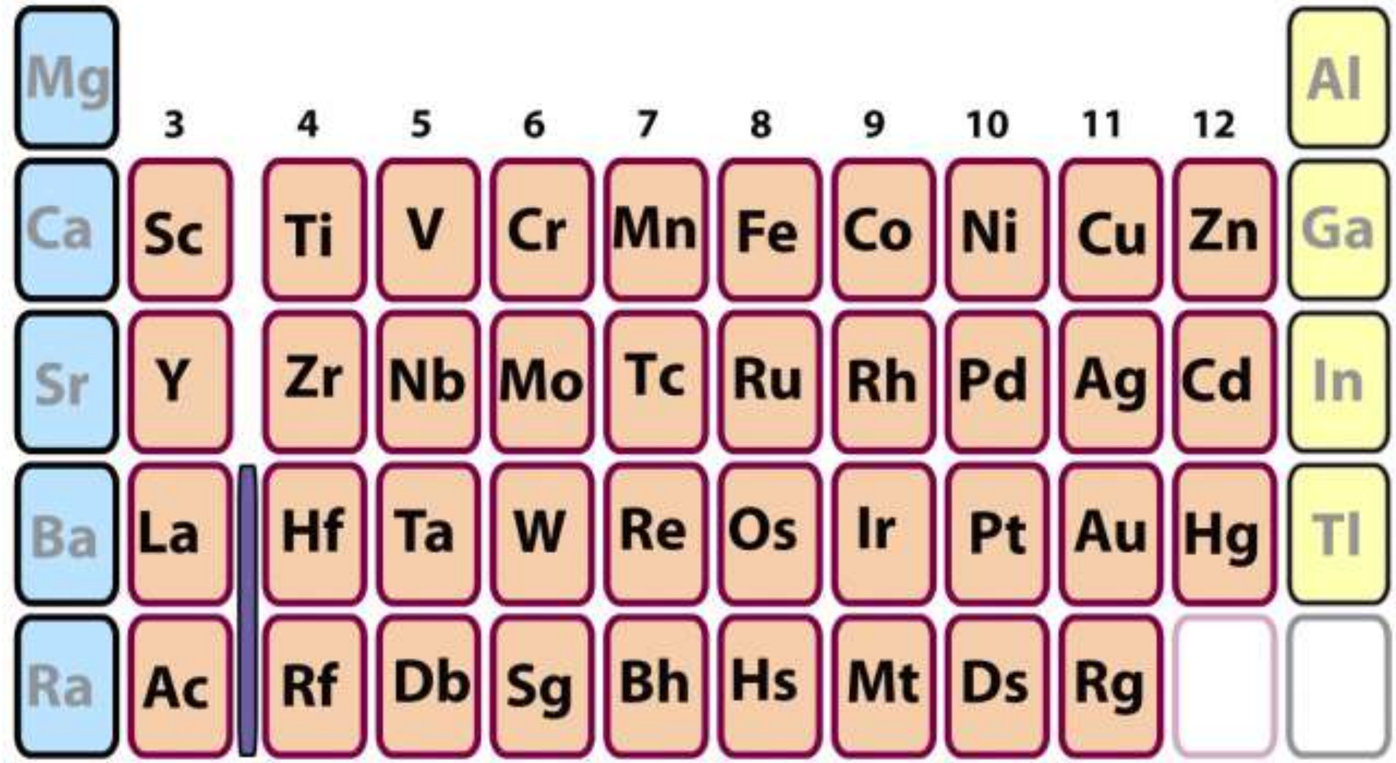
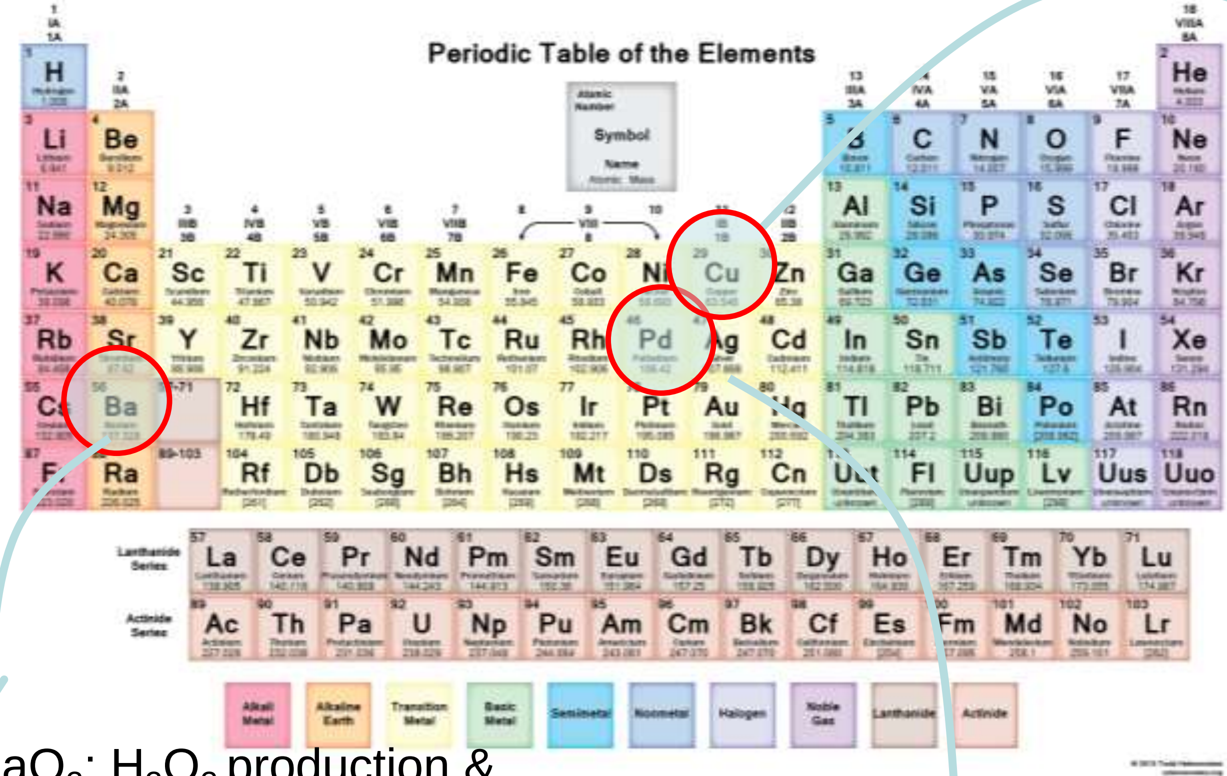
Chemistry of Transition Metals

Part 1. General Considerations



- Filling of 3d, 4d, and 5d shells
- In s- and p-block, electrons added to outer shell
- In d-block, electrons added to penultimate shell expanding it from 8-18
- Most elements have incompletely filled d-shell (interesting properties)

Inorganic compounds in Industry: Selected examples



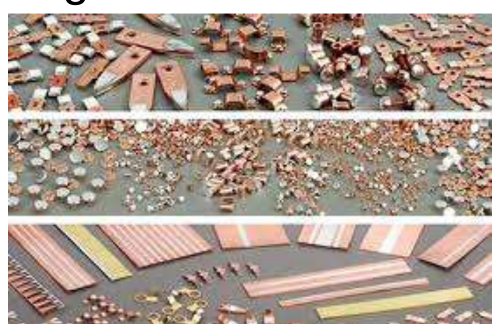
Cuprous Oxide: Fungicide, pigments and an antifouling agent for marine paints

$Cu(NO_3)_2$: Light-sensitive papers, textile dyeing, paints, and as a catalyst in pharma preparations

BaO_2: H_2O_2 production & Pyrotechnics

$Ba(OH)_2$: in waste-water

Used low voltage electrical contacts. & Catalysis



Some general properties of TM elements

1. Metals
2. Almost all: HARD, STRONG, High m.p., b.p.
3. Conduct heat & electricity
4. Form Alloys
5. Show variable oxidation states
6. At least one of the ions & compounds colored.
7. Form paramagnetic species because of partially filed shells
8. Form coordination compounds (complexes) and organometallic compounds.

