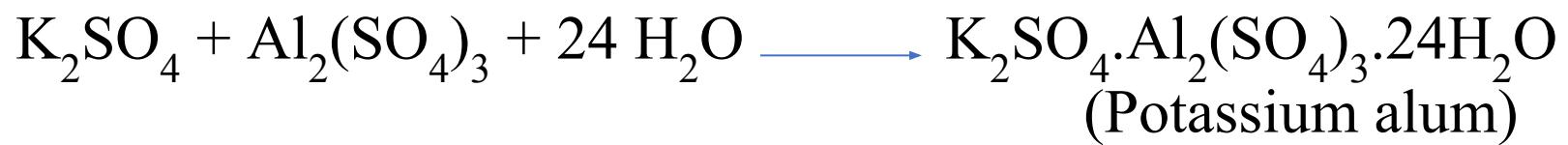


COORDINATION NUMBERS AND GEOMETRIES

Dt. 22/23-11-2021

Double salts and coordination compounds

Addition compounds are formed when stoichiometric amounts of two or more stable compounds join together

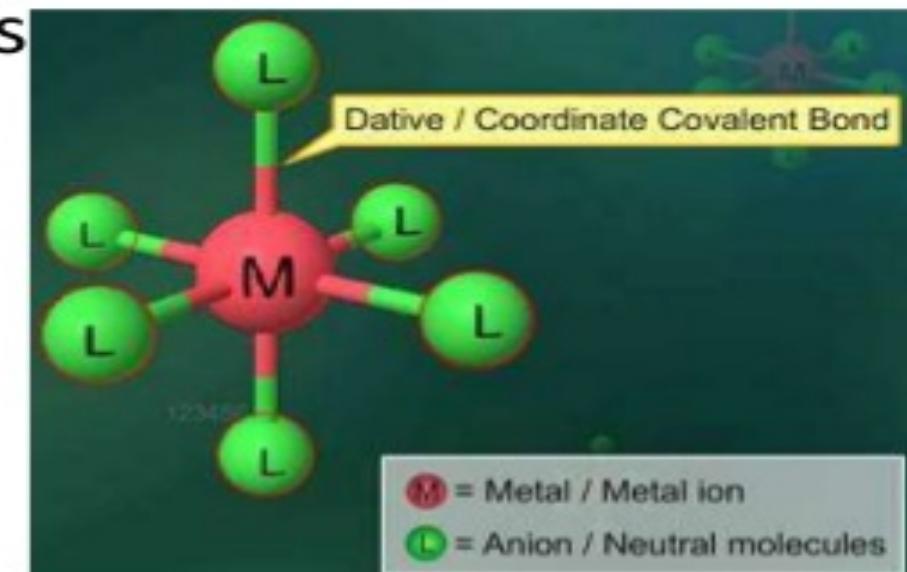


Two types:

1. Double salts: Those which lose their identity in solution
2. Complexes: Those which retain their identity in solution

Coordination compound

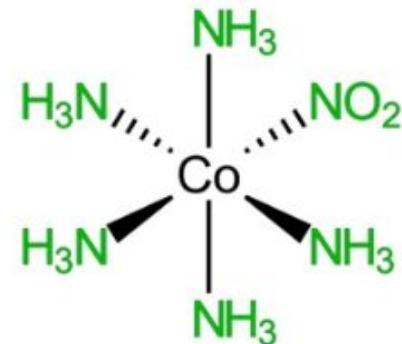
- Complex compounds are a special class of compounds in which the metal atoms (or) ions are bound to a number of anions (or) neutral molecules.
- In modern terminology, these compounds are called coordination compounds
- Coordination compounds (or) complex compounds are a type of addition compounds.



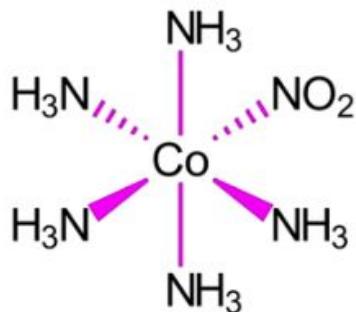
Coordination Compounds



- central **metal ion** (Lewis acid)
- some **ligands** (Lewis bases)

