

# CH103: Introductory Chemistry



Instructors: Dr. Debajit Sarma & Dr. Ranganathan Subramanian

Email: [debajit@iitp.ac.in](mailto:debajit@iitp.ac.in)

# INORGANIC CHEMISTRY

# PERIODIC TABLE

<div>Hydrogen H 1.008 1</div>																		<div>Helium He 4.003 2</div>																							
<div>Lithium Li 6.941 3</div>				<div>Beryllium Be 9.012 4</div>														<div>Boron B 10.81 5</div>				<div>Carbon C 12.01 6</div>				<div>Nitrogen N 14.01 7</div>				<div>Oxygen O 16.00 8</div>				<div>Fluorine F 18.99 9</div>				<div>Neon Ne 20.18 10</div>			
<div>Sodium Na 22.99 11</div>				<div>Magnesium Mg 24.31 12</div>														<div>Aluminum Al 26.98 13</div>				<div>Silicon Si 28.09 14</div>				<div>Phosphorus P 30.97 15</div>				<div>Sulfur S 32.07 16</div>				<div>Chlorine Cl 35.45 17</div>				<div>Argon Ar 39.95 18</div>			
<div>Potassium K 39.10 19</div>		<div>Calcium Ca 40.08 20</div>		<div>Scandium Sc 44.96 21</div>		<div>Titanium Ti 47.88 22</div>		<div>Vanadium V 50.94 23</div>		<div>Chromium Cr 52.01 24</div>		<div>Manganese Mn 54.94 25</div>		<div>Iron Fe 55.85 26</div>		<div>Cobalt Co 58.93 27</div>		<div>Nickel Ni 58.69 28</div>		<div>Copper Cu 63.55 29</div>		<div>Zinc Zn 65.39 30</div>		<div>Gallium Ga 69.72 31</div>		<div>Germanium Ge 72.64 32</div>		<div>Arsenic As 74.92 33</div>		<div>Selenium Se 78.96 34</div>		<div>Bromine Br 79.90 35</div>		<div>Krypton Kr 83.80 36</div>							
<div>Rubidium Rb 85.47 37</div>		<div>Sr 87.62 38</div>		<div>Y 88.91 39</div>		<div>Zr 91.22 40</div>		<div>Nb 92.91 41</div>		<div>Mo 95.94 42</div>		<div>Tc 98 43</div>		<div>Ru 101.07 44</div>		<div>Rh 102.91 45</div>		<div>Pd 106.42 46</div>		<div>Ag 107.87 47</div>		<div>Cd 112.41 48</div>		<div>In 114.82 49</div>		<div>Sn 118.71 50</div>		<div>Sb 121.76 51</div>		<div>Te 127.60 52</div>		<div>I 126.91 53</div>		<div>Xe 131.29 54</div>							
<div>Cesium Cs 132.91 55</div>		<div>Ba 137.33 56</div>		<div>LANTHANIDES ▼</div>		<div>Hf 178.49 72</div>		<div>Ta 180.95 73</div>		<div>W 183.84 74</div>		<div>Re 186.21 75</div>		<div>Os 190.23 76</div>		<div>Ir 192.22 77</div>		<div>Pt 195.08 78</div>		<div>Au 196.97 79</div>		<div>Hg 200.59 80</div>		<div>Tl 204.38 81</div>		<div>Pb 207.2 82</div>		<div>Bi 208.98 83</div>		<div>Po 209 84</div>		<div>At 210 85</div>		<div>Rn 222 86</div>							
<div>Francium Fr 223 87</div>		<div>Ra 226 88</div>		<div>ACTINIDES ▼</div>		<div>Rf 261 104</div>		<div>Db 262 105</div>		<div>Sg 266 106</div>		<div>Bh 264 107</div>		<div>Hs 277 108</div>		<div>Mt 268 109</div>		<div>Ds 271 110</div>		<div>Rg 272 111</div>		<div>Cn 285 112</div>		<div>Uut 288 113</div>		<div>Fl 289 114</div>		<div>Uup 294 115</div>		<div>Lv 293 116</div>		<div>Uus 294 117</div>		<div>Og 294 118</div>							

Lanthanum <b>La</b> 138.91 57	Cerium <b>Ce</b> 140.12 58	Praseodymium <b>Pr</b> 140.91 59	Neodymium <b>Nd</b> 144.24 60	Promethium <b>Pm</b> 144.91 61	Samarium <b>Sm</b> 150.36 62	Europium <b>Eu</b> 151.96 63	Gadolinium <b>Gd</b> 157.25 64	Terbium <b>Tb</b> 158.93 65	Dysprosium <b>Dy</b> 162.50 66	Holmium <b>Ho</b> 164.93 67	Erbium <b>Er</b> 167.26 68	Thulium <b>Tm</b> 168.93 69	Ytterbium <b>Yb</b> 173.04 70	Lutetium <b>Lu</b> 174.97 71
Actinium <b>Ac</b> 227.03 89	Thorium <b>Th</b> 232.04 90	Protactinium <b>Pa</b> 231.04 91	Uranium <b>U</b> 238.03 92	Neptunium <b>Np</b> 237.05 93	Plutonium <b>Pu</b> 244.06 94	Americium <b>Am</b> 243.06 95	Curium <b>Cm</b> 247.07 96	Berkelium <b>Bk</b> 247.07 97	Californium <b>Cf</b> 251.08 98	Einsteinium <b>Es</b> 252.08 99	Fermium <b>Fm</b> 257.10 100	Mendelevium <b>Md</b> 258.10 101	Nobelium <b>No</b> 259.10 102	Lawrencium <b>Lr</b> 262.11 103

 ALKALI METAL	 ACTINIDE	 METALLOID	 NOBLE GAS	* SOLID	*** GAS
 ALKALINE EARTH METAL	 TRANSITION METAL	 OTHER NONMETAL	 UNKNOWN	** LIQUID	**** UNKNOWN
 LANTHANIDE	 POST-TRANSITION METAL	 HALOGEN			

# PERIODIC TABLE OF THE ELEMENTS

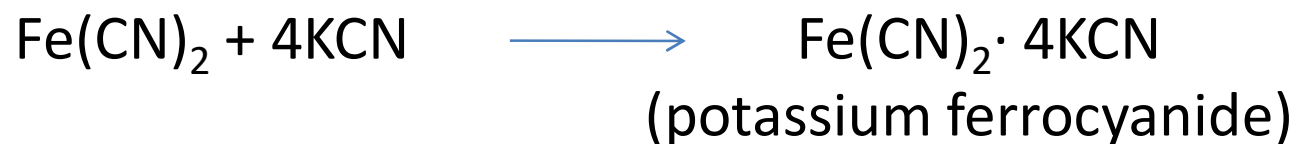


Source: <https://www.sigmaaldrich.com/technical-documents/articles/biology/periodic-table-of-elements-names.html>

## Coordination chemistry:

Ligands, nomenclature, isomerism, stereochemistry,  
valence bond, crystal field and molecular orbital  
theories.