Variable oxidation states

			+7				
		+6	+6	+6			
	+5	+5	+5	+5	+5		
+4	+4	+4	**+4**	+4	+4	+4	
+3	**+3**	**+3**	+3	**+3**	**+3**	+3	+3
+2	+2	+2	**+2**	**+2**	**+2**	**+2**	**+2**
							+1
Ti	V	Cr	Mn	Fe	Co	Ni	Cu
[Ar] $3d^2 4s^2$	[Ar] $3d^3 4s^2$	[Ar] $3d^5 4s^1$	[Ar] $3d^5 4s^2$	[Ar] $3d^6 4s^2$	[Ar] $3d^7 4s^2$	[Ar] $3d^8 4s^2$	[Ar] $3d^{10} 4s^1$

1. Increase in the number of oxidation states from Sc to Mn. All are possible only in case of Mn.

2. Decrease in the number of oxidation states from Mn to Zn, due to the pairing of d-e's after Mn

3. Stability of higher oxidn states decreases along Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizers.

4. Down the group, the stability of high oxidation states increases (easier availability of both d and s electrons for ionization).

Oxidation states of TM elements: Comparison

Sc 3	Ti 3,4	V 2, 3, 4, 5	Cr 2, 3, 4, 6	Mn 2, 3, 4, 6, 7	Fe 2, 3	Co 2, 3	Ni 2	Cu 1, 2	Zn 2
Y 3	Zr 4	Nb 3,4, 5	Mo 2,3,4, 5, 6	Tc 2,3,4, 5,6,7	Ru 2,3,4, 5,6,7, 8	Rh 1, 3	Pd 2, 4	Ag 1	Cd 2
La 3	Hf 4	Ta 3, 4, 5	W 2,3,4, 5, 6	Re 2,3,4, 5,6,7	Os 3,4,5, 6,7,8	Ir 1, 3	Pt 2, 4	Au 1, 3	Hg 1, 2

This is NOT an exhaustive list

Low oxidation states of heavy elements, such as, Nb, Ta, Mo, W , Re, exhibit metal – metal bonding in their compounds

Reasons for colour by TM Elements

1. The d-orbitals of the metal interact with the electron cloud of the ligands in such a manner that the d-orbitals become non-degenerate. When the d-level is not completely filled, it is possible to promote an electron from a lower energy d-orbital to a higher energy d-orbital by absorption of a photon of electromagnetic radiation having an appropriate energy (*d-d transitions).*

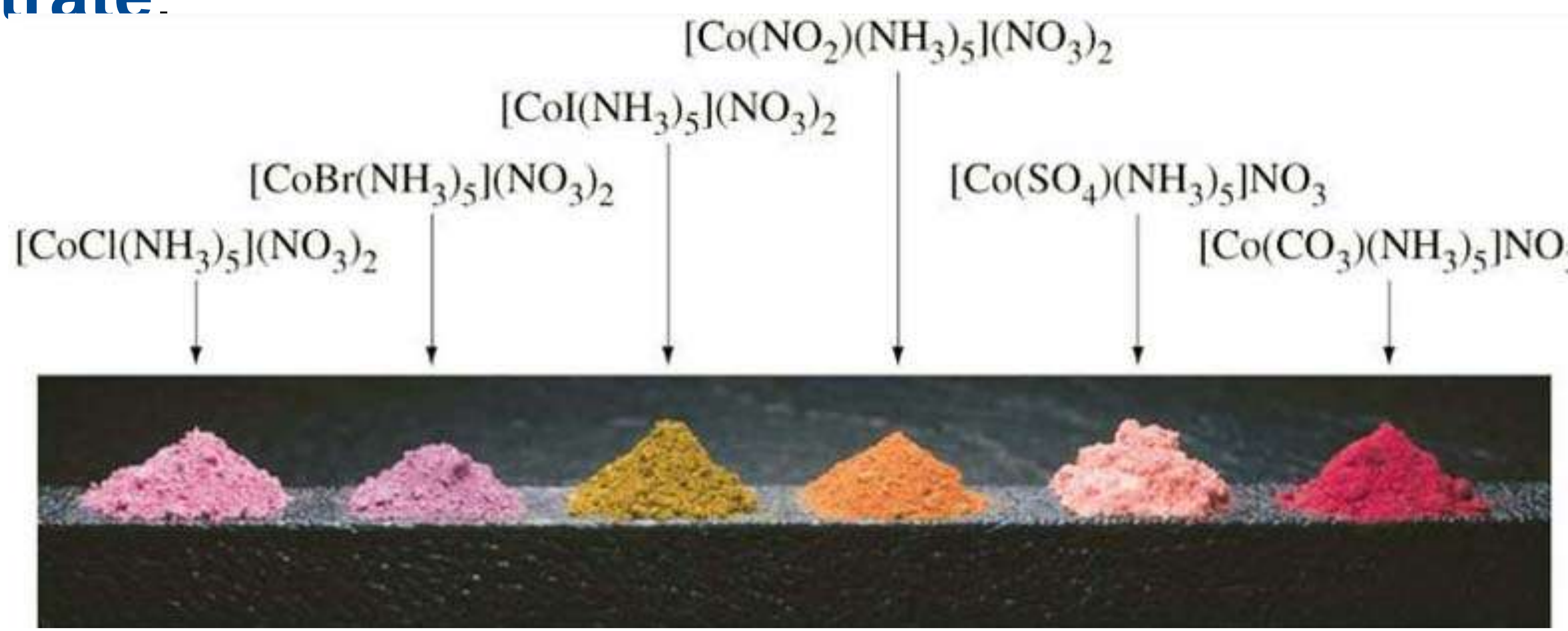
***2. Metal to Ligand and Ligand to Metal Charge Transfer (LMCT and MLCT) transitions* ($KMnO_4$)**

3. Electromagnetic radiations in the visible region of the spectrum often possess the appropriate energy for the above transitions.