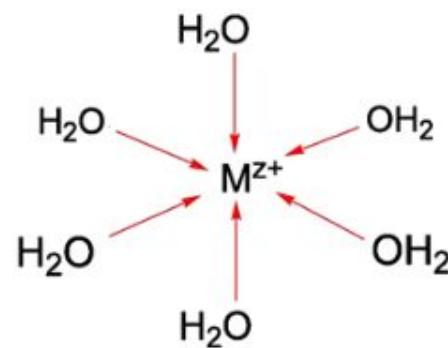


- some **ligands** (Lewis bases)
- can be **atoms/molecules/ions**

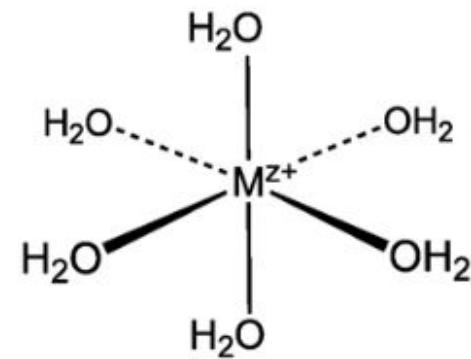


- some **ligands** (Lewis bases)
- coordinate **covalent bond/dative bond**

Coordination Compounds

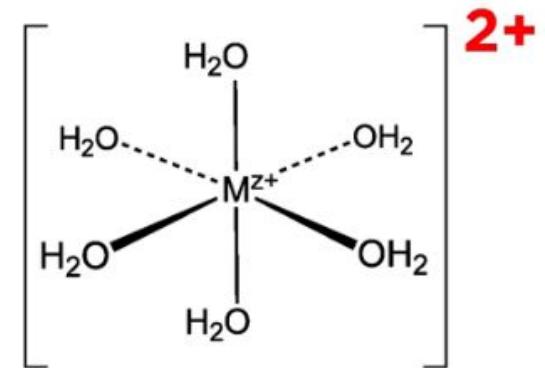


Octahedral Complex



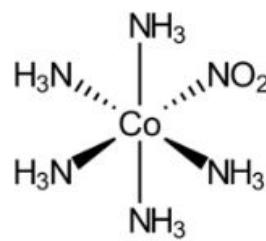
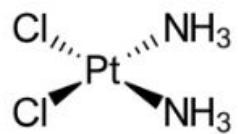
coordinate covalent bonds
both electrons come from ligand

Coordination Compounds



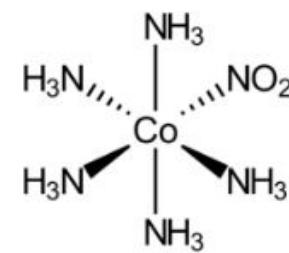
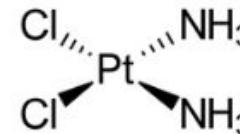
coordination sphere

Coordination Compounds



coordination number

number of donor atoms bound to the central atom



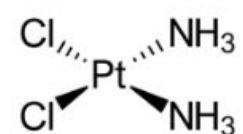
monodentate ligands

interact with the central atom through one atom

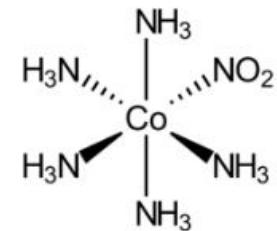
2



4

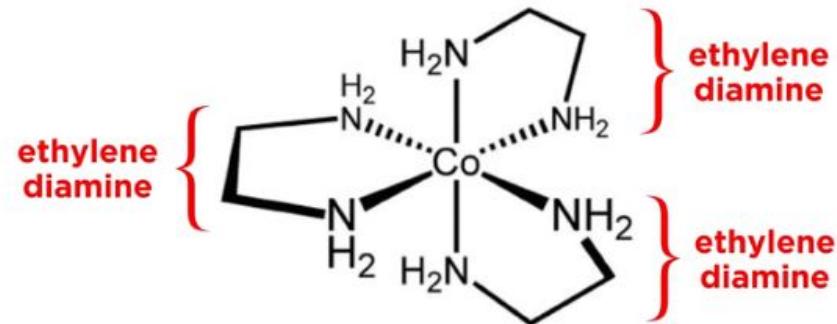


6



coordination number

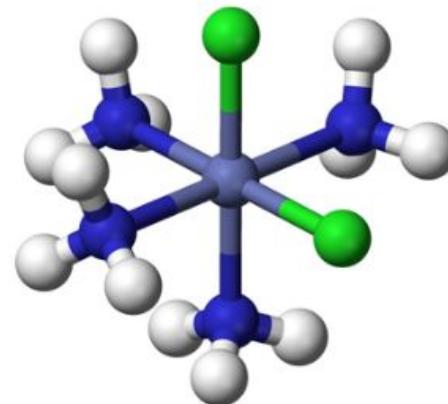
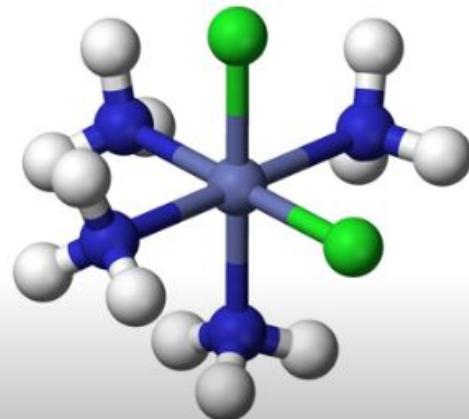
number of donor atoms bound to the central atom



