



CHEM F111 : General Chemistry

Semester II: AY 2017-18

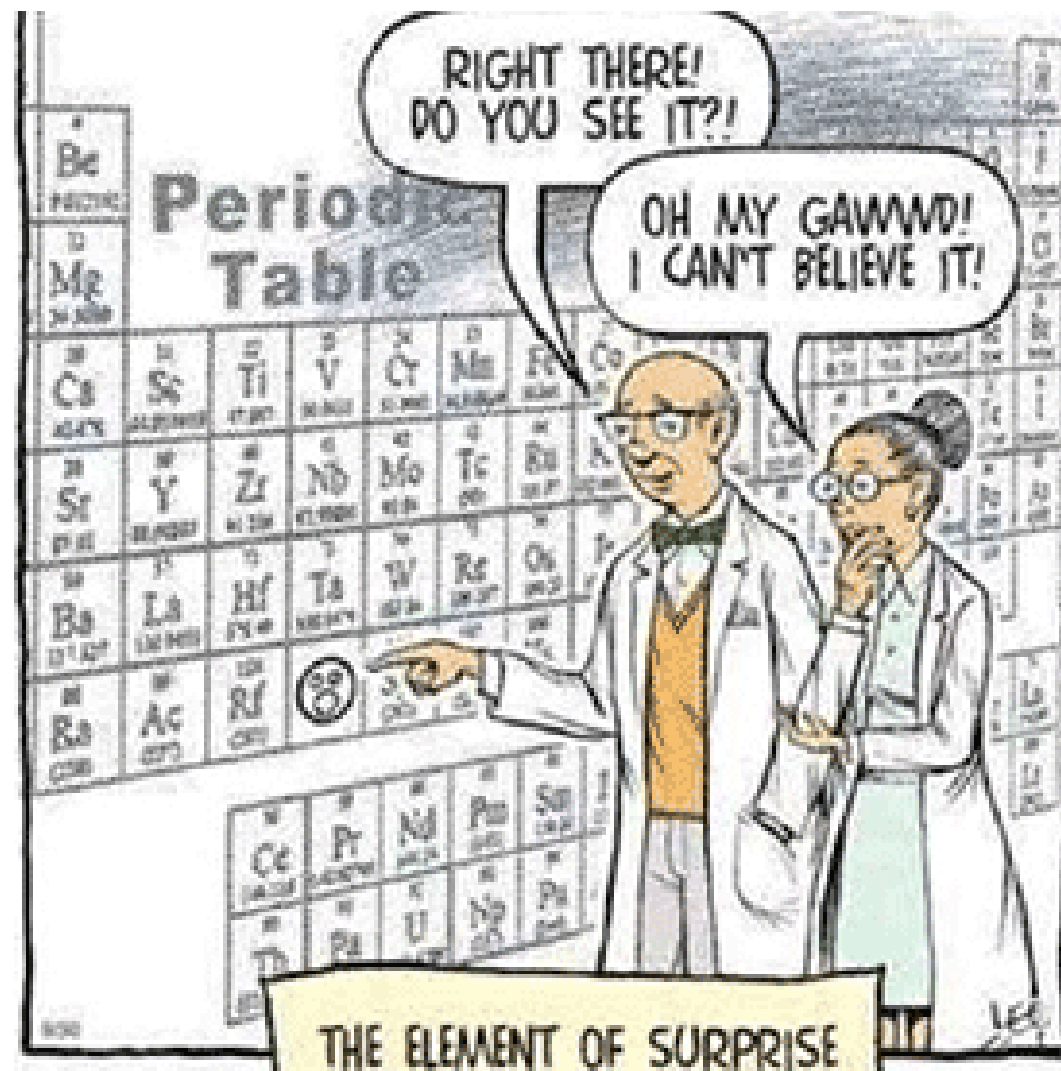
Lecture-21, 12-03-2018

Notice:


Assignment-02 will be conducted on
28-03-2018 at 17.30 hrs

You learned so far (10+2)