Diversity in colour: Ligand variation

$[Co(NH_3)_6]Cl_3$ and $[CoCl(NH_3)_5]Cl_2$

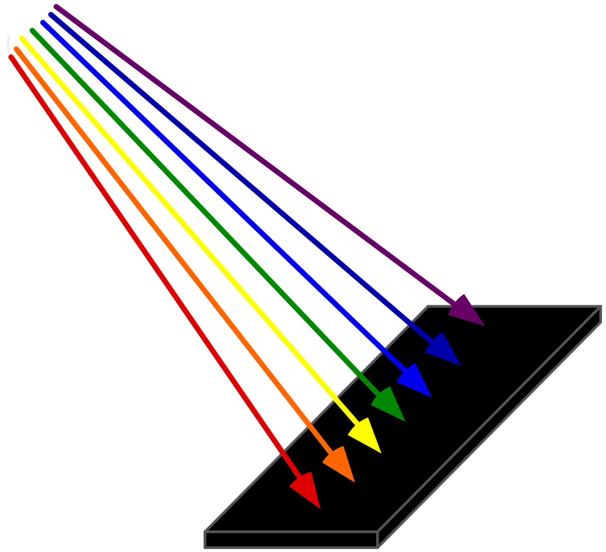
Two compounds made of the same chemicals, yet **they look different**, and **react differently with silver nitrate**.

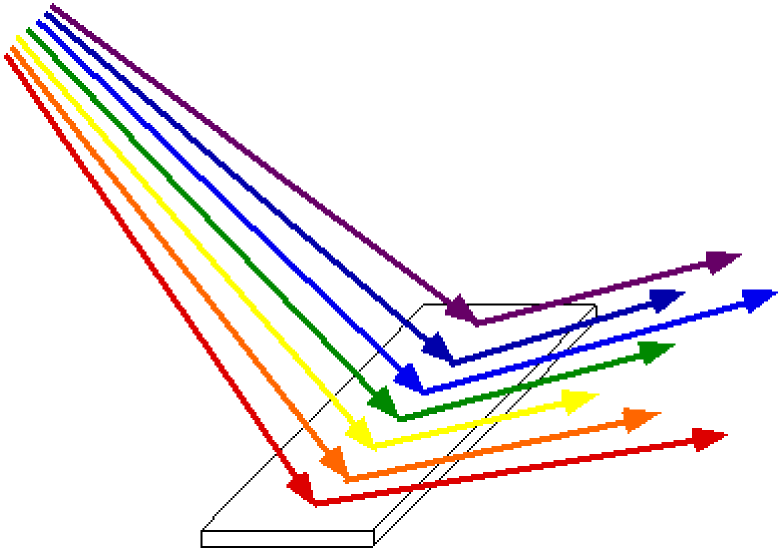


Colors & How We perceive it

Black and White

When a sample absorbs light, what we see is the sum of the remaining colors that strikes our eyes.

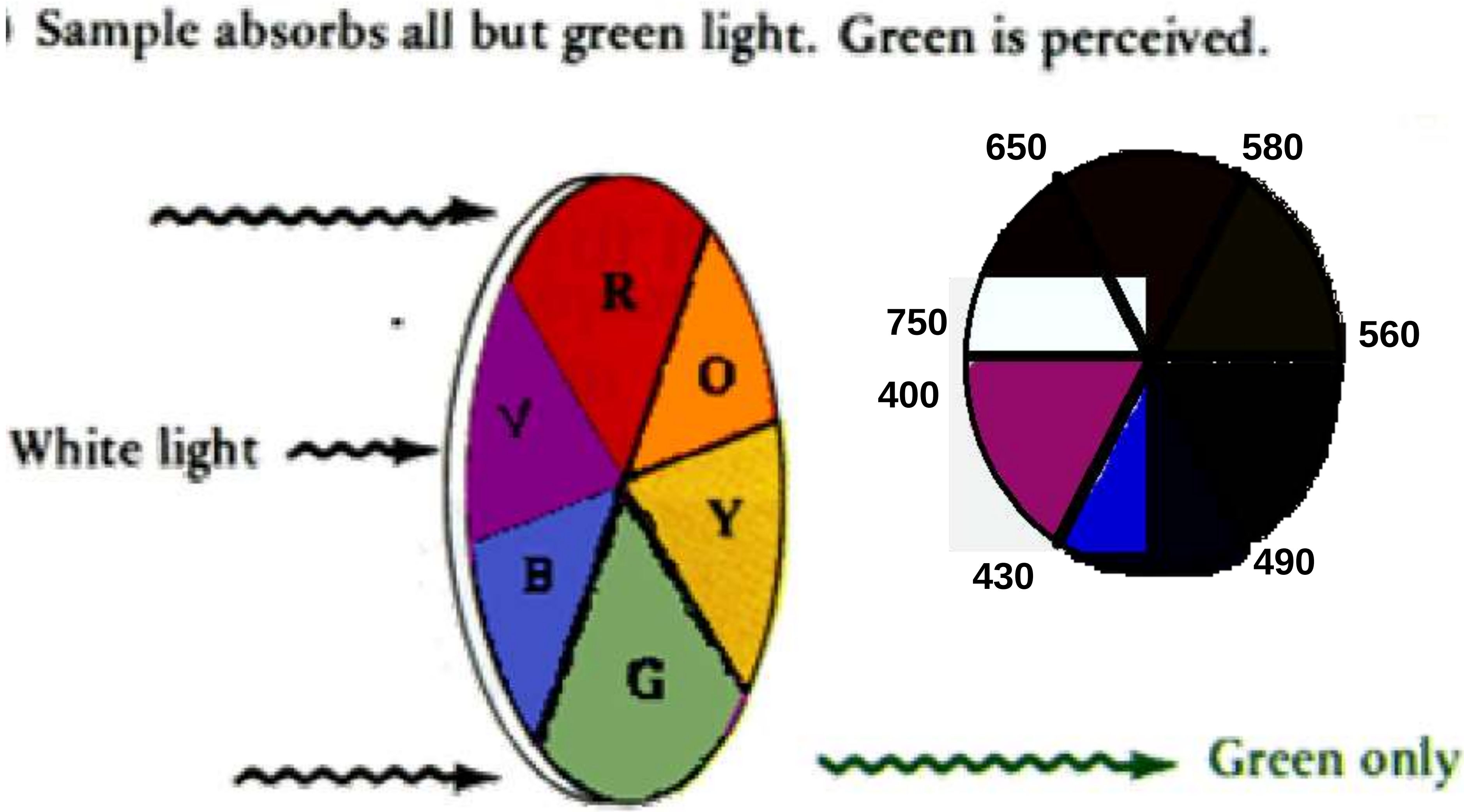




If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample. Consequently, it appears black.

If the sample absorbs no visible light, it is white or colorless.