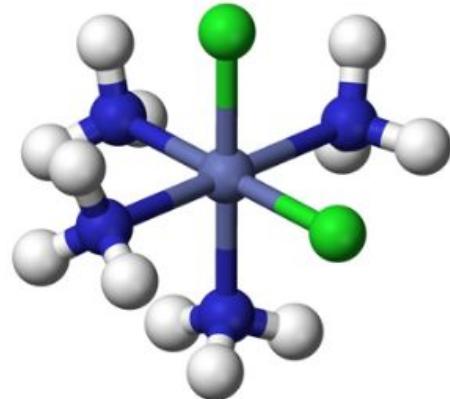
bidentate ligands

interact with the central atom through two atoms

Coordination Compounds

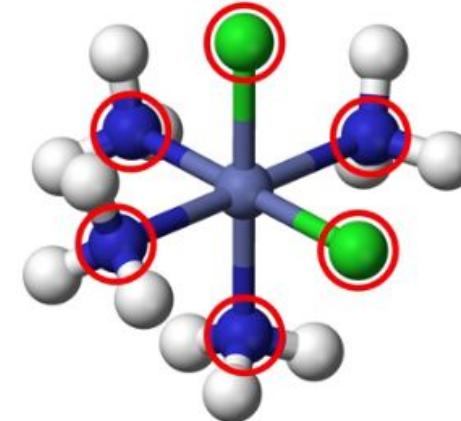


What determines this geometry?



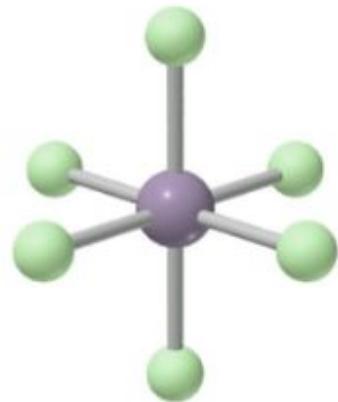
geometry is determined by coordination number

6

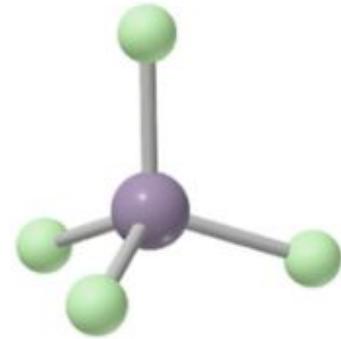


geometry is determined by coordination number

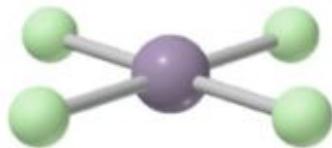
Coordination Compounds



octahedral
(6)



tetrahedral
(4)



square planar
(4)

coordination
compounds



- ✗ VSEPR theory
- ✗ valence bond theory
- ✓ crystal field theory

Geometry and bonding pattern will be explained by using Crystal Field Theory

Werner's main Study

Primary Valencies



Secondary Valencies

Normally fixed for a particular ion and oxidation state.

The primary valency in coordination compounds is the number of negative ions which are equivalent to the charge on the metal ion.