# Coordination Chemistry



*Compounds containing these ions are called coordination compounds. The chemistry of metal ions in solution is essentially the chemistry of their complexes. Transition metal ions, in particular, form many stable complexes.*

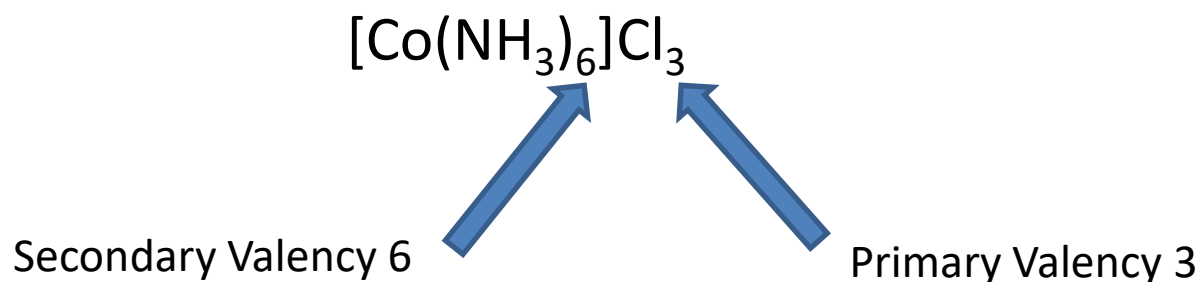
# Coordination Chemistry

## WERNER'S WORK

*Werner was able to explain the nature of bonding in complexes, and he concluded that in complexes the metal shows two different sorts of valency-*

*1. Primary valencies. These are non-directional.*

*2. Secondary valencies. These are directional. In modern terms the number of secondary valencies equals the number of ligand atoms coordinated to the metal. This is now called the coordination number.*



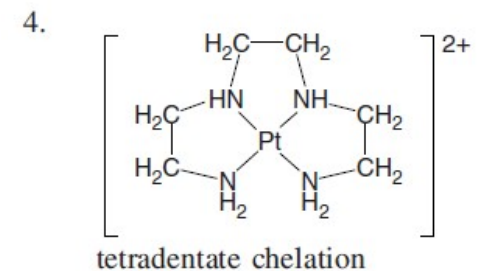
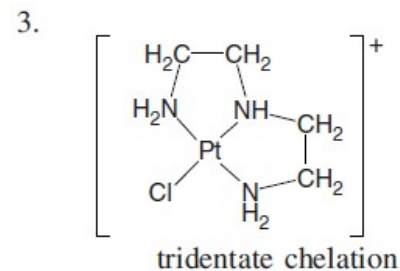
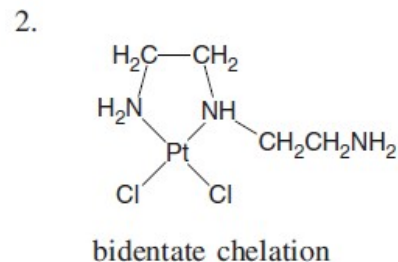
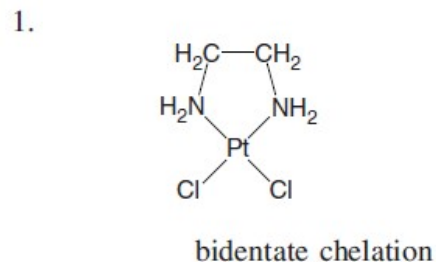
## Coordination Chemistry

- *A coordination compound is any compound that contains a coordination entity*
- *A coordination entity is an ion or neutral molecule: composed of a **central metal atom** to which is attached a surrounding array of other **atoms or groups of atoms**, each of which is called a ligand.*

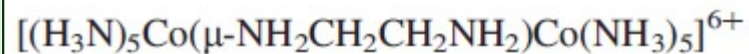
# Coordination Chemistry

**Coordination number:** the number of  $\sigma$ -bonds between ligands and the central atom.

**Chelation:** coordination of more than one non-contiguous  $\sigma$ -electron pair donor atom from a given ligand to the same central atom.