Example: When the colour is green



General consideration of TM complexes

A TM complex is a species consisting of a transition metal or its ion coordinated to (bonded to) one or more ligands (generally neutral or anionic non-metal species)

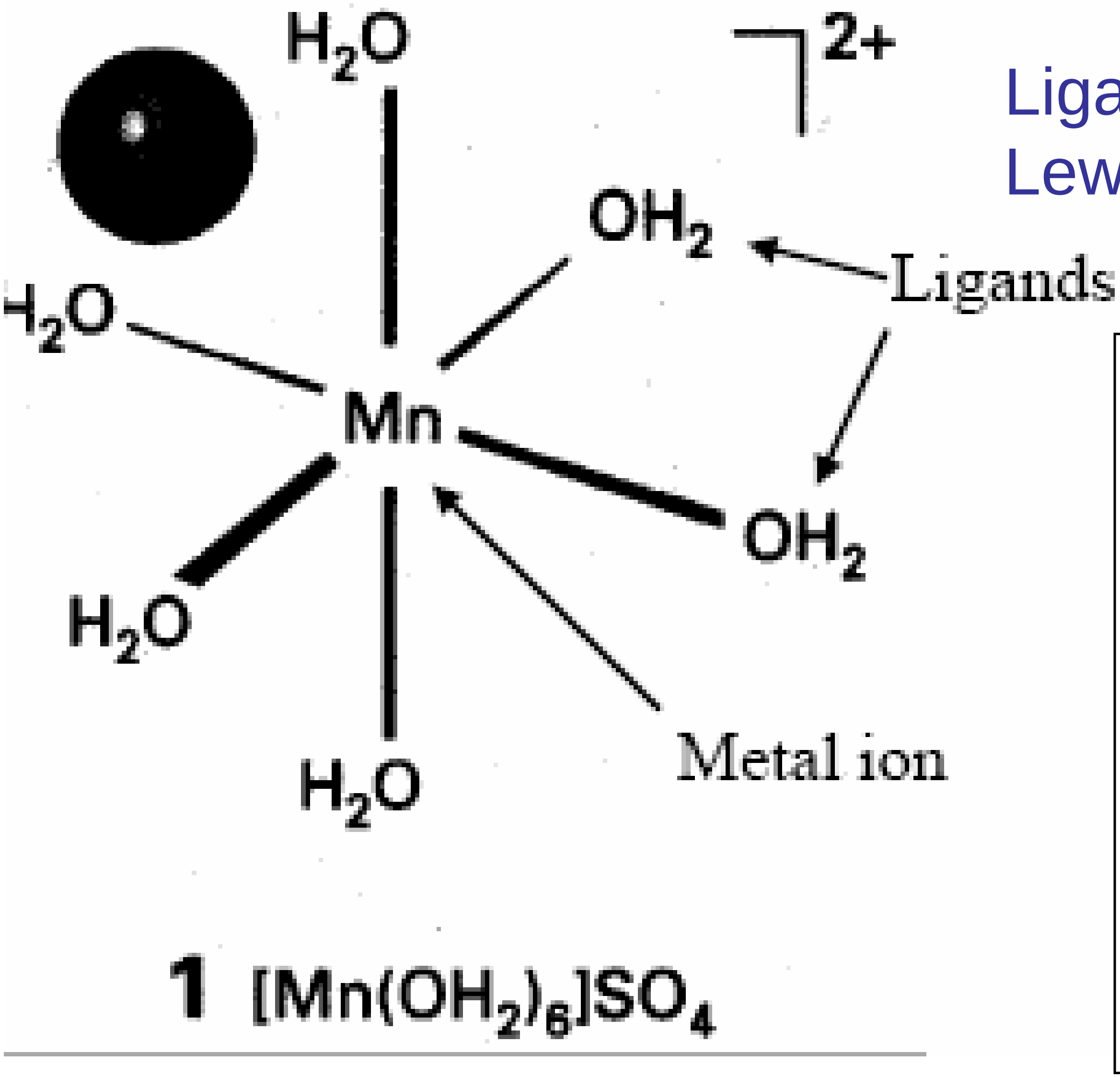
TM complexes are important in catalysis, materials synthesis, photochemistry, and biological systems

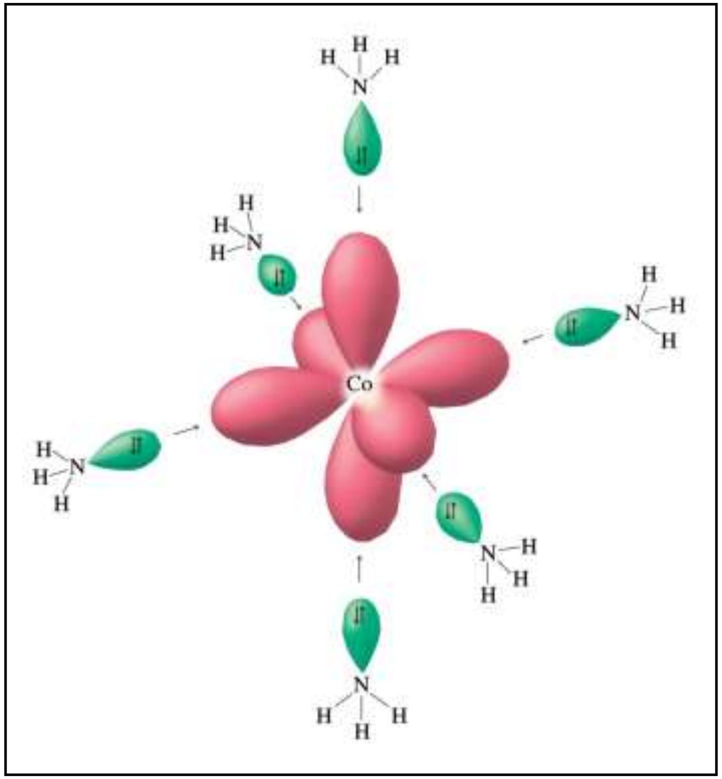
Display diverse chemical, optical and magnetic properties

An example of a metal complex

Metal ion: Central & is a Lewis Acid

Ligand: Is Attached & is a Lewis Base





General features of TM compounds

TM ions generally form complexes with well defined number of ligands

Complexes with coordination numbers of 4 and 6 are the most common (for TM), although two to five have also been very well established. Rarely higher than 6 is found.

The coordination number & geometry are determined by a combination of
---Metal ion size & its charge & its type
---Ligand size & type
---Electronic factors

Ligands

Ligands are species (neutral or anionic) bonded to the central metal ion

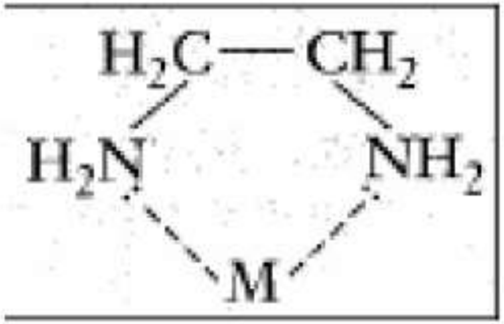
They may be attached to the metal center through a single atom (monodentate) or two or three atoms or higher (bidentate, tridentate, etc.)

