INDIAN INSTITUTE OF TECHNOLOGY PATNA
DEPARTMENT OF CHEMISTRY

CH 103

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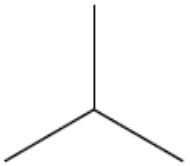
Coordination number and geometry

Three-coordination

trigonal plane

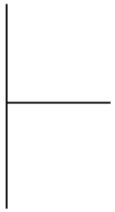


TP-3

trigonal pyramid

TPY-3

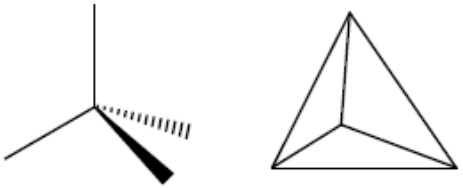
T-shape



TS-3

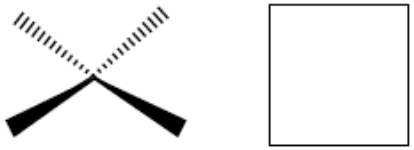
Four-coordination

tetrahedron



T-4

square plane

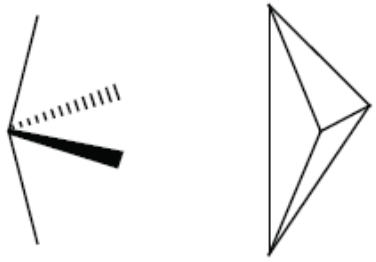


SP-4

square pyramid

SPY-4

see-saw

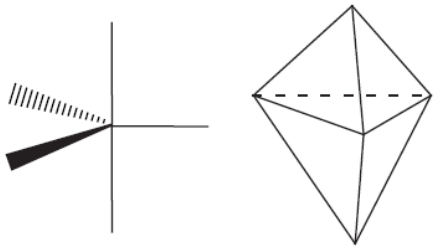


SS-4

Coordination number and geometry

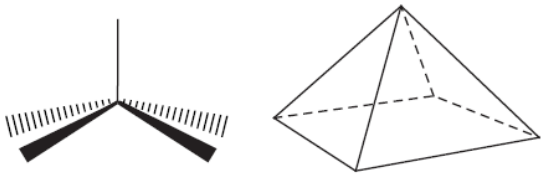
Five-coordination

trigonal bipyramid



TBPY-5

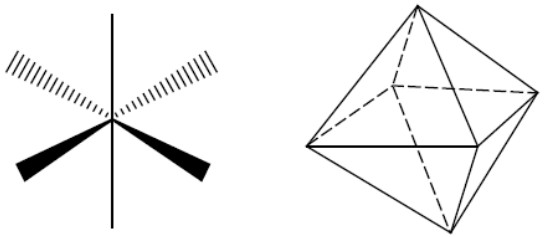
square pyramid



SPY-5

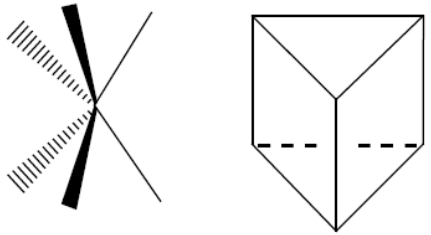
Six-coordination

octahedron