## Chelating vs Bridging

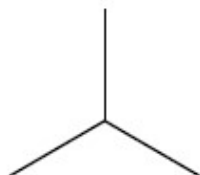




# Coordination Chemistry

## *Three-coordination*

trigonal plane



*TP-3*

trigonal pyramid



*TPY-3*

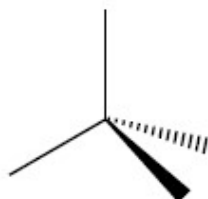
T-shape



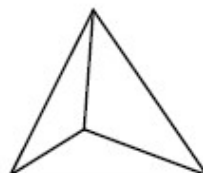
*TS-3*

## *Four-coordination*

tetrahedron



*T-4*



square plane



*SP-4*



square pyramid



*SPY-4*

see-saw



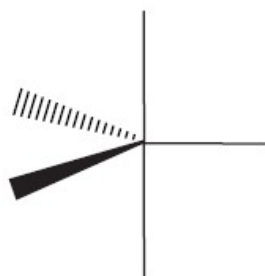
*SS-4*



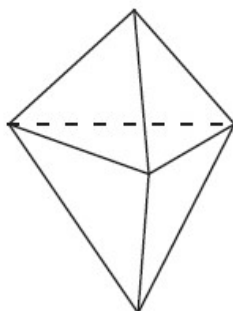
# Coordination Chemistry

## *Five-coordination*

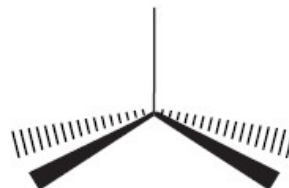
trigonal bipyramid



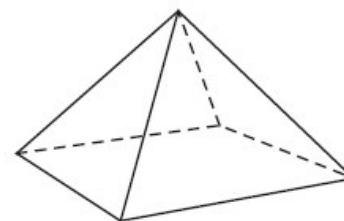
*TBPY-5*



square pyramid

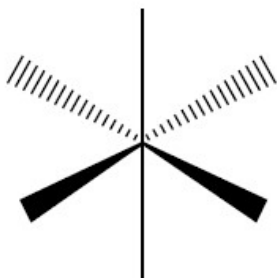


*SPY-5*

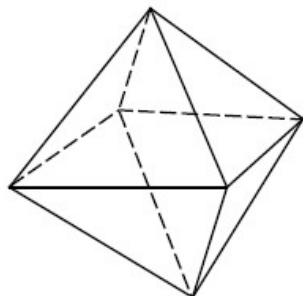


## *Six-coordination*

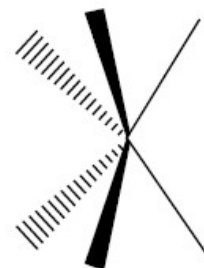
octahedron



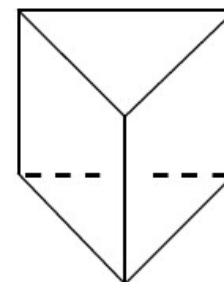
*OC-6*



trigonal prism



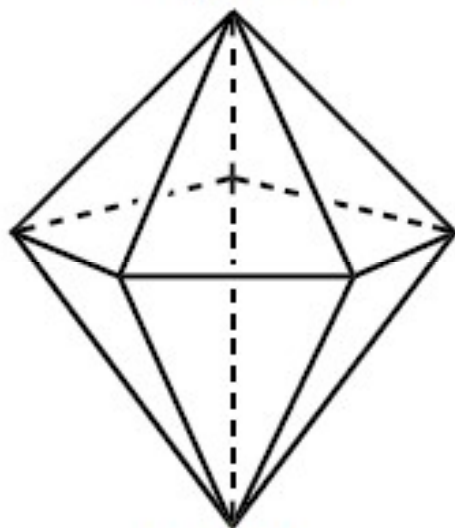
*TPR-6*



# Coordination Chemistry

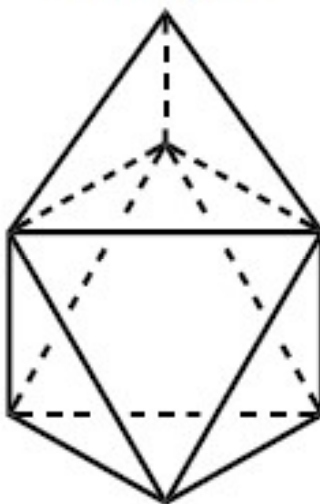
*Seven-coordination*

pentagonal  
bipyramid



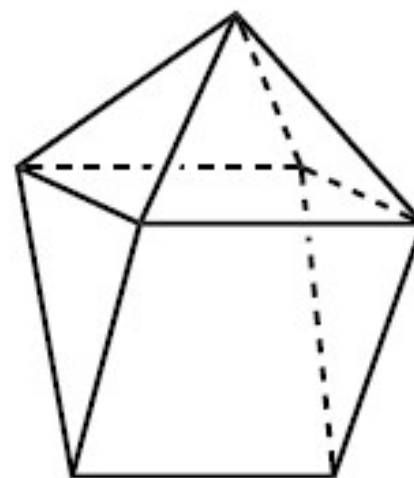
*PBPY-7*

octahedron, face  
monocapped



*OCF-7*

trigonal prism,  
square-face monocapped

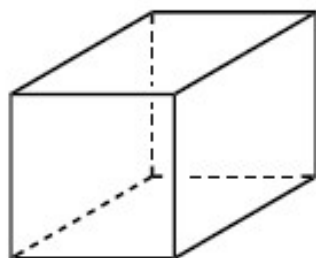


*TPRS-7*

# Coordination Chemistry

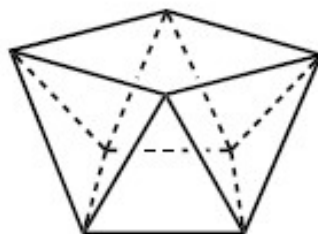
*Eight-coordination*

cube



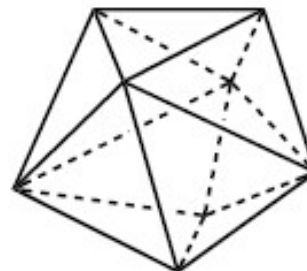
*CU-8*

square  
antiprism



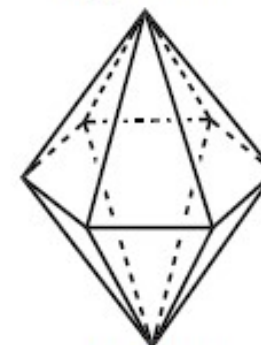
*SAPR-8*

dodecahedron



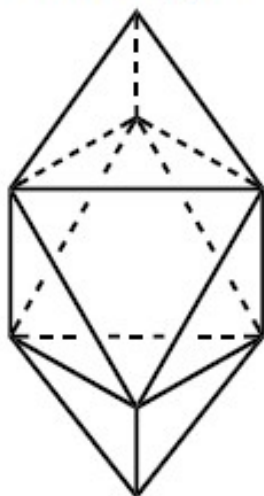
*DD-8*

hexagonal  
bipyramid



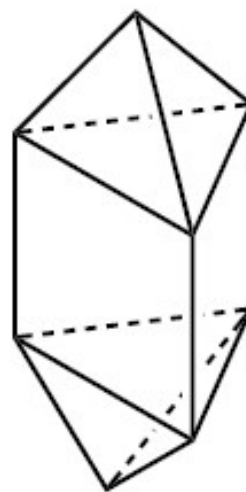
*HBPY-8*

octahedron,  
*trans*-bicapped



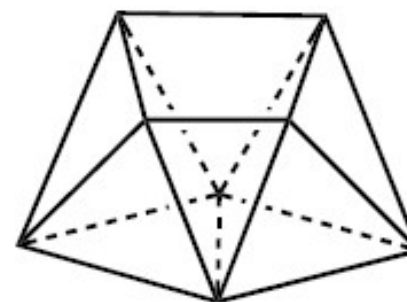
*OCT-8*

trigonal prism,  
triangular-face bicapped



*TPRT-8*

trigonal prism,  
square-face bicapped

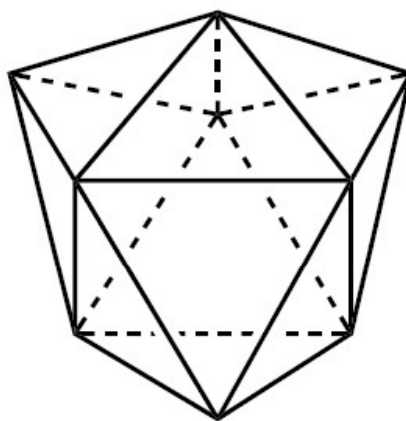


*TPRS-8*

# Coordination Chemistry

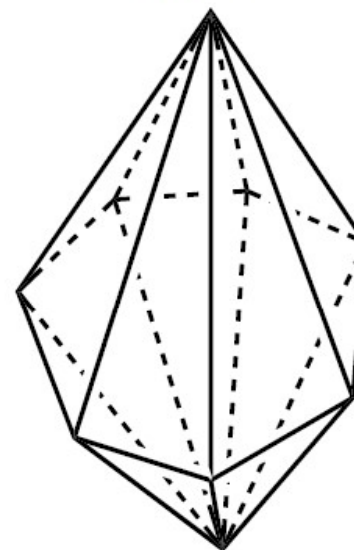
*Nine-coordination*

trigonal prism,  
square-face tricapped



*TPRS-9*

heptagonal  
bipyramid



*HBPY-9*

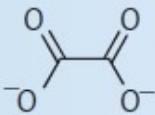
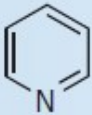
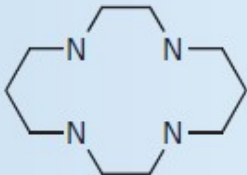
# Coordination Chemistry

## Oxidation State

	<i>Formula</i>	<i>Ligands</i>	<i>Central atom oxidation state</i>
1.	$[\text{Co}(\text{NH}_3)_6]^{3+}$	6 $\text{NH}_3$	III
2.	$[\text{CoCl}_4]^{2-}$	4 $\text{Cl}^-$	II