Such polydentate (bidentate or higher) ligands are called chelating ligands

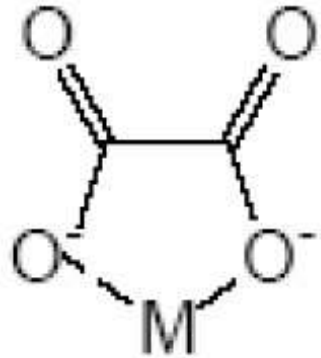
Some very common & simple ligands

Neutral Molecules		Anions	
Aqua	H_2O	Fluoro	F^-
Ammine	NH_3	Chloro	Cl^-
Methylamine	CH_3NH_2	Bromo	Br^-
Carbonyl	CO	Iodo	I^-
Nitrosyl	NO	Hydroxo	OH^-
		Cyano	CN^-

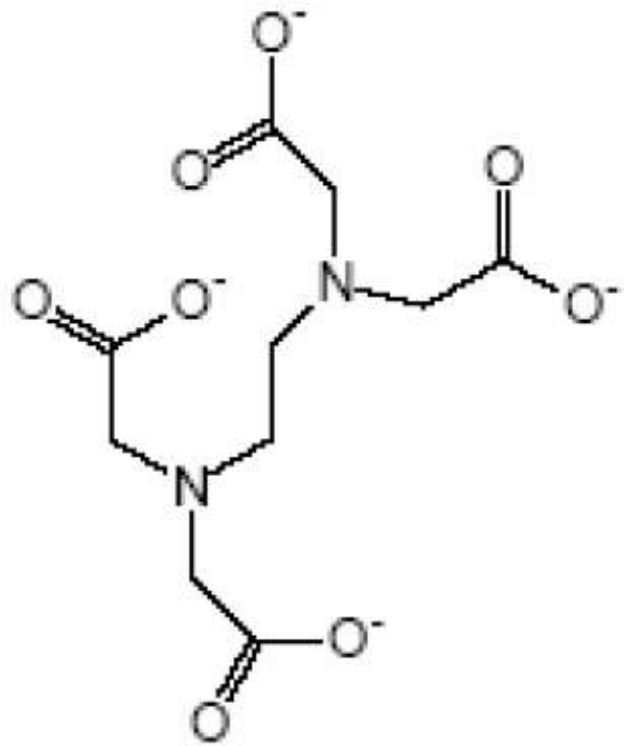
Some very common but chelating ligands



Ethylenediamine acting as a bidentate ligand

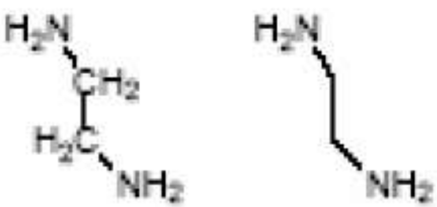


Oxalate acting as a bidentate ligand



Ethylenediaminetetraacetate

Can act as hexadentate ligand



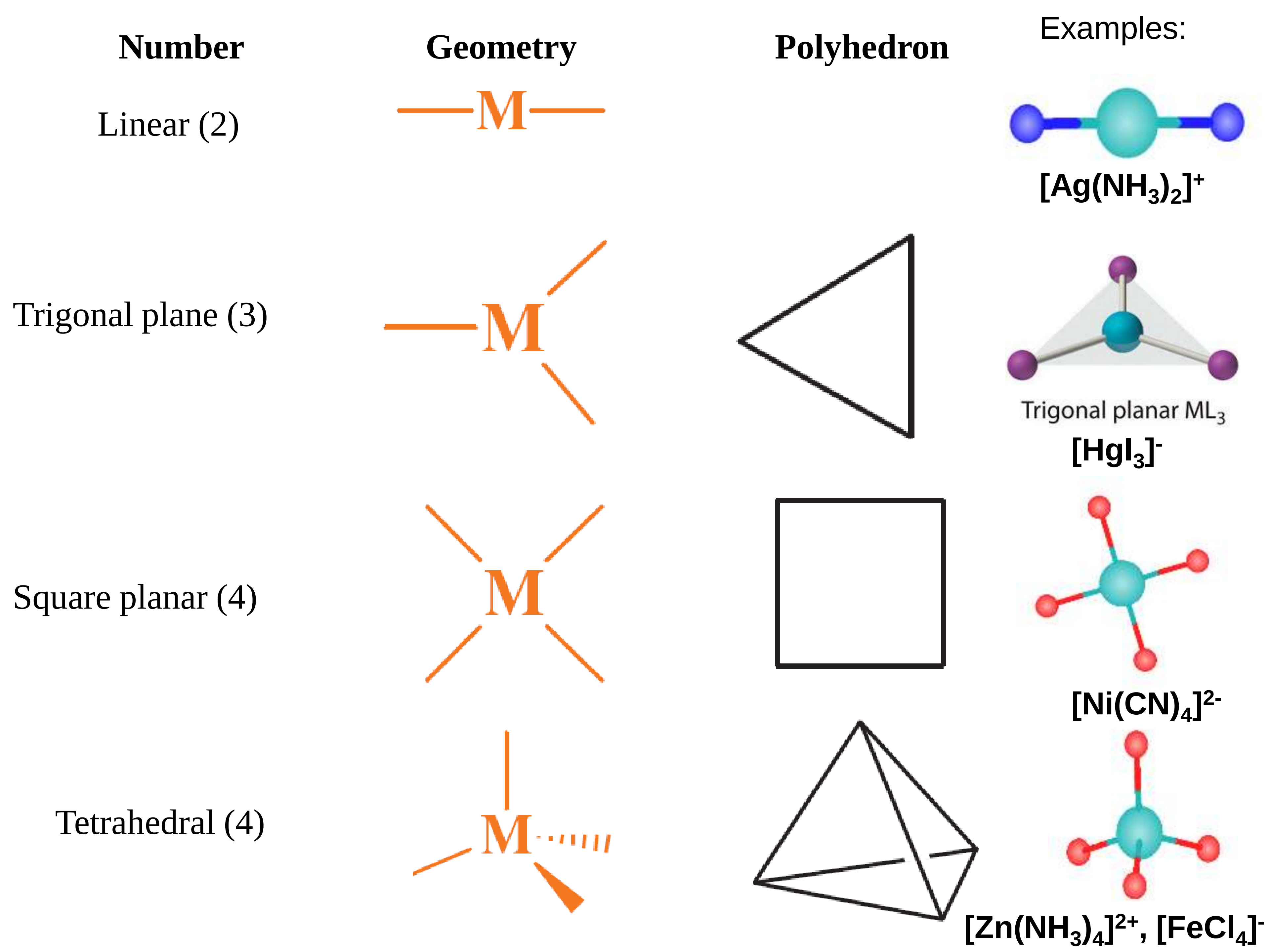
Note both of these drawing imply the same thing

Oxidation states: Role of ligands

Low oxidation state complexes can be stabilized by using ligands such as cyanide and carbon monoxide (pi-acceptor ligands -- Later on explained)

Intermediate oxidation state complexes often have ligands such as chloride, ammonia or water

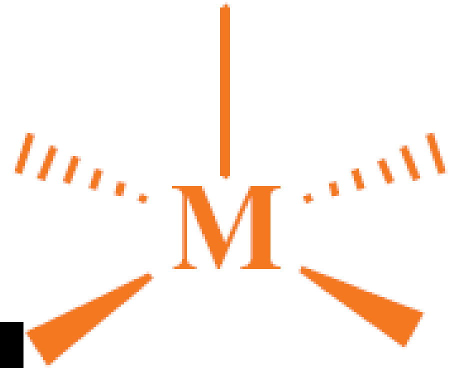
High oxidation state complexes usually have oxide or fluoride ligands