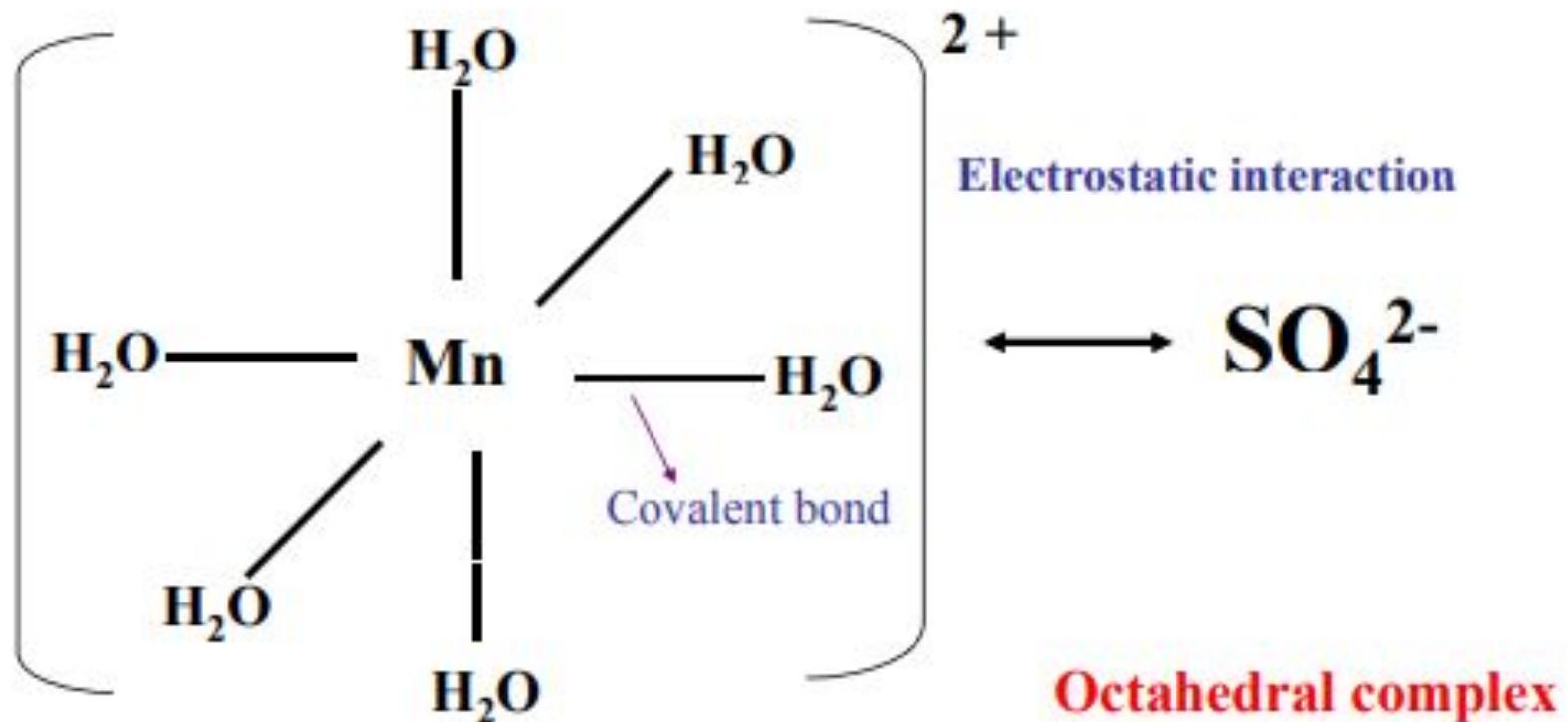
The secondary valency is the number of ions or molecules that are coordinated to the metal ion or it is the number of ligands attached or coordinated to metal ions.

Werner's Theory

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

TABLE 24.1 Properties of Some Ammonia Complexes of Cobalt(III)

Original Formulation	Color	Ions per Formula Unit	“Free” Cl ⁻ Ions per Formula Unit	Modern Formulation
CoCl ₃ ·6 NH ₃	Orange	4	3	[Co(NH ₃) ₆]Cl ₃
CoCl ₃ ·5 NH ₃	Purple	3	2	[Co(NH ₃) ₅ Cl]Cl ₂
CoCl ₃ ·4 NH ₃	Green	2	1	<i>trans</i> -[Co(NH ₃) ₄ Cl ₂]Cl
CoCl ₃ ·4 NH ₃	Violet	2	1	<i>cis</i> -[Co(NH ₃) ₄ Cl ₂]Cl



Coordination number is 6 (secondary valency)

Mn^{2+} ————— Central metal ion (lewis acid)

H_2O ————— Ligand (Lewis base)

Types of Ligands

Monodentate ligands

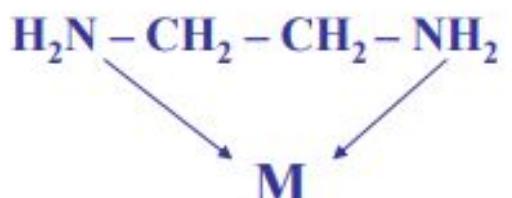
Donate one pair of electrons to a central metal ion.