3.	$[\text{MnO}_4]^-$	4 $\text{O}^{2-}$	VII
4.	$[\text{MnFO}_3]$	3 $\text{O}^{2-}$ + 1 $\text{F}^-$	VII
5.	$[\text{Co}(\text{CN})_5\text{H}]^{3-}$	5 $\text{CN}^-$ + 1 $\text{H}^-$	III
6.	$[\text{Fe}(\text{CO})_4]^{2-}$	4 $\text{CO}$	-II

# Coordination Chemistry

## Common Ligands

Fluorido	$\text{F}^-$		F	1
Glycinato	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	gly	N, O	1N, 1O
Hydrido	$\text{H}^-$		H	1
Hydroxido	$\text{OH}^-$		O	1
Iodido	$\text{I}^-$		I	1
Nitrato	$\text{NO}_3^-$		O	1 or 2
Nitrito- $\kappa\text{O}$	$\text{NO}_2^-$		O	1
Nitrito- $\kappa\text{N}$	$\text{NO}_2^-$		N	1
Oxido	$\text{O}^{2-}$		O	1
Oxalato		ox	O	2
Pyridine		py	N	1
Sulfido	$\text{S}^{2-}$		S	1
Tetraazacyclotetradecane		cyclam	N	4

# Coordination Chemistry

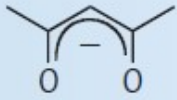
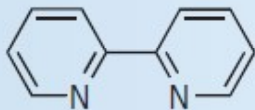
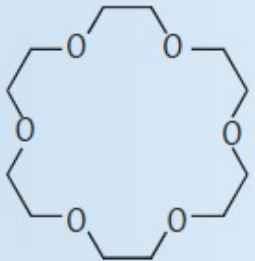
## Common Ligands

Thiocyanato— $\kappa N$	$NCS^-$		N	1
Thiocyanato— $\kappa S$	$SCN^-$		S	1
Thiolato	$RS^-$		S	1
Triaminotriethylamine	$N(CH_2CH_2NH_2)_3$	tren	N	4
Tricyclohexylphosphine	$P(C_6H_{11})_3$	$PCy_3$	P	1
Trimethylphosphine	$P(CH_3)_3$	$PMe_3$	P	1
Triphenylphosphine	$P(C_6H_5)_3$	$PPh_3$	P	1



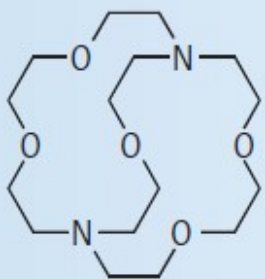
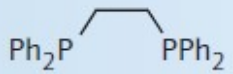
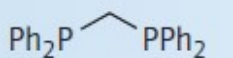
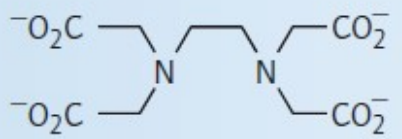
# Coordination Chemistry

## Common Ligands

Name	Formula	Abbreviation	Donor atoms	Number of donors
Acetylacetonato		acac <sup>-</sup>	O	2
Ammine	NH <sub>3</sub>		N	1
Aqua	H <sub>2</sub> O		O	1
2,2-Bipyridine		bpy	N	2
Bromido	Br <sup>-</sup>		Br	1
Carbanato	CO <sub>3</sub> <sup>2-</sup>		O	1 or 2
Carbonyl	CO		C	1
Chlorido	Cl <sup>-</sup>		Cl	1
1,4,7,10,13,16-Hexaoxa-cyclooctadecane		18-crown-6	O	6

# Coordination Chemistry

## Common Ligands

Name	Formula	Abbreviation	Donor atoms	Number of donors
4,7,13,16,21-Pentaoxa-1,10-diaza-bicyclo[8.8.5]tricosane		2.2.1 crypt	N, O	2N, 5O
Cyanido	CN <sup>-</sup>		C	1
Diethylenetriamine	NH(CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub>	dien	N	3
Bis(diphenylphosphino)ethane		dppe	P	2
Bis(diphenylphosphino)methane		dppm	P	2
Cyclopentadienyl	C <sub>5</sub> H <sub>5</sub> <sup>-</sup>	Cp <sup>-</sup>	C	5
Ethylenediamine (1,2-diaminoethane)	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	en	N	2
Ethylenediaminetetraacetato		edta <sup>4-</sup>	N, O	2N, 4O

