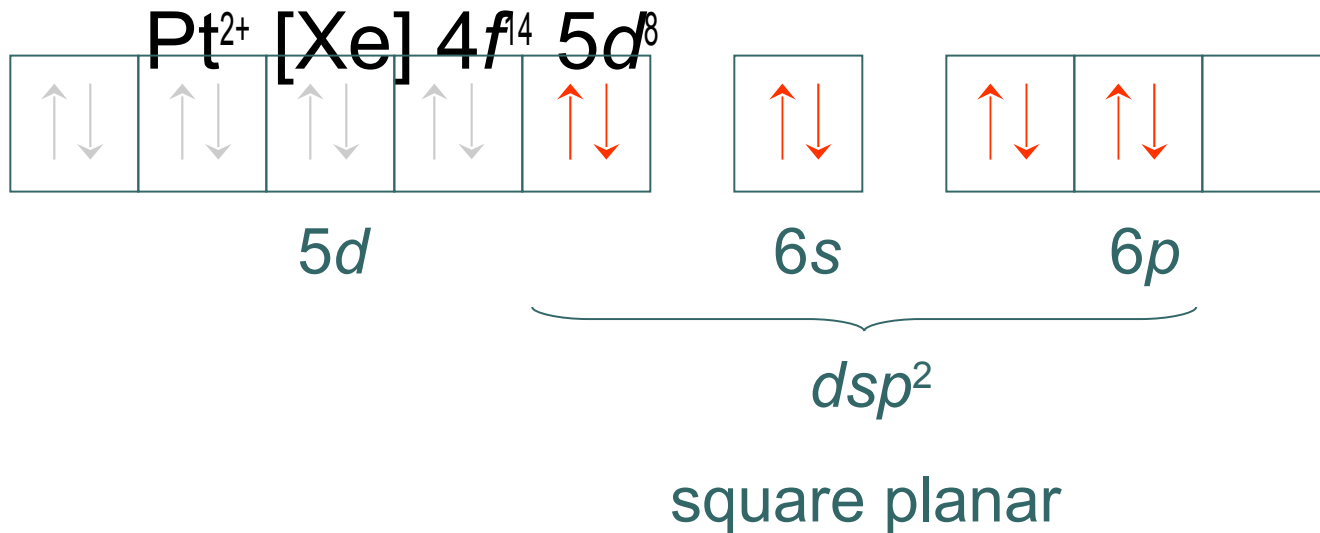
Co^{3+} $[\text{Ar}] 3d^6$



if complex is paramagnetic

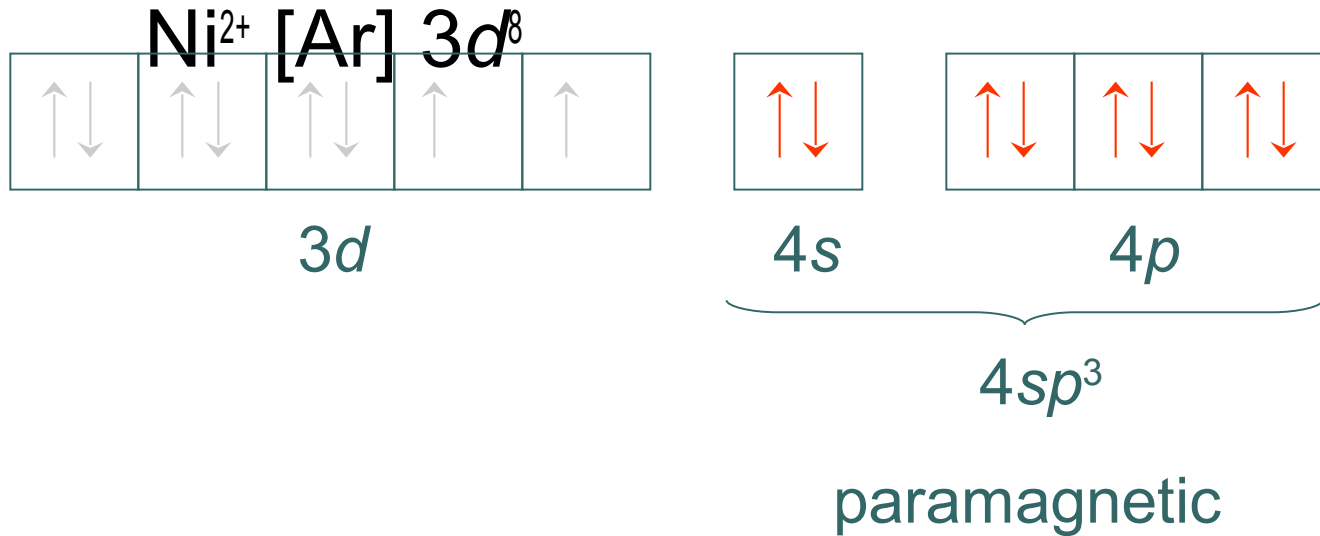
Valence Bond Theory

Example 3: $[\text{PtCl}_4]^{2-}$, diamagnetic