e.g. Cl⁻, Br⁻, I⁻, NH₃, H₂O

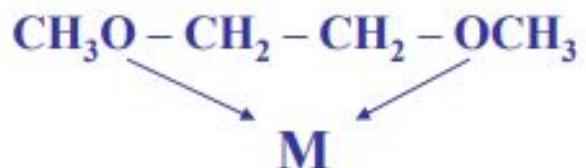
Bidentate ligands

They have two donor atoms

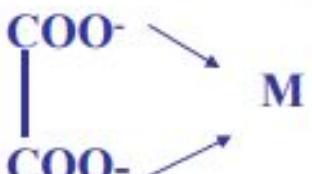
Ethylenediamine (en)



Dimethyl glycol (glyme)

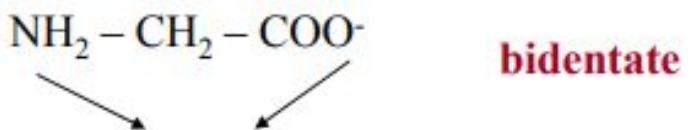


Oxalate ion (oxalato)

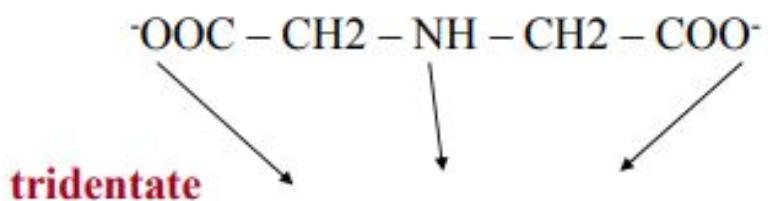


More Examples

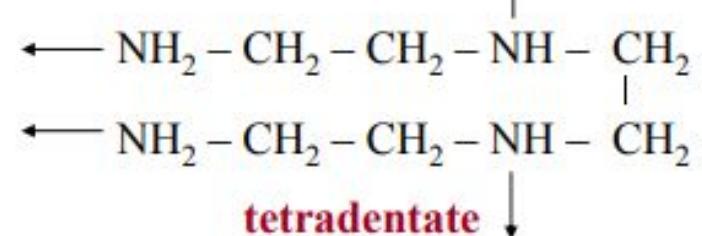
Glycinato (gly)



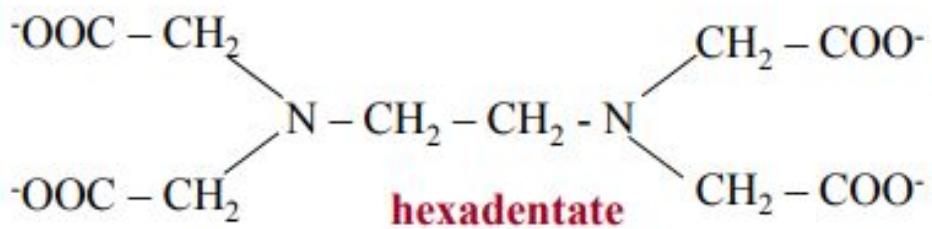
Iminodiacetato (imda)



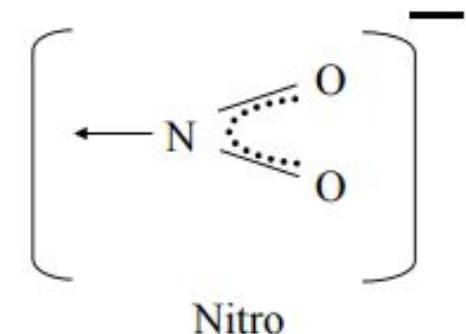
Triethylenetetramine (tren)



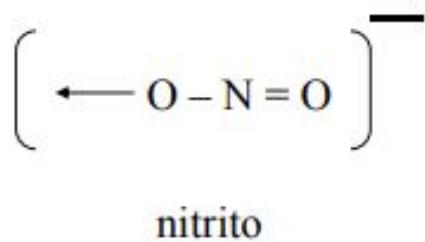
Ethylenediamine
tetraacetate (edta)