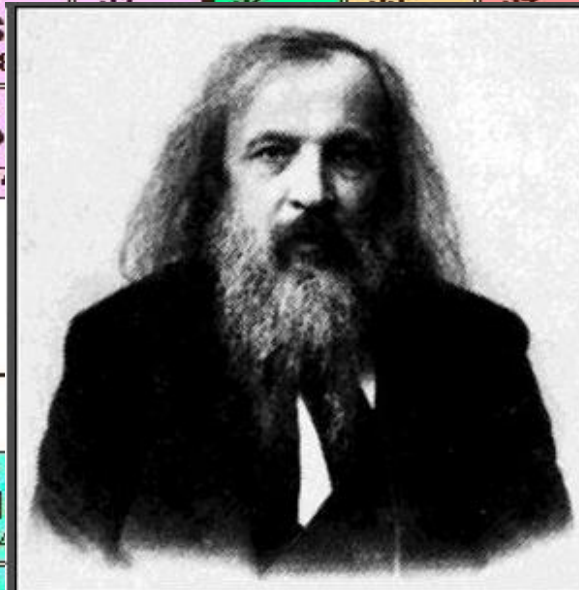
- Redox reactions
- Hydrogen and related compounds
- s-block elements
- *p* block elements
- d and f block elements
- Metals, non-metals, Alloy etc.



1/IA																18/VIIIA										
1	1 H 1.008																2 He 4.003									
2/IIA																13/IIIA		14/IVA		15/VA		16/VIA		17/VIIA		
2	3 Li 6.941	4 Be 9.012															5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18				
3	11 Na 22.99	12 Mg 24.30	VIII										13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95								
4	19 K 39.10	20 Ca 40.08	3/IIIB	4/IVB	5/VB	6/VIB	7/VIIB	8	9	10	11/IB	12/IIB	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80								
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3								
6	55 Cs 132.9	56 Ba 137.3	La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 208.98	84 Po 209	85 At 210	86 Rn 222								
7	87 Fr 223.0	88 Ra 226.0	Ac-Lr	104 Db 262	105 JI 261	106 Rf 261	107 Bh 264	108 Hn 277	109 Mt 268	110 Uun 289	111 Uuu 288															
<div><div>s</div><div>d</div><div>f</div></div>																										
Lanthanides			57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm 146.9	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9													
Actinides			89 Ac 227.0	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu 239.1	95 Am 241.1	96 Cm 244.1	97 Bk 249.1	98 Cf 252.1	99 Es 252													
<div><div>f</div></div>																										