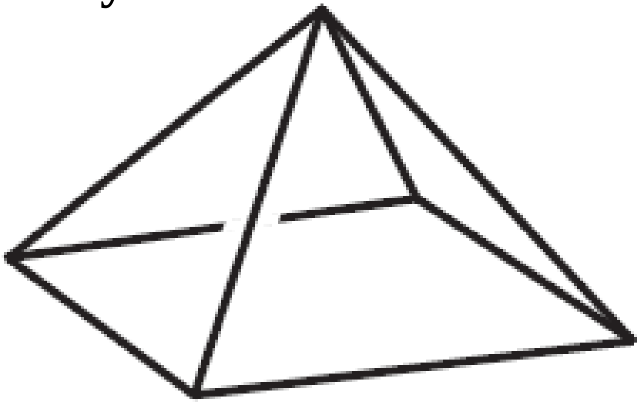

Number
Geometry
Polyhedron
Examples:
Linear (2)
M
[Ag(NH3)2]+
Trigonal plane (3)
M
Trigonal planar ML3
[HgI3]-
Square planar (4)
M
[Ni(CN)4]2-
Tetrahedral (4)
M
[Zn(NH3)4]2+, [FeCl4]-

Coordination No. 5

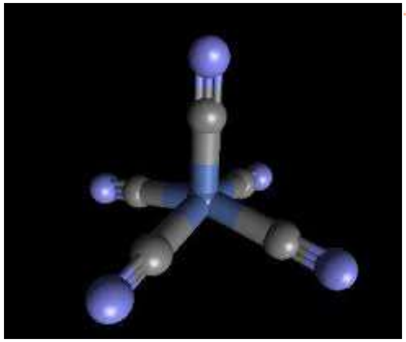
Number | **Geometry** | **Polyhedron**

Square pyramid (5)



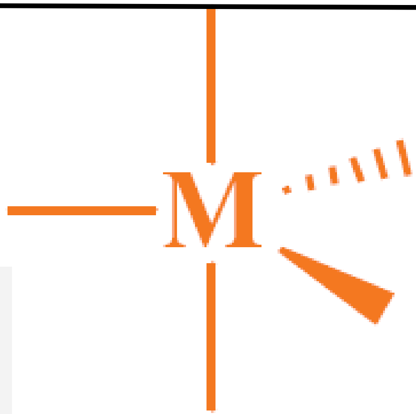


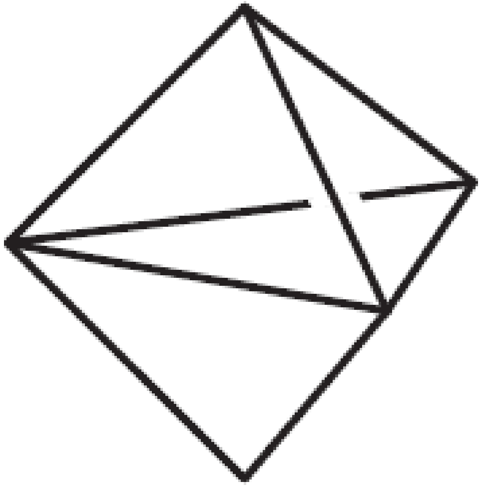
Example:



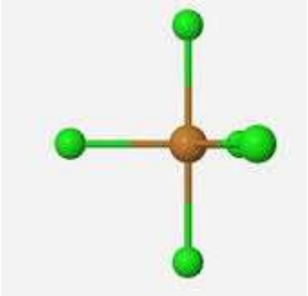
$[Ni(CN)_5]^{3-}$

Trigonal bipyramid (5)





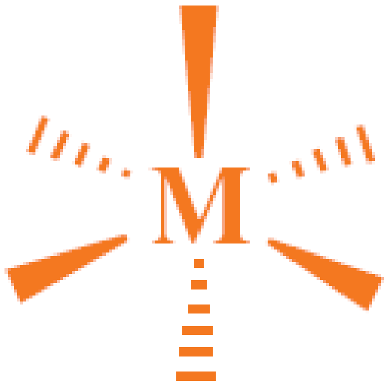
Example:

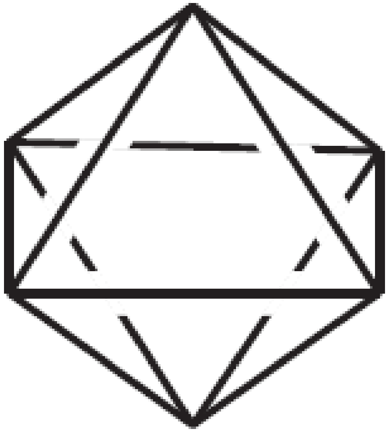


$[Cu(Cl)_5]^{3-}$

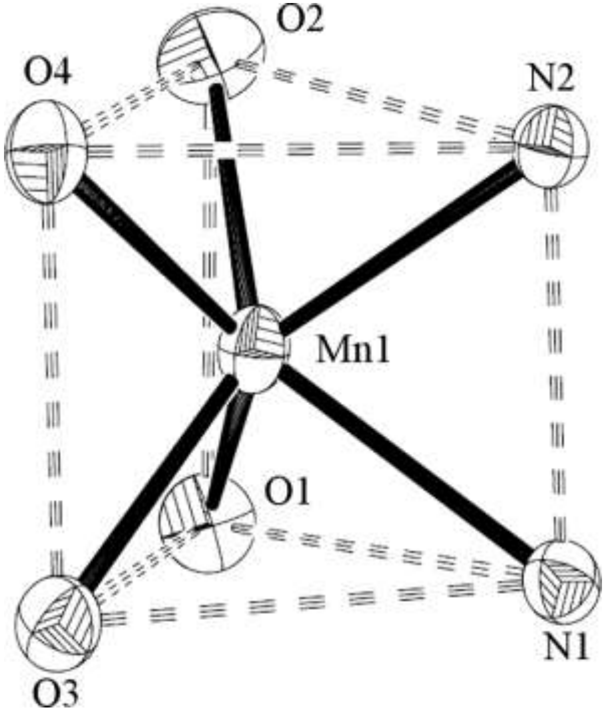
Coordination No. 6

Octahedral (6)