OC-6

trigonal prism

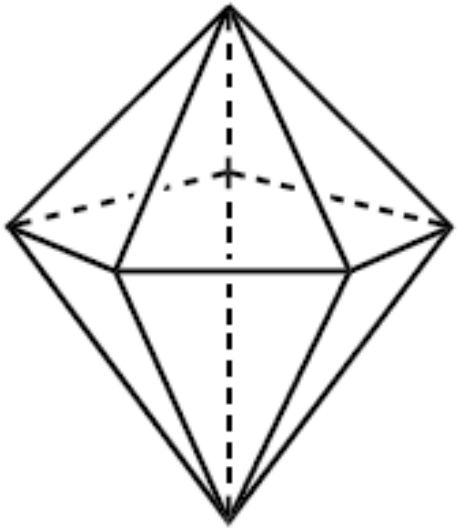


TPR-6

Coordination number and geometry

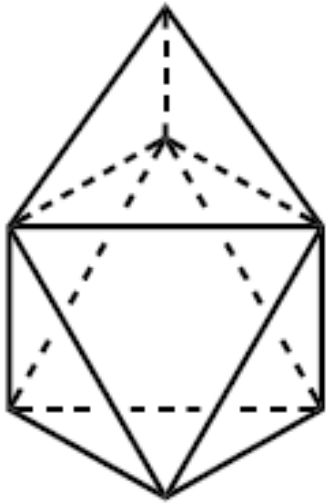
Seven-coordination

pentagonal bipyramid



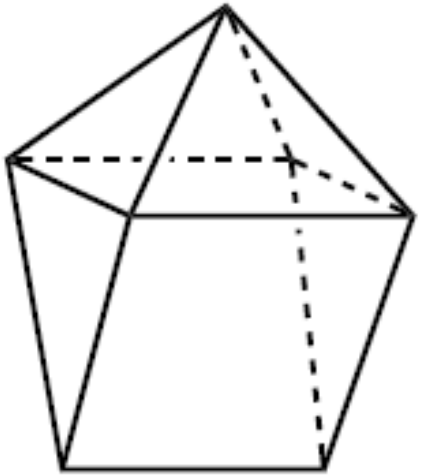
PBPY-7

octahedron, face monocapped



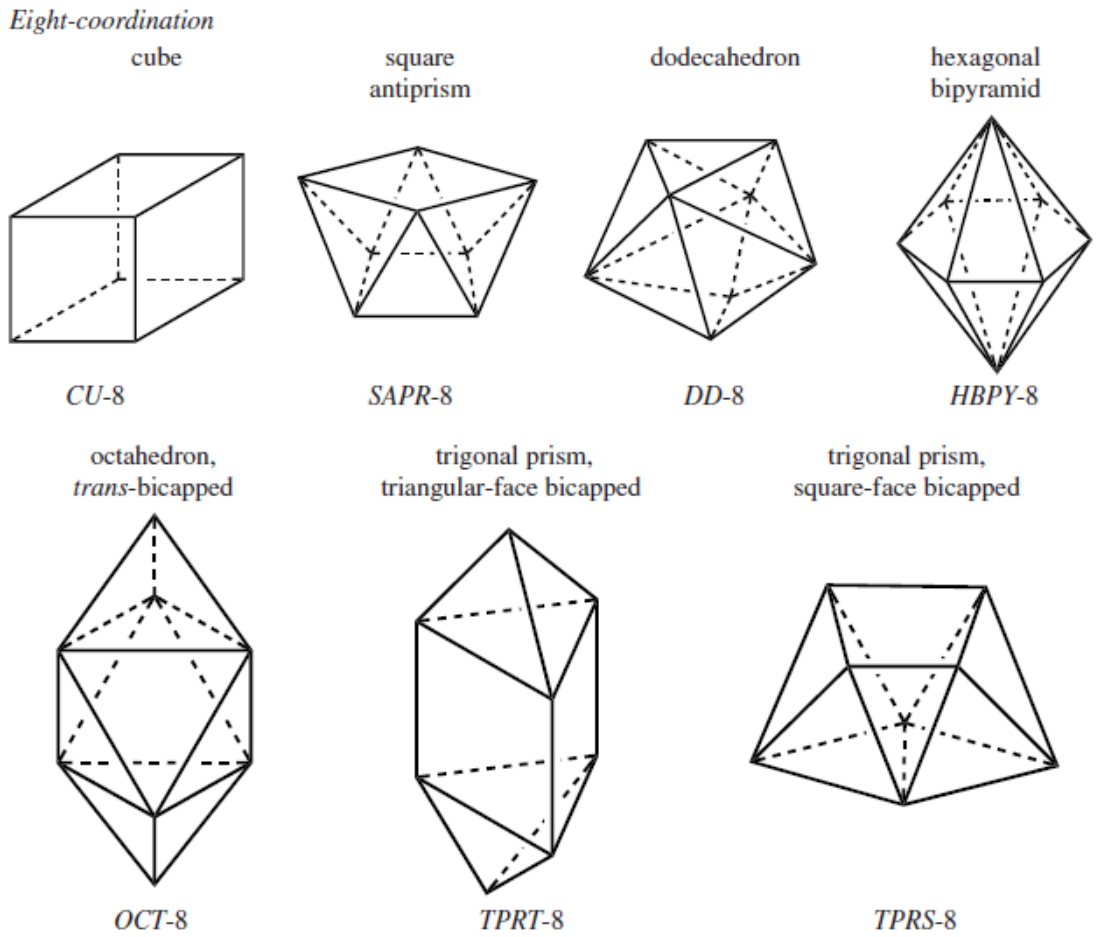
OCF-7

trigonal prism, square-face monocapped



TPRS-7

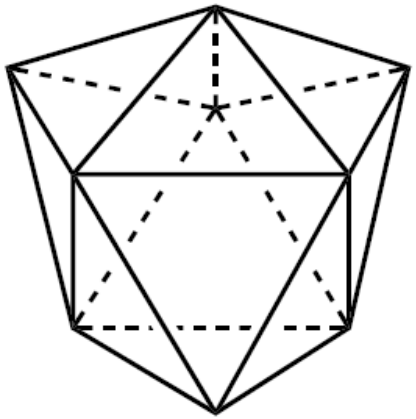
Coordination number and geometry



Coordination number and geometry

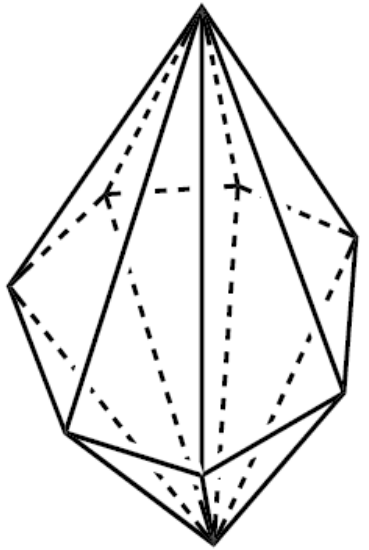
Nine-coordination

trigonal prism,
square-face tricapped



TPRS-9

heptagonal
bipyramid



HBPY-9

Coordination nomenclature

- an additive nomenclature
- To name a coordination compound, no matter whether the complex ion is the cation or the anion, **always name the cation before the anion**

Example:

1. Addition of ligands to a central atom:

$$Ni^{2+} + 6H_2O \longrightarrow [Ni(OH_2)_6]^{2+}$$

Addition of ligand names to a central atom name:

hexaaquanickel(II)

Naming Coordination Compounds

- **ligand** names are listed **before** the name(s) of the **central atom**
- **no spaces** are left between parts of the name that refer to the same coordination entity,
- **ligand names** are listed in **alphabetical order** (multiplicative prefixes indicating the number of ligands are not considered in determining that order),
- Names of anionic coordination entities are furthermore given the ending 'ate'.

1. $[CoCl(NH_3)_5]Cl_2$
   pentaamminechloridocobalt(2+) chloride
2. $[AuXe_4]^{2+}$
   tetraxenonidogold(2+)

$K_4[Fe(CN)_6]$
potassium hexacyanidoferrate(II)

Number of ligands

- Greek prefixes used to designate the number of each type of ligand in the complex ion.