Dmitri Mendeleev

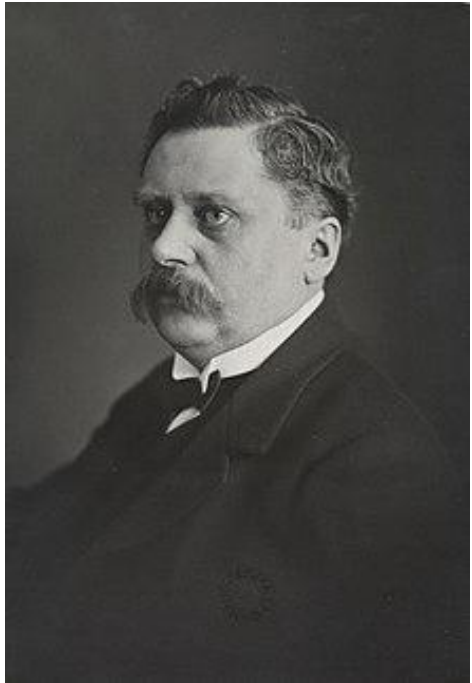


Dmitri Mendeleev

Topics to be discussed



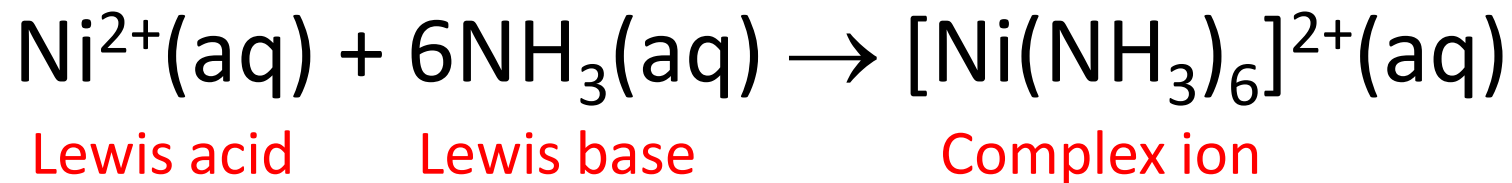
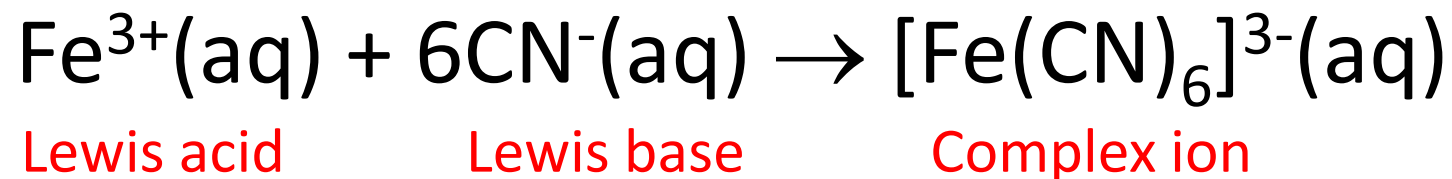
21-23	Coordination Chemistry: Coordination compounds	Double salts and coordination compounds. Werner's work; effective atomic no. concept.; Chelates and isomerism; shapes of d orbitals, crystal field theory, octahedral complexes, spectrochemical series	R1: p194-200 (SS); p202-214; p222-224, p232-235	<ul style="list-style-type: none"> The concept of chelates and coordination compounds Development of coordination complexes in light of various theories
24-26	Distortion of Complexes; Tetrahedral, Octahedral, and Square planar arrangement	Jahn-Teller distortion: Effect of geometrical distortions on stability, stability in other geometries	R1: p214-222	<ul style="list-style-type: none"> Nature of ligand, idea of different orbitals and their effect in inorganic complexes Idea of distortion in tetrahedral, octahedral, and square planar complexes
27-29	Coordination Chemistry: Octahedral complex, CFSE, and Electronic spectroscopy of Oh complexes	CFSE, effects of crystal field splitting, Electronic spectra of octahedral complexes, Applications of term symbols, Thermodynamic and kinetic aspects of Inorganic complexes, Latimer and Frost diagram	R1: p210-214, p219-222 R1: p947-960 R3: p262-264, 380-381, 385-389	<ul style="list-style-type: none"> Spectral nature of inorganic complexes Effect of strength and the symmetry of ligand field on various energy levels Identify the nature of stable and unstable complexes



Alfred Werner

- ❖ Alfred Werner was a Swiss chemist and a professor at the University of Zurich.
- ❖ He won the **Nobel Prize in Chemistry in 1913** for proposing the octahedral configuration of transition metal complexes.
- ❖ Werner developed the basis for modern coordination chemistry.
- ❖ He was the first inorganic chemist to win the Nobel prize, and the only one prior to 1973

- Transition metals act as Lewis acids
 - Form complexes/complex ions



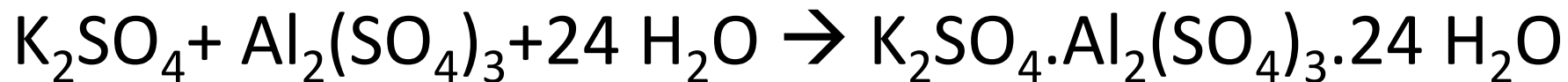
- Complex with a net charge = complex ion
- Complexes have distinct properties

Addition Compounds



When stoichiometric amounts of two or more stable compounds join together **two** types of addition compounds are formed.