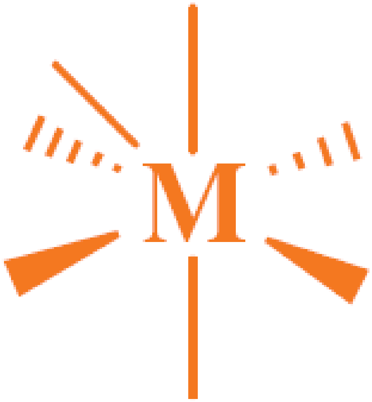
Triagonal prism

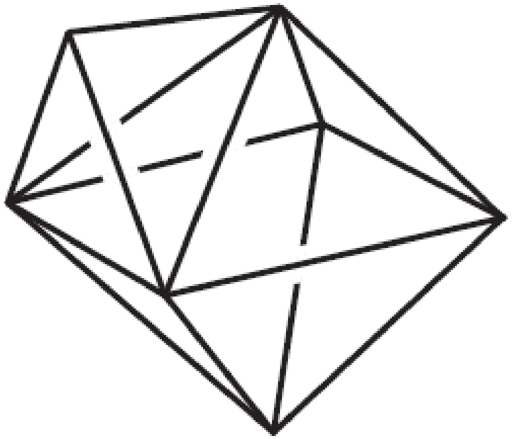


Coordination No. 7

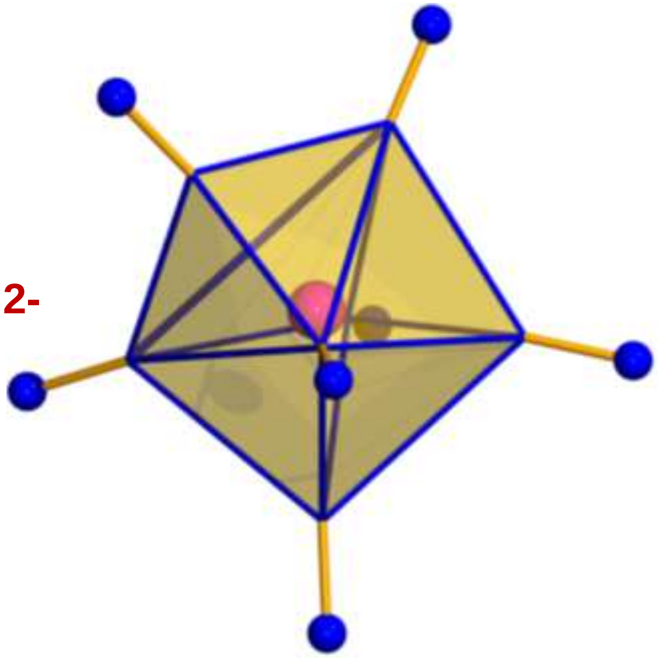
Number | **Geometry** | **Polyhedron**

Singly capped octahedron (7)

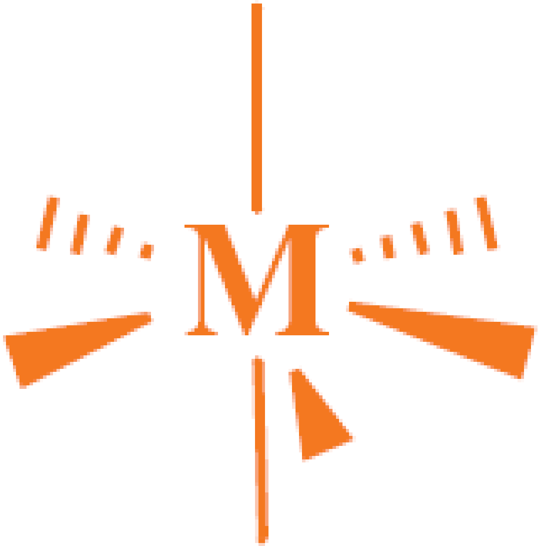


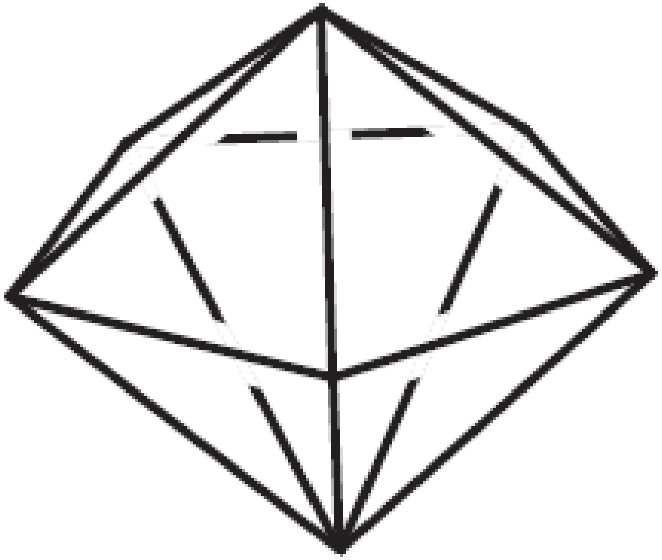


$[Mo(CN)_7]^{2-}$

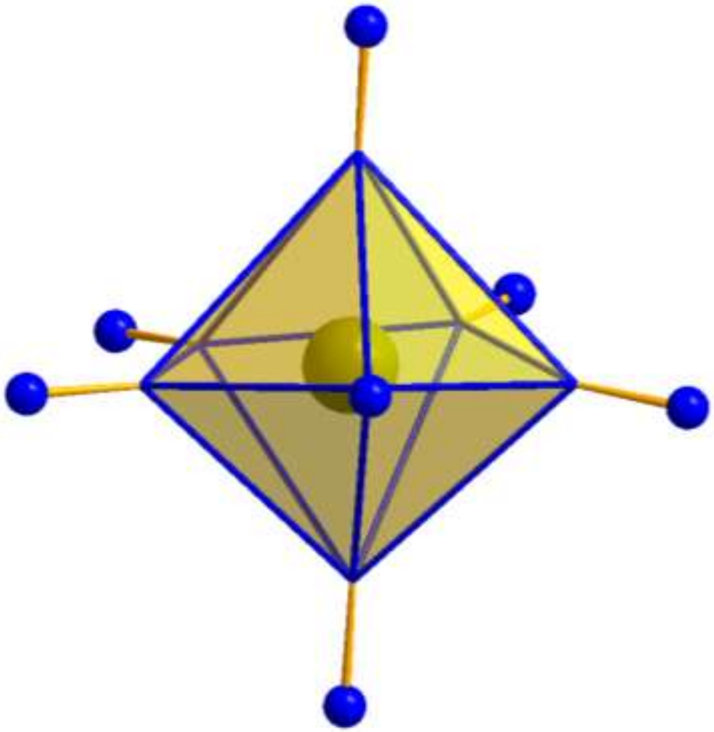


Pentagonal bipyramidal (7)