Number	Prefix	Number	Prefix	Number	Prefix
1	mono	5	penta (pentakis)	9	nona (ennea)
2	di (bis)	6	hexa (hexakis)	10	deca
3	tri (tris)	7	hepta	11	undeca
4	tetra (tetrakis)	8	octa	12	dodeca

Number of ligands

- Two kinds of multiplicative prefix are available
  - Prefixes di, tri, etc. are generally used with the names of simple ligands. Enclosing marks are not required.
  - Prefixes bis, tris, tetrakis, etc. are used with complex ligand names and in order to avoid ambiguity, **enclosing marks must be placed around the multiplicand.**
  - **for $(NH_3)_2$**
  - **diammine, or**
  - **bis(methylamine)**

Representing ligands in names

- Names of anionic ligands: modified to end in ‘o’.
- In general, if the anion name ends in ‘ide’, ‘ite’ or ‘ate’, the final ‘e’ is replaced by ‘o’, giving ‘ido’, ‘ito’ and ‘ato’, respectively.

  – **alcoholates, thiolates, phenolates, carboxylates, phosphanes, etc.**

- neutral and cationic ligands, including organic ligands, are used without modification

naming the central metal

- If the complex ion is a cation, the metal is named same as the element.
  - Co in a complex cation is called cobalt.
- If the complex ion is an anion, the name of the metal ends with the suffix –ate.
  - Co in a complex anion is called cobaltate.
- For some metals, the Latin names are used in the complex anions
  - Fe is called ferrate (not ironate).

Name of Metal	Name in an Anionic Complex
Iron	Ferrate
Copper	Cuprate
Lead	Plumbate
Silver	Argenate
Gold	Aurate
Tin	Stannate

Charge numbers and oxidation numbers

- **The oxidation number of the central atom**: a Roman numeral appended in parentheses to the central atom name (including the ending 'ate', if applicable)
- Arabic zero indicates the oxidation number zero.
- Alternatively, the charge on a coordination entity may be indicated.
- The net charge is written in arabic numbers, with the number preceding the charge sign, and enclosed in parentheses.
- It follows the name of the central atom (including the ending 'ate', if applicable) without the intervention of a space.

$K_4[Fe(CN)_6]$
potassium hexacyanidoferrate(II), or
potassium hexacyanidoferrate(4−), or
tetrapotassium hexacyanidoferrate

$[Co(NH_3)_6]Cl_3$
hexaamminecobalt(III) chloride

$[CoCl(NH_3)_5]Cl_2$
pentaamminechloridocobalt(2+) chloride

Exceptions ...

- For historic reasons, some coordination compounds are called by their common names.

- For example, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ are named ferricyanide and ferrocyanide respectively

- $Fe(CO)_5$ is called iron carbonyl.

Formulae of coordination compounds

- A (line) formula of a compound:
  - provides basic information about the constitution of the compound in a concise and convenient manner
  - The central atom symbol is listed first
  - The ligand symbols are then listed in alphabetical order
  - single letter symbols precede two letter symbols.
  - Example: CO precedes Cl

sodium amminebromidochloridonitrito-κ*N*-platinate(1−)

$Na[PtBrCl(NH_3)(NO_2)]$

Formulae of coordination compounds

- Use of enclosing marks
  - **Square brackets: []**
  - formula for the entire coordination entity, whether charged or not
  - **Parentheses: ()**
  - polyatomic ligands formulae and abbreviations of ligands.

$Na[PtBrCl(NH_3)(NO_2)]$
sodium amminebromidochloridonitrito-κ*N*-platinate(1−)

$[Fe(CNMe)_6]Br_2$
hexakis(methyl isocyanide)iron(II) bromide

$[Co(en)_3]Cl_3$
tris(ethane-1,2-diamine)cobalt(III) trichloride

Ionic charges and oxidation numbers

- If the **formula** of a charged coordination entity is to be written **without any counterion**, the charge is indicated outside the square bracket as a right superscript (number before the sign).

- The **oxidation number** of a central atom *may be* represented by a Roman numeral, which should be placed as a right superscript on the element symbol.