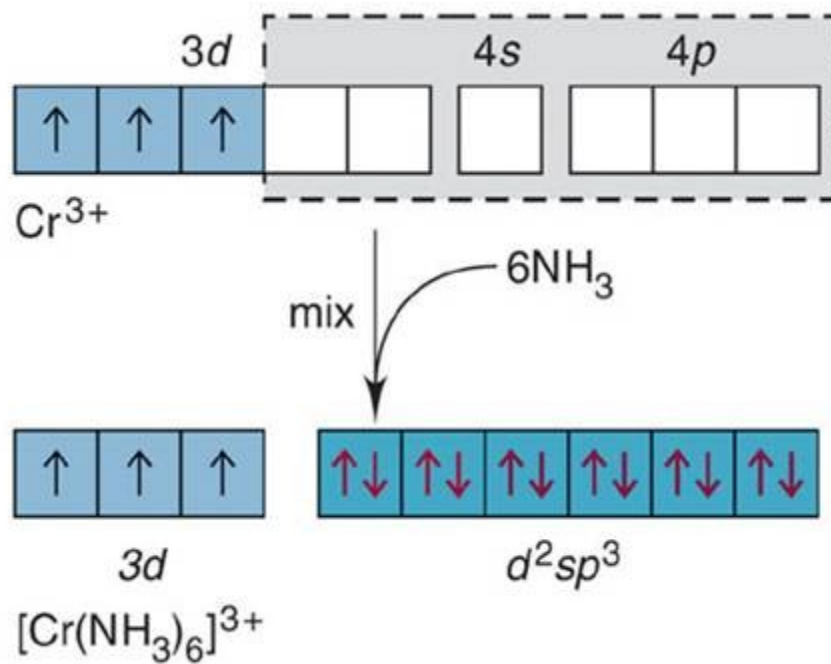
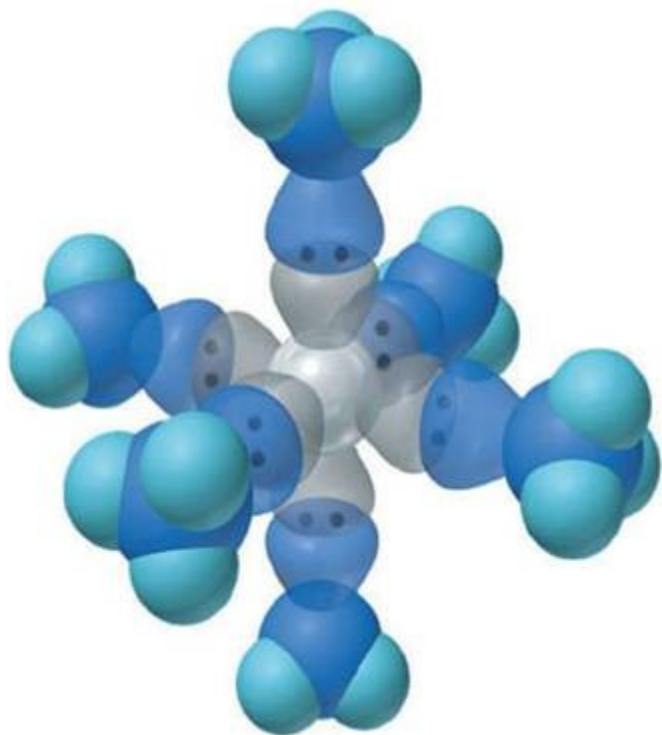


Valence Bond Theory

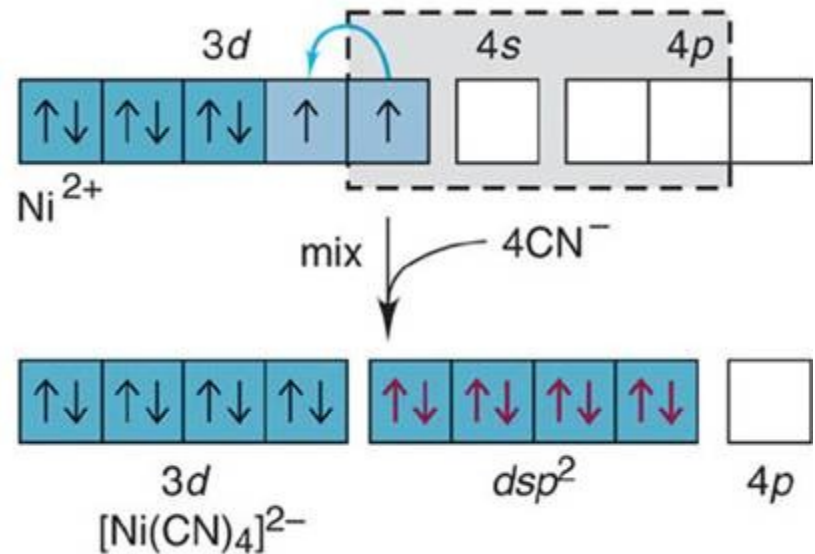
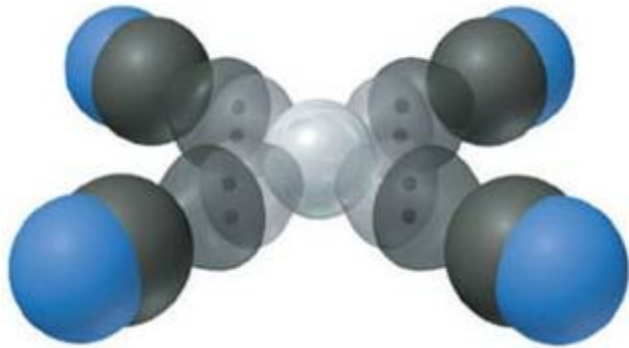
Example 4: $[\text{NiCl}_4]^{2-}$, tetrahedral