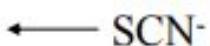
Ambidentate Ligands



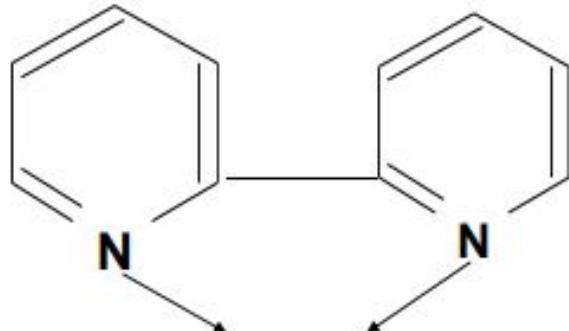
Nitro



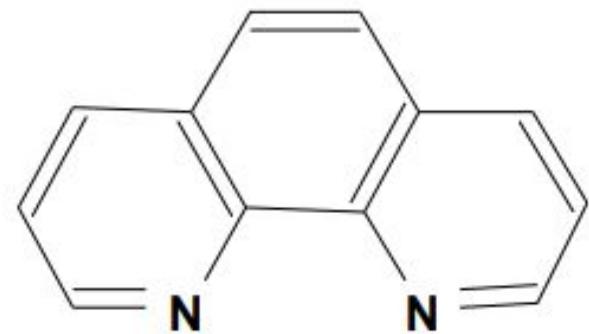
nitrito



Organic Ligands



2, 2'-Bipyridine (bpy)

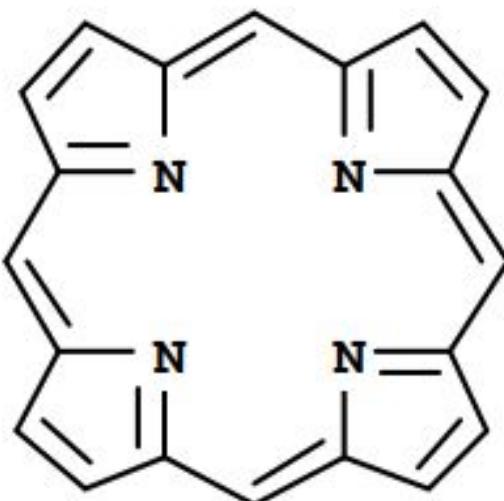


1,10 – Phenanthroline (phen)

Alkyl groups as ligands

CH_3 (methyl), CH_3CH_2 (ethyl), C_6H_5 (Phenyl)

Macrocyclic ligands



Porphyrin

tetradeятate

Nomenclature of Transition metal Compounds

A. Writing the name of the complex compound

1. Designation of ligands

(a) Anionic ligands end with ‘o’

NO_2^-	nitro,	CN^-	cyano
Cl^-	chloro,	NO_3^-	nitrato

(b) Organic ligands retained their names

Pyridine (py) or ethylenediamine (en)

alkyl groups: methyl, phenyl

(c) Special names

H_2O (aqua), NO (nitrosyl), CO (carbonyl), NH_3 (ammine)

2. Designation of metal

- (a) Cationic and neutral complexes end in the english name followed by the oxidation state of the metal in brackets.
e.g. nickel(II) or iron(II).

- (b) Anionic complexes have the latin name of the metal
ferrate(), Stannate ()
Cuprate (), Argentate ()

3. Numerical prefixes

- (a) For two similar ligands di or bis
(b) three similar ligands tri or tris
(c) four similar ligands tetra or tetrakis etc.

3. Order of listing

The ligands are to be written in alphabetical order (irrespective of charge)



dichlorotetraamminecobalt(III) chloride. *wrong*

tetraamminedichlorocobalt(III) chloride. *right*

A. Writing the formulae of the complex compound

1. First central metal atom , then anionic ligands and then neutral ligands (Cl⁻,NH₃)



Rules for naming:

- 1. The positive ion is named first followed by the negative ion**
- 2. The ligands are quoted in alphabetical order followed by the metal**
- 3. The complex ion should be enclosed by square brackets. The order of ligands is negative, neutral and then positive**
- 4. If there are several ligands of the same kind, the prefixes such as di, tri, tetra, etc. are used to show the number of that ligands**
- 5. The oxidation state of metal is shown by a Roman numeral in brackets following its name (without any space)**
- 6. Complex positive ion and neutral molecules have no special ending, but complex negative ions end in –ate.**

7. Sometimes a ligand can be attached through different atoms.

Ex: M-NO₂ is called nitro and M-ONO is called nitrito.

Similarly, M-SCN as thiocyanato and M-NCS as isothiocyanato

8. If a complex contains two or more metal atoms, it is termed as polynuclear. The bridging ligands which link the two metal atoms together are indicated by the prefix μ -.

If there are two or more bridging groups of the same kind, this is indicated by di- μ , tri- μ etc.

If a bridging group bridges more than two metal atoms, it is shown as $\mu 3$, $\mu 4$ or $\mu 5$, to indicate how many atoms it is bonded to.