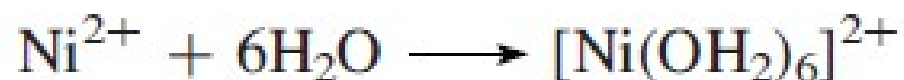
# Coordination Chemistry

## Nomenclature

### Additive nomenclature

*Example:*

1. Addition of ligands to a central atom:

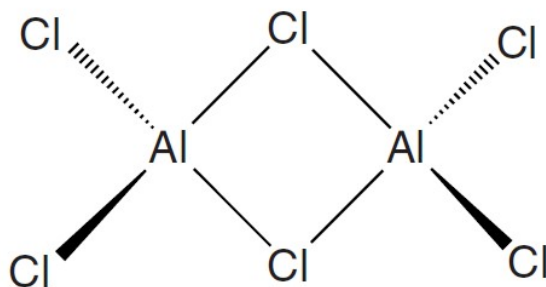


Addition of ligand names to a central atom name:

hexaaquanickel(II)

## Bridging Ligands

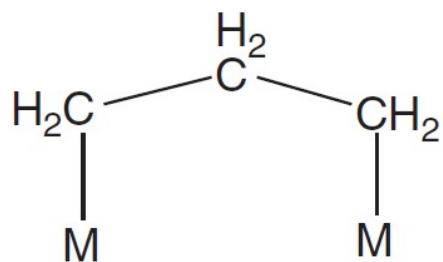
- Form polynuclear species
- $\mu$  as a prefix to the ligand formula or name
  - The number of central atoms joined into a single coordination entity by bridging ligands: indicated by using the terms dinuclear, trinuclear, tetranuclear, etc



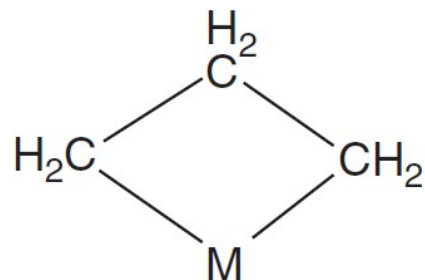
di- $\mu$ -chlorido-tetrachlorido- $1\kappa^2\text{Cl}, 2\kappa^2\text{Cl}$ -dialuminium

# Bridging Ligands

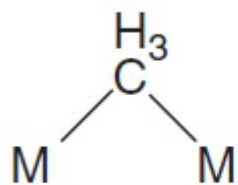
- mu ( $\mu$ ) convention



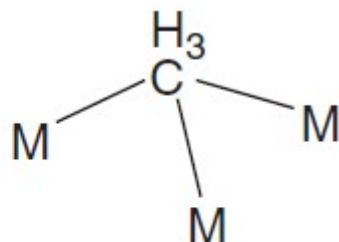
$\mu$ -propane-1,3-diyl  
(bridging)



propane-1,3-diyl  
(chelating)



$\mu$ -methyl



$\mu_3$ -methyl

## Metal–metal bonds

1.  $[\text{Br}_4\text{ReReBr}_4]^{2+}$   
bis(tetrabromidorhenium)(*Re*—*Re*)(2+)
2.  $[(\text{OC})_5\overset{1}{\text{Re}}\overset{2}{\text{Co}}(\text{CO})_4]$   
nonacarbonyl-1 $\kappa^5\text{C}$ , 2 $\kappa^4\text{C}$ -rheniumcobalt(*Re*—*Co*)

# Naming Coordination Compounds

- Ligand names are listed before the name(s) of the central atom(s)
- **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),
- The use of **abbreviations** in names is **discouraged**.
- Names of **anionic coordination entities** are furthermore given the ending '**ate**'.



penta**ammine**chloridocobalt(2+) chloride

## 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.**
  - **diammine for  $(\text{NH}_3)_2$ , but bis(methylamine)**



## Representing ligands in names

- **Names of anionic ligands**, are 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.
  - In particular, alcoholates, thiolates, phenolates, carboxylates, partially dehydronated amines, phosphanes, etc. are in this category.
- **Neutral and cationic ligands**, including organic ligands, are used without modification
- **Enclosing marks are required for**
  - neutral and cationic ligand names,
  - for names of inorganic anionic ligands containing multiplicative prefixes (such as triphosphato), for compositional names (such as carbon disulfide),
  - for names of substituted organic ligands
- Ligands binding to metals through carbon atoms to be discussed in organometallic compounds

# Examples

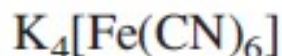
<i>Formula</i>	<i>Ligand name</i>
1. $\text{Cl}^-$	chlorido
2. $\text{CN}^-$	cyanido
3. $\text{H}^-$	hydrido <sup>3</sup>
4. $\text{D}^-$ or $^2\text{H}^-$	deuterido <sup>3</sup> or [ <sup>2</sup> H]hydrido <sup>3</sup>
5. $\text{PhCH}_2\text{CH}_2\text{Se}^-$	2-phenylethane-1-selenolato
6. $\text{MeCOO}^-$	acetato or ethanoato
7. $\text{Me}_2\text{As}^-$	dimethylarsanido
8. $\text{MeCONH}_2$	acetamide ( <i>not</i> acetamido)
9. $\text{MeCONH}^-$	acetylazanido or acetylamido ( <i>not</i> acetamido)
10. $\text{MeNH}_2$	methanamine

## Examples

- |                         |  |
|-------------------------|--|
| 11. $\text{MeNH}^-$     | methylazanido, or methylamido, or methanaminido<br>( <i>cf.</i> Example 3 of Section IR-6.4.6) |
| 12. $\text{MePH}_2$     | methylphosphane  |
| 13. $\text{MePH}^-$     | methylphosphanido  |
| 14. $\text{MeOS(O)OH}$  | methyl hydrogen sulfite  |
| 15. $\text{MeOS(O)O}^-$ | methyl sulfite, or methanolatodioxidosulfato(1–)   |

## 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)
- **Zero** indicates the oxidation number zero.
- Alternatively, the charge on a coordination entity may be indicated.
- The net charge is written in 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.



potassium hexacyanidoferrate(II), or  
potassium hexacyanidoferrate(4-), or  
tetrapotassium hexacyanidoferrate



hexaamminecobalt(III) chloride



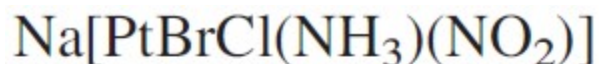
pentaamminechloridocobalt(2+) chloride

## 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(s) is (are) listed first
  - The ligand symbols are then listed in alphabetical order
    - Thus,  $\text{CH}_3\text{CN}$ ,  $\text{MeCN}$  and  $\text{NCMe}$  would be ordered under C, M and N respectively, and  $\text{CO}$  precedes  $\text{Cl}$  because single letter symbols precede two letter symbols.