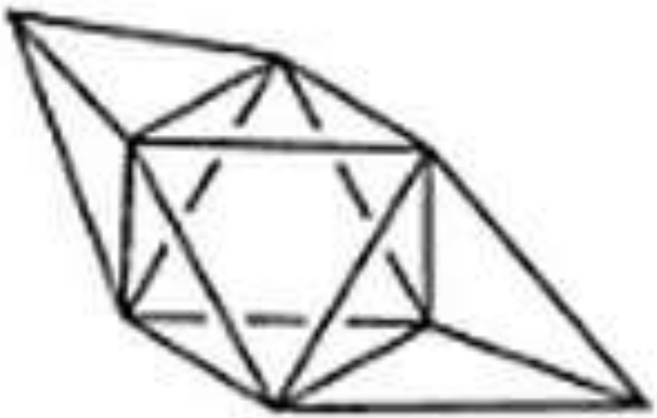


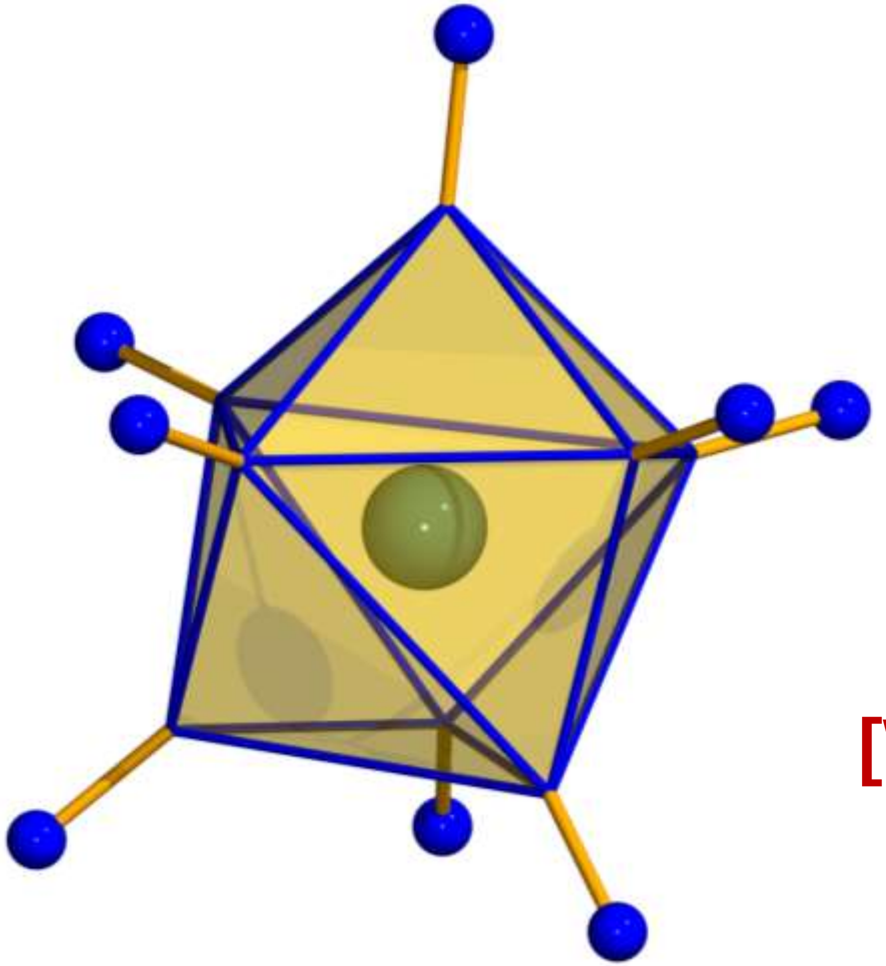
$[Re(CN)_7]^{2-}$



Coordination No. 8

Doubly capped octahedral (8)





$[W(CN)_8]^{3-}$

Self Study
Isomerism
Naming of complexes

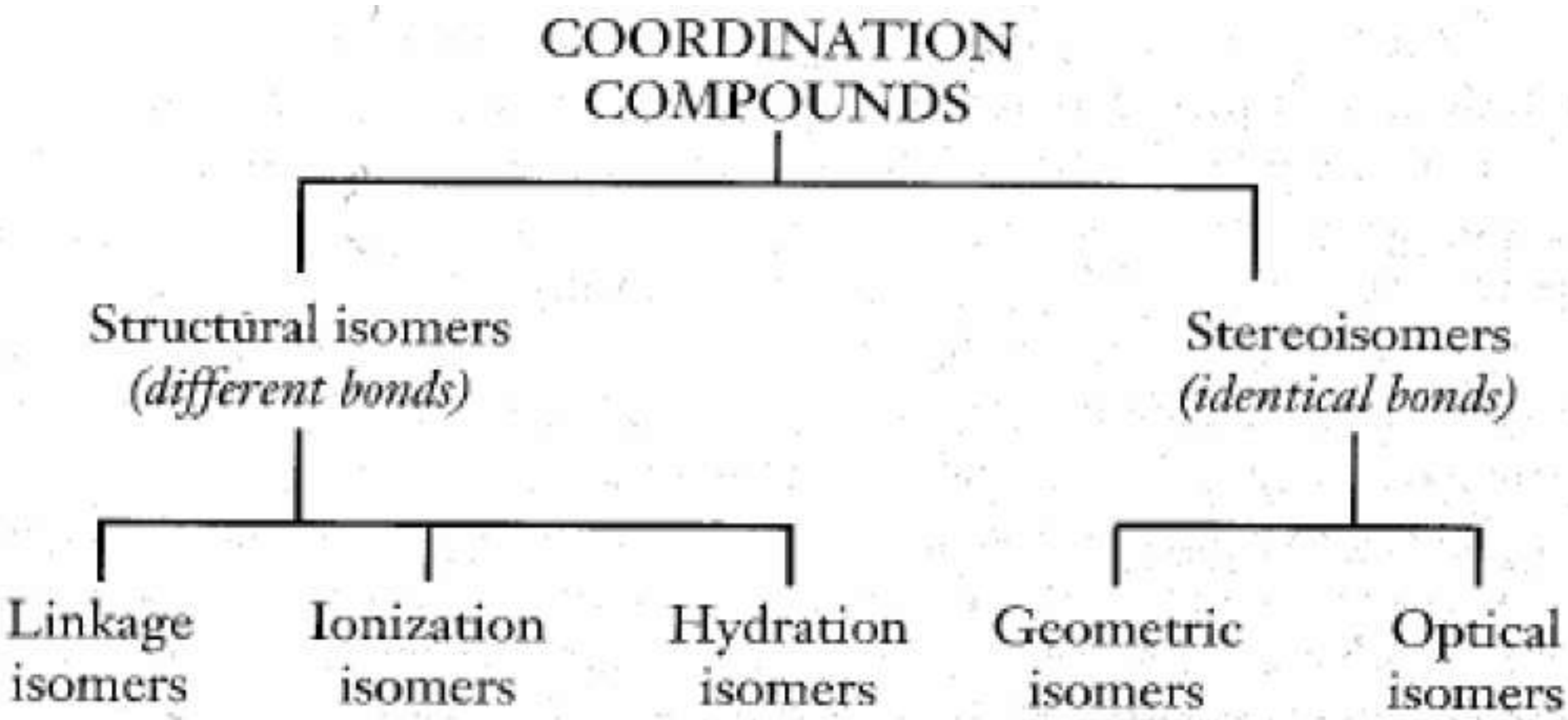
Self Study

Isomerism in metal complexes

Isomers are compounds with the same chemical formula but different structures

Note that as they have different structures, they will have different physical and chemical properties.

Self Study


COORDINATION
COMPOUNDS
Structural isomers
(different bonds)
Stereoisomers
(identical bonds)
Linkage
isomers
Ionization
isomers
Hydration
isomers
Geometric
isomers
Optical
isomers

Self Study

Naming of complexes

The naming of compounds containing coordination complexes follows a set of well defined norms

1) In a salt, the cation is always named before the anion
2) The names of ligands are given in alphabetical order

*The names of coordinated anions end “o”, e.g., chloro, cyano, etc.

*The names of neutral ligands are just the names of the ligand molecule

*Some ligands have special names when they are in complexes, eg., H_2O -- Aquo, NH_3 -- ammine

Self Study

3) The number of ligands that are present is indicated by a prefix, di, tri, etc. However, if these prefixes are already exist in the name of the ligand, then use bis, tris, tetrakis, etc.
   >Dichloro means two chloride ligands
   > Bisethylenediamine means two ethylenediamine ligands

4) After the ligands, we specify the metal and its oxidation state as a roman numeral in brackets
   >Platinum(II) indicates that the platinum is in an oxidation state of two

$[Cr(NH_3)_3(H_2O)_3]Cl_3$ ***triamminetriaquachromium(III) chloride***