Examples



hexanitro cobalt (III) chloride



tetra amminecopper(II)sulphate



bis pyrridinedichlorocopper(II)

dichloro dipyridine copper (II)

dichloro bis (pyridine) copper (II)



cis-diamminedichloroplatinum(II)

More Examples:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$: Hexamminecobalt(III) chloride

$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$: Triaminetrinitrocobalt(III)

$[\text{CoCl.CN.NO}_2.(\text{NH}_3)_3]$: Triamminechlorocyanonitrocobalt(III)

$\text{K}_4[\text{Fe}(\text{CN})_6]$: Potassium hexacyanoferrate(II)

$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$: Potassium pentacyanonitrosylferrate(II)

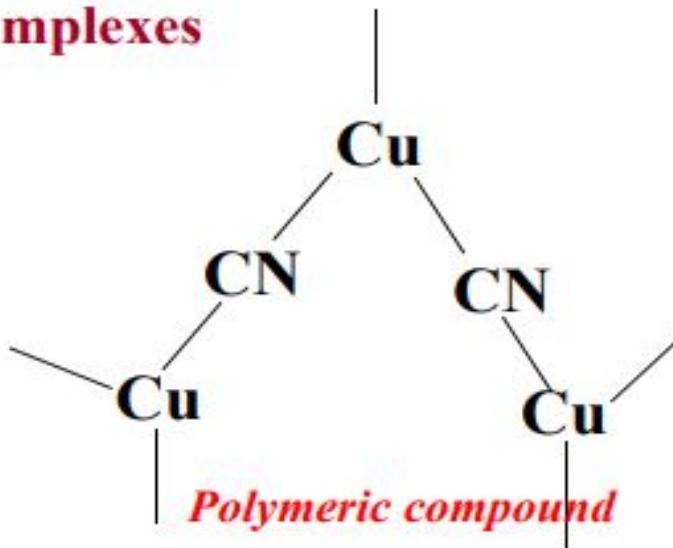
$[\text{Pt}(\text{py})_4] [\text{PtCl}_4]$: Tetrapyridineplatinum(II) tetrachloroplatinate(II)

$[\text{CuCl}_2(\text{CH}_3\text{NH}_2)_2]$: Dichlorobis(methylamine)copper(II)

Geometry of complexes

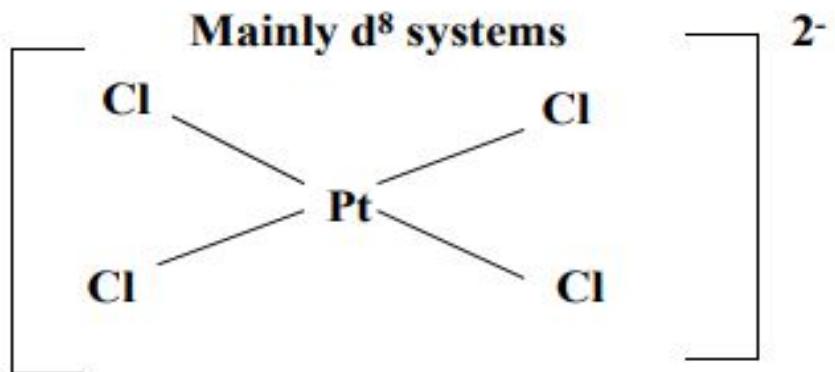
Coordination No.2

(linear)