# Formulae of coordination compounds

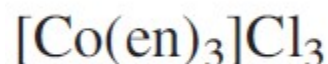
- Use of enclosing marks
  - Square brackets: formula for the entire coordination entity, whether charged or not
  - Parentheses: polyatomic ligands formulae and abbreviations of ligands.



sodium amminebromidochloridonitrito- $\kappa N$ -platinate(1-)



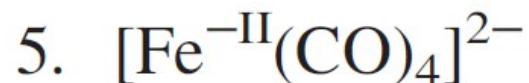
hexakis(methyl isocyanide)iron(II) bromide



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 that of any counterion, the charge is indicated outside the square bracket as a right superscript, with the 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.



## Specifying donor atoms

- only 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,  $\kappa$
  - $\kappa$  placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found



dibromido[ethane-1,2-diylbis(dimethylphosphane- $\kappa P$ )]nickel(II)

## Specifying donor atoms

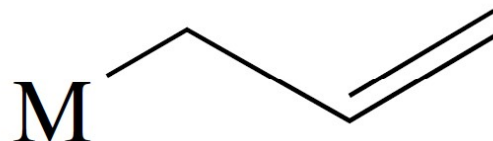
- The kappa convention
  - thiocyanato- $\kappa N$  for nitrogen-bonded NCS
  - thiocyanato-  $\kappa S$  for sulfur-bonded NCS.
  - Nitrogen-bonded nitrite is named nitrito- $\kappa N$
  - Oxygen-bonded nitrite is named nitrito- $\kappa O$ , as in pentaamminenitrito-  $\kappa O$  -cobalt(III)

# Specifying donor atoms

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



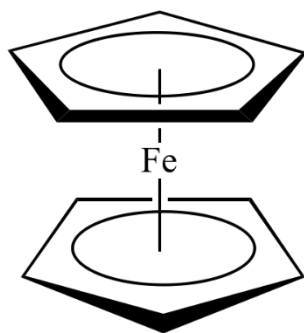
M



bis- $\eta^3$ -allyl nickel, or  $[\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2]$

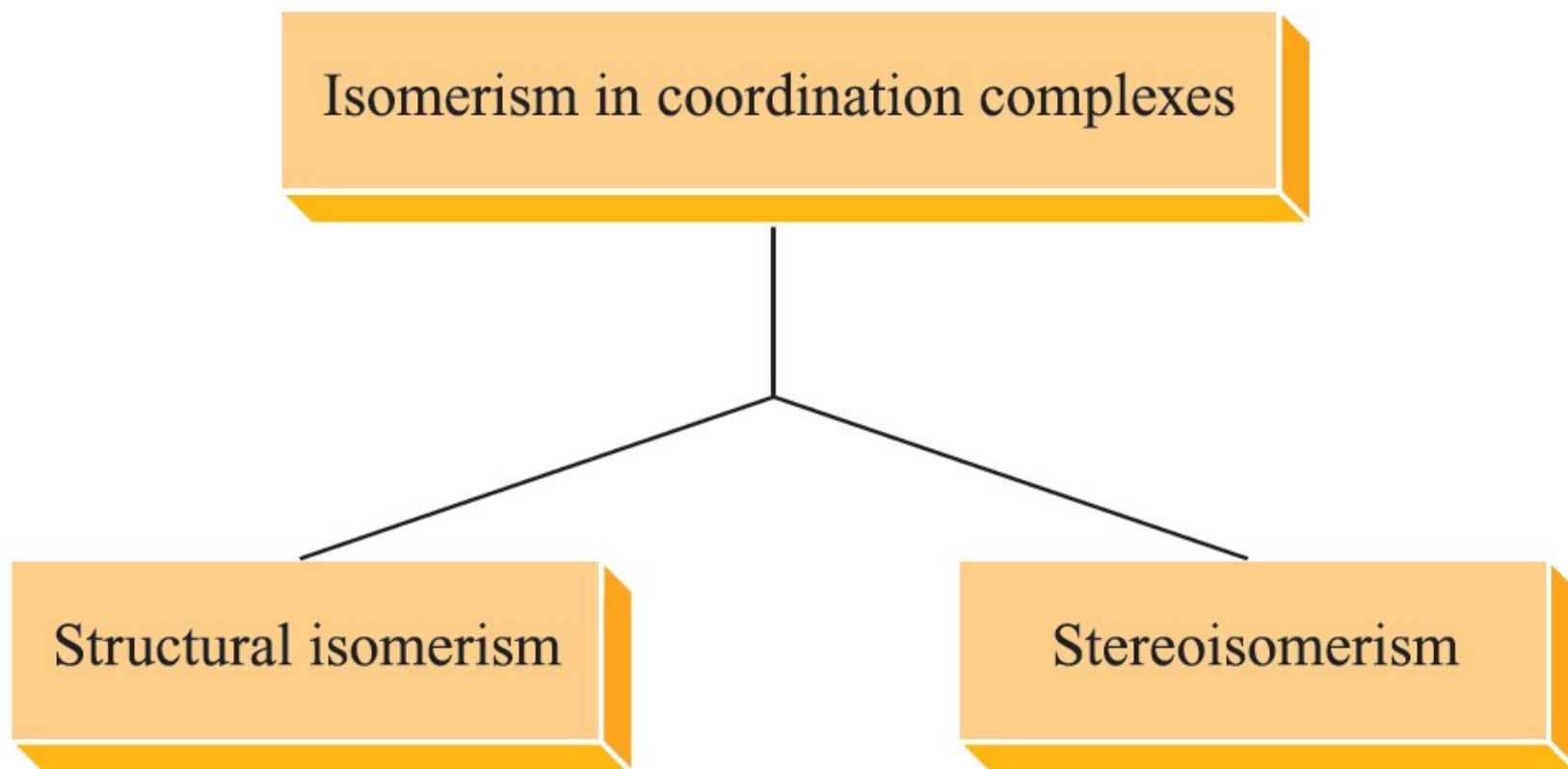
4 electron donor and anionic

2 electron donor and anionic



$[\text{Fe-}\eta^5\text{-C}_5\text{H}_5)_2]$

# Isomerism in coordination complexes



# Isomerism in coordination complexes

Structural isomerism



```
graph TD; A[Isomerism in coordination complexes] --> B[Structural isomerism]; A --> C[Stereoisomerism]; B --> D[Ionization isomerism]; B --> E[Hydration isomerism]; B --> F[Coordination isomerism]; B --> G[Linkage isomerism]; B --> H[Polymerization isomerism]; C --> I[Geometrical isomerism]; C --> J[Optical isomerism];
```

Stereoisomerism

Ionization isomerism  
Hydration isomerism  
Coordination isomerism  
Linkage isomerism  
Polymerization isomerism