Hybrid orbitals and bonding in the octahedral $[\text{Cr}(\text{NH}_3)_6]^{3+}$ ion.

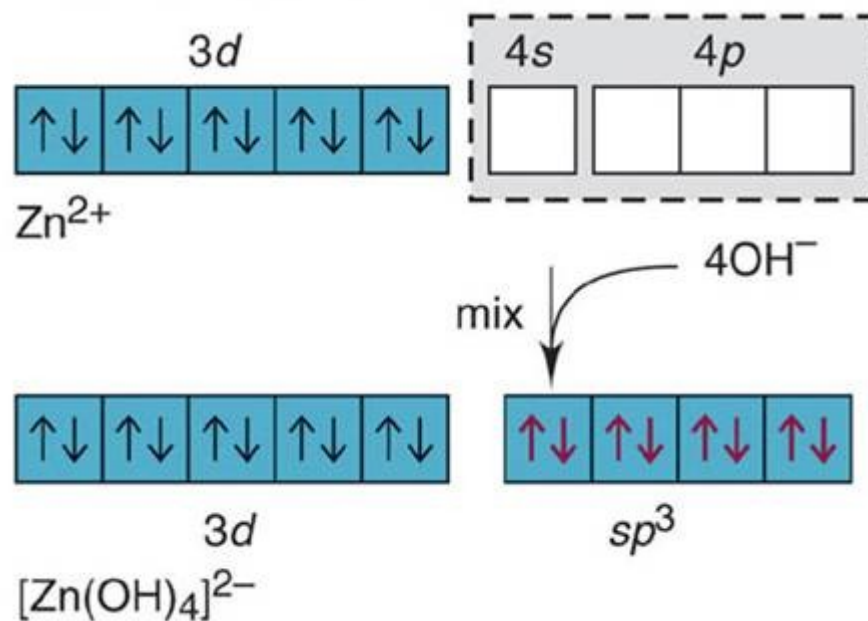
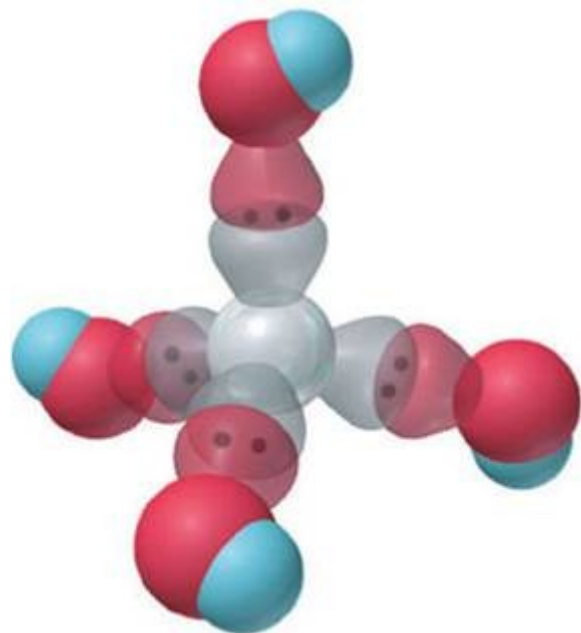


Hybrid orbitals and bonding in the square planar $[\text{Ni}(\text{CN})_4]^{2-}$ ion



The 3d metal electrons are unhybridized thus diamagnetic and the ligand electrons fit into the leftover hybridized dsp^2 orbitals of the metal. $\text{CN}=4$ and square planar.

Hybrid orbitals and bonding in the tetrahedral $[\text{Zn}(\text{OH})_4]^{2-}$ ion.





DRAWBACKS OF VALENCE BOND THEORY

- It provides only qualitative explanations for complexes
- It does not explain the electronic spectra of complexes.
- It is unable to predict the relative stabilities of different ligands
- It does not explain the colour of complexes.
- It does not take into account the splitting of **d**- energy level
- It does not predict the relative stabilities of different structures