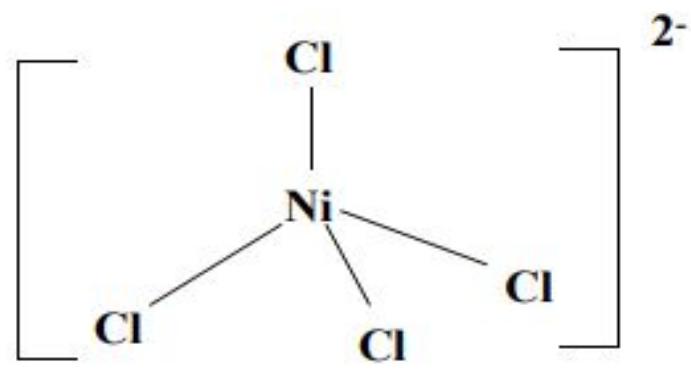


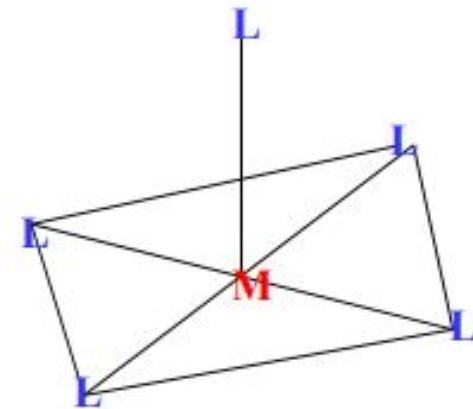
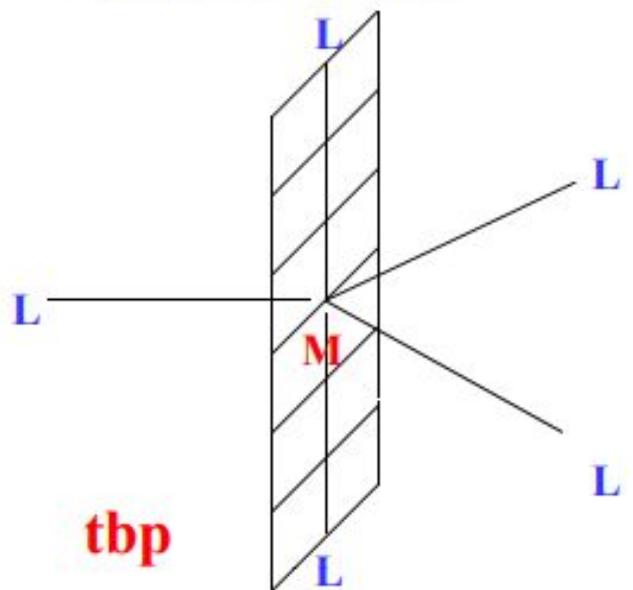
Coordination no. 4 (large ligands)

(a) Square planar

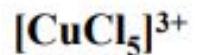


(b) Tetrahedral



Coordination no. 5**Sq. pyramidal**

$[\text{Ni}(\text{CN})_5]^{2-}$ shows both structures (little energy difference)



TBP structure

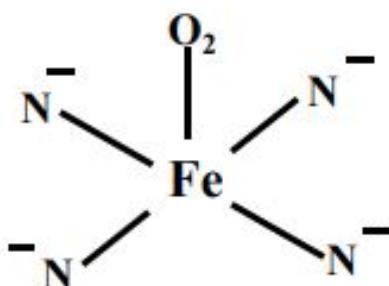


TBP structure

Biologically important molecules

Haemoglobin,

Oxomyoglobin

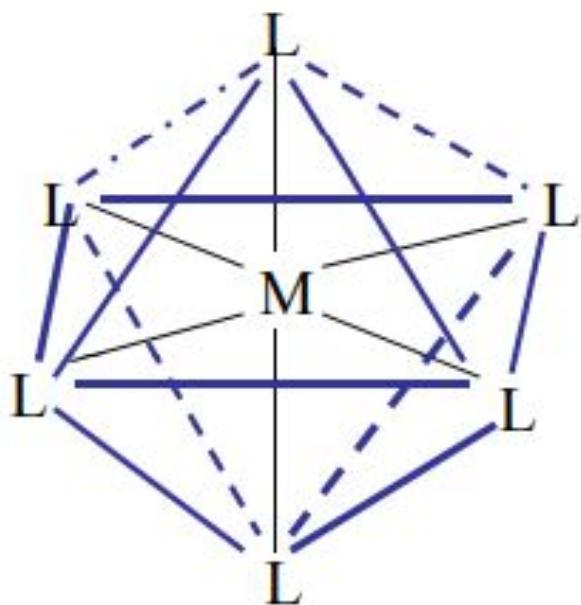


Coordination no. 6

ML₆ octahedral complex

Most important from d¹ to d⁹

e. g. [Cr(NH₃)₆]³⁺, [Fe(CN)₆]³⁻



- **Hexagonal planar Geometry:** Unknown for first row transition metal ions, although the arrangement of six groups in a plane is found in some higher coordination number geometries.
- **Trigonal prism Geometry:** Most trigonal prismatic compounds have three bidentate ligands such as dithiolates or oxalates and few are known for first row transition metal ions.
- **Octahedral (Oh):** The most common geometry found for first row transition metal ions, including all aqua ions. In some cases distortions are observed and these can sometimes be explained in terms of the Jahn-Teller Theorem.

Coordination Number 8

- Dodecahedron (D_{2d}) Geometry
- Cube (O_h) Geometry
- Square antiprism (D_{4d}) Geometry
- Hexagonal bipyramidal (D_{6h}) Geometry

Coordination Number 9

- Three-face centered trigonal prism (D_{3h}) Geometry

Coordination Number 10

- Bicapped square antiprism (D_{4d}) Geometry

Coordination Number 11

- All-faced capped trigonal prism (D_{3h}) Geometry: This is not a common stereochemistry.

Coordination Number 12

- cubooctahedron (O_h) Geometry