Geometrical isomerism  
Optical isomerism

## Structural isomerism: Ionization Isomers

- Ionization isomers result from the interchange of an anionic ligand within the first coordination sphere with an anion outside the coordination sphere.*

Violet  $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and red  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$

The isomers are also easily distinguished by IR spectroscopy; free and coordinated sulfate ions give rise to one or three IR active SO stretching vibrations respectively

## Structural isomerism:

### Hydration isomers

- *Hydration isomers result from the interchange of  $H_2O$  and another ligand between the first coordination sphere and the ligands outside it.*



When this is dissolved in water, the chloride ions in the complex are slowly replaced by water to give blue-green  $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$  and finally violet  $[Cr(H_2O)_6]Cl_3$

## Structural isomerism: Coordination isomer

*Coordination isomers are possible only for **salts in which both cation and anion are complex ions**; the isomers arise from interchange of ligands between the two metal centres.*

Examples of coordination isomers are:

- $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$  and  $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$ ;
- $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$  and  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]$ ;
- $[\text{Pt}^{\text{II}}(\text{NH}_3)_4][\text{Pt}^{\text{IV}}\text{Cl}_6]$  and  $[\text{Pt}^{\text{IV}}(\text{NH}_3)_4\text{Cl}_2][\text{Pt}^{\text{II}}\text{Cl}_4]$ .

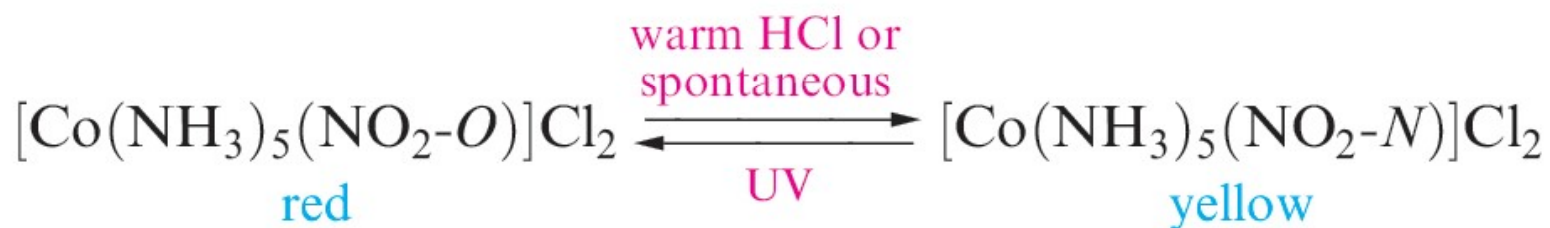


# Structural isomerism:

## Linkage Isomer

*Linkage isomers may arise when one or more of the ligands can coordinate to the metal ion in more than one way.*

Linkage isomers of  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$



- distinguished by using IR spectroscopy.
  - For the O-bonded ligand, characteristic absorption bands at 1065 and 1470  $\text{cm}^{-1}$
  - while for the N-bonded ligand, the corresponding vibrational wavenumbers are 1310 and 1430  $\text{cm}^{-1}$ .

## Structural isomerism: Polymerization isomer

- *Polymerization isomers denote complexes which have the same empirical formulae but different molecular masses.*

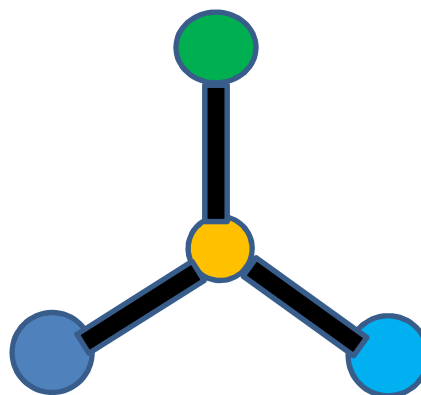
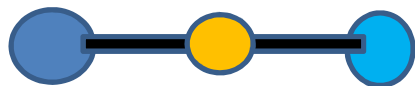
Examples of polymerization isomers are:

- $[\text{PtCl}_2(\text{NH}_3)_2]$  and  $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ ;
- $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  and  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{NO}_2)_6]$ .

# Stereoisomerism: Geometrical isomers

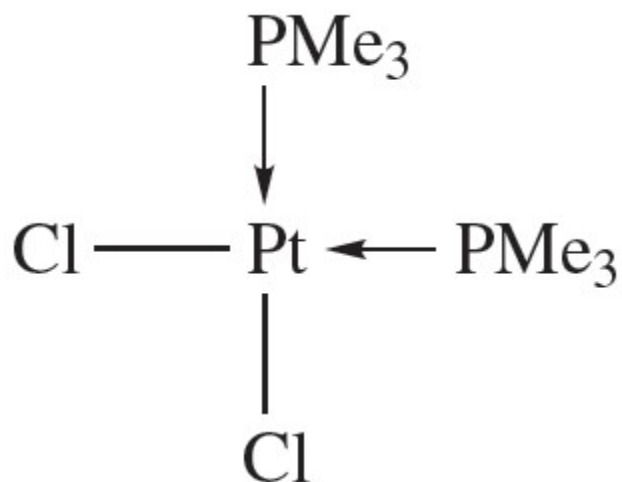
*If two species have the same molecular formulae and the same structural framework, but **differ in the spatial arrangement** of different atoms or groups about a central atom or a double bond, then the compounds are geometrical isomers.*

- Square planar , Octahedral and Trigonal Bipyramidal species

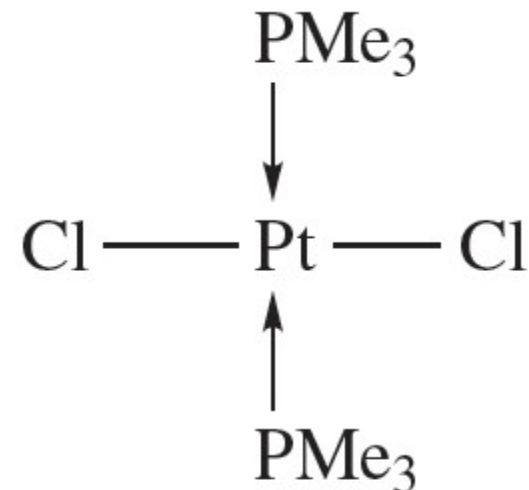


## Stereoisomerism: Geometrical isomers

*Square planar species of the general form  $EX_2Y_2$  or  $EX_2YZ$  may possess cis- and trans-isomers.*