1. $[PtCl_6]^{2-}$
2. $[Cr(OH_2)_6]^{3+}$
3. $[Cr^{III}(NCS)_4(NH_3)_2]^{-}$
4. $[Cr^{III}Cl_3(OH_2)_3]$
5. $[Fe^{-II}(CO)_4]^{2-}$

Specifying donor atoms

- Cases where specification of the donor atom is not required for a ligand that can bind to a central atom in more than one way

  - monodentate O-bound carboxylate groups
  - monodentate C-bound cyanide (ligand name ‘cyanido’)

  - monodentate C-bound carbon monoxide (ligand name ‘carbonyl’)
  - monodentate N-bound nitrogen monoxide (ligand name ‘nitrosyl’).

Specifying donor atoms

- The kappa convention
  - **Single ligating atoms** are indicated by the italicized element symbol preceded by a Greek kappa, κ
  - Placing the symbol κ
  - κ placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found

$[NiBr_2(Me_2PCH_2CH_2PMe_2)]$

dibromido[ethane-1,2-diylbis(dimethylphosphane-κ*P*)]nickel(II)

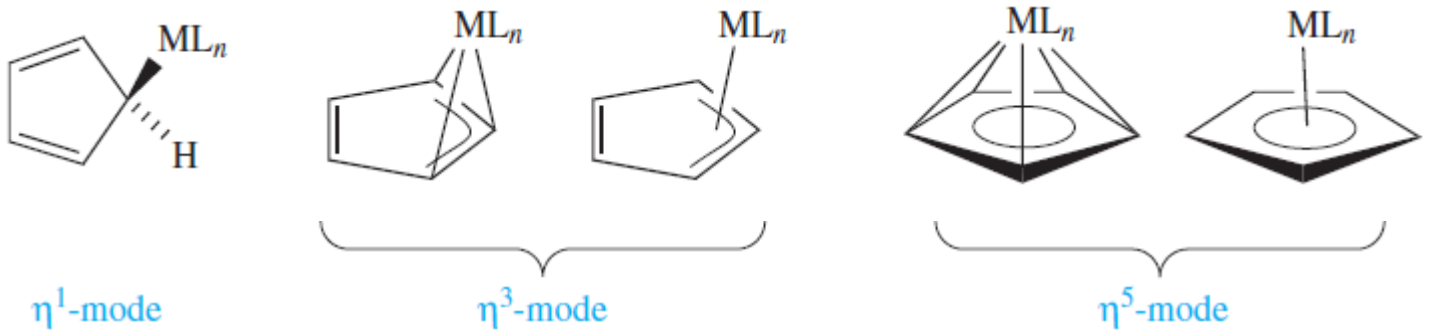
Specifying donor atoms

- The kappa convention
  - thiocyanato-κ*N* for nitrogen-bonded NCS
  - thiocyanato- κ*S* for sulfur-bonded NCS.

  - Nitrogen-bonded nitrite is named nitrito- κ*N*
  - Oxygen-bonded nitrite is named nitrito- κ*O*, as in pentaamminenitrito- κ*O* -cobalt(III)

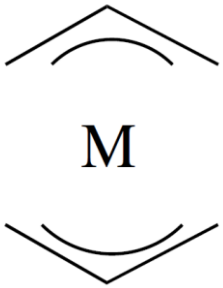
hapticity of a ligand

- The hapticity of a ligand is the number of atoms that are directly bonded to the metal centre



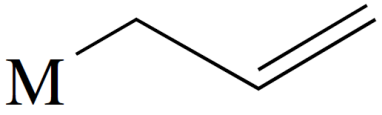
Specifying donor atoms

- The eta (η) convention: ('hapticity')
  - applied in cases where adjacent donor atoms within a given ligand are involved in bonding to a central atom



4 electron donor and anionic

bis-η^3-allyl nickel, or $[Ni(\eta^3\text{-}C_3H_5)_2]$



2 electron donor and anionic

Metal–metal bonds

1. $[Br_4ReReBr_4]^{2+}$
   bis(tetrabromidorhenium)(*Re*—*Re*)(2+)

2. $[(OC)_5\overset{1}{Re}\overset{2}{Co}(CO)_4]$
   nonacarbonyl-1κ^5C,2κ^4C-rheniumcobalt(*Re*—*Co*)