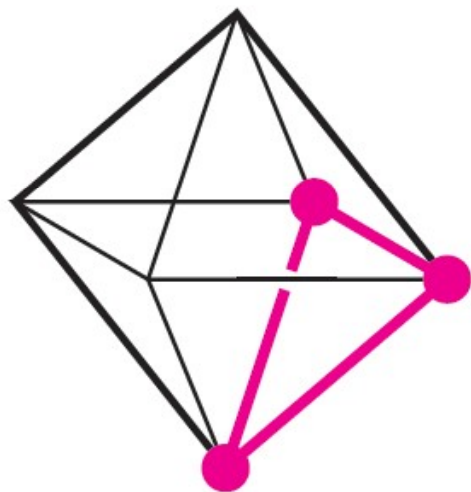
*cis-isomer*



*trans-isomer*

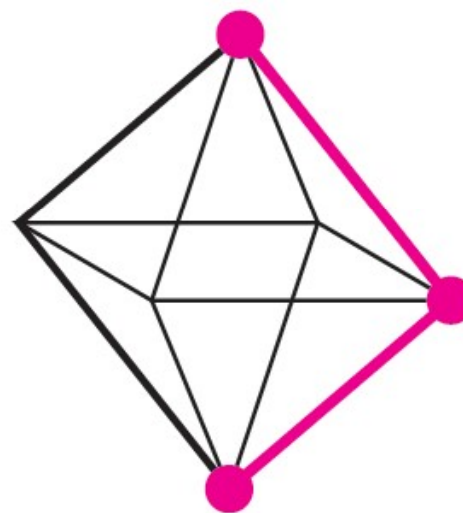
# Stereoisomerism: Geometrical isomers

*An octahedral species containing three identical groups (e.g. of type  $EX_3Y_3$ ) may possess fac- and mer-isomers.*



*Facial*  
arrangement

*fac-isomer*



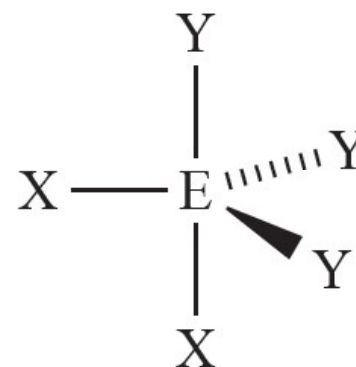
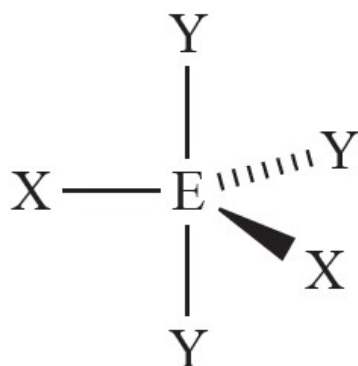
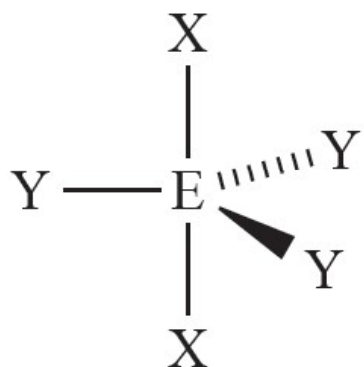
*Meridional*  
arrangement

*mer-isomer*

# Stereoisomerism:

## Geometrical isomers

*In a trigonal bipyramidal species, geometrical isomerism arises because of the presence of axial and equatorial*



Steric factors may dictate which isomer is preferred for a given species  
e.g. static structure of  $\text{PCl}_3\text{F}_2$ .

# Stereoisomerism:

## Optical isomers

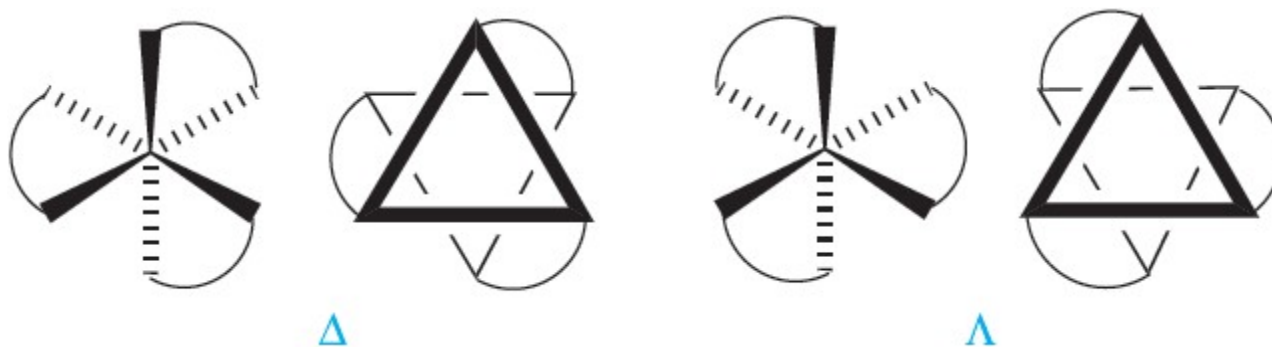
*Optical isomerism is concerned with chirality, and some important terms relating to chiral complexes*

- **Enantiomers** are a pair of stereoisomers that are nonsuperposable mirror images.
- (+) and (-) prefixes  
specific rotation  
Sign of  $[\alpha]_D$ .
- *d* and *l* prefixes :  
dextro- and laevo- (derived from the Latin for right and left)  
refer to right- and left-handed rotation of the plane of polarized light respectively
- The +/- or *d/l* notation is not a direct descriptor of the absolute configuration of an enantiomer (the arrangement of the substituents or ligands) for which the following prefixes are used.

# Stereoisomerism:

## Optical isomers

- *R* and *S* prefixes: Cahn–Ingold–Prelog notation
  - notation is used for chiral organic ligands, and also for tetrahedral complexes
  - The *R*- and *S*-labels for the enantiomers refer to a clockwise (*rectus*) and anticlockwise (*sinister*) sequence of the prioritized atoms, working from high to low.
- $\Delta$  and  $\Lambda$  prefixes:
  - enantiomers of octahedral complexes containing three equivalent bidentate ligands (tris-chelate complexes)
  - octahedron is viewed down a three-fold axis, and the chelates then define either a right- or left-handed helix.





# Stereoisomerism:

## Optical isomers

- Bis-chelate octahedral complexes : cis- and trans-isomers
  - $[\text{Co}(\text{en})_2\text{Cl}_2]^+$
- The first purely inorganic complex to be resolved into its optical isomers was