(i) Double salts



Double salts lose their identity in solution

(ii) Co-ordination compounds



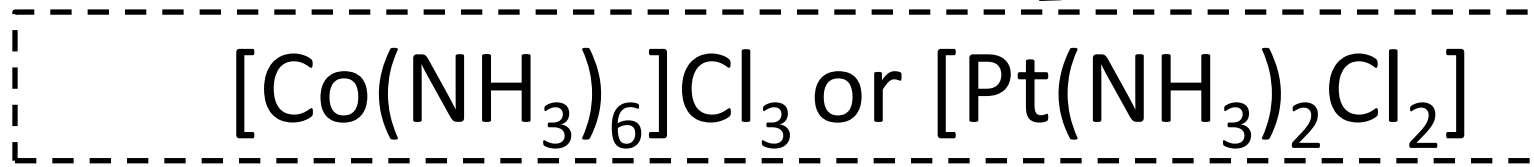
$[\text{Fe}(\text{CN})_6]^{4-}$ is stable in solution

Coordination Compounds



Compound that contains
one or more complexes

Coordination sphere: Metal
and ligands bound to it



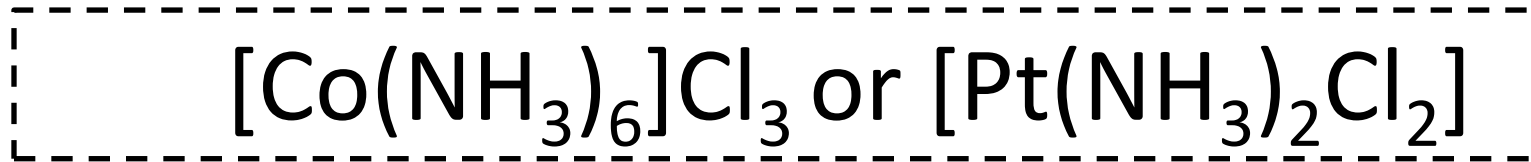
Coordination number: number of
donor atoms bonded to the central
metal atom or ion in the complex

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

Werner's work



- ❖ Metal ions exhibit **two** kinds of valence: primary and secondary



- ❖ The **primary** valence is the number of charges on the complex ion, **Non-directional**
- ❖ The **secondary** valence is the number of atoms that are directly bonded (coordinated) to the metal, **Directional**
- ❖ The secondary valence is also termed the “coordination number” of the metal in a coordination complex

Classification of Ligands

innovate

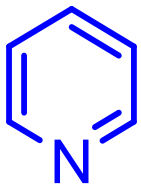
achieve

lead

Ligands: classified according to the number of donor atoms

monodentate

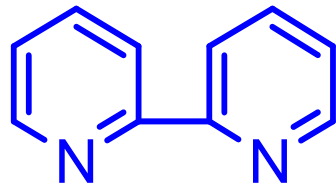
NH_3
ammonia
or ammine



pyridine
(py)

bidentate

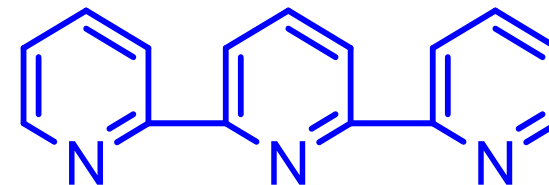
$\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$
ethylenediamine
(en)



2,2'-bipyridine
(bipy)

tridentate

$\text{NH}(\text{CH}_2\text{NH}_2)_2$
diethylenetriamine
(dien)



2,2':6',6''-terpyridine
(terpy)

An Illustration of Primary and Secondary valency



Conductivity and Cryoscopic Measurement

Formula	Cryoscopic Measurement	Molar Conductivity	Structure
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4 particles	6 charges	$[\text{Co}(\text{NH}_3)_6]^{3+} 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3 particles	4 charges	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2 particles	2 charges	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1 particle	0 charge	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
$\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$	4 particles	6 charges	$3\text{K}^+ [\text{Co}(\text{NO}_2)_6]^{3-}$

Effective Atomic Number (EAN)



Effective atomic number (EAN) rule : based on the octet theory of Lewis this is the first attempt to account for the bonding in complexes

Sum of the electrons on the **central atom** (*Lewis acid*) including those donated from the **ligands** (*Lewis base*) should be equal to the number of electrons on a noble gas



At. No of Cu = 29, Cu = +1, 4 L = 8 electrons gained

$$\text{EAN} = 29 - 1 + 8 = 36 \text{ (Atomic No. of Kr)}$$

- ❖ Gives stable compound
- ❖ Violated in many places

EAN: few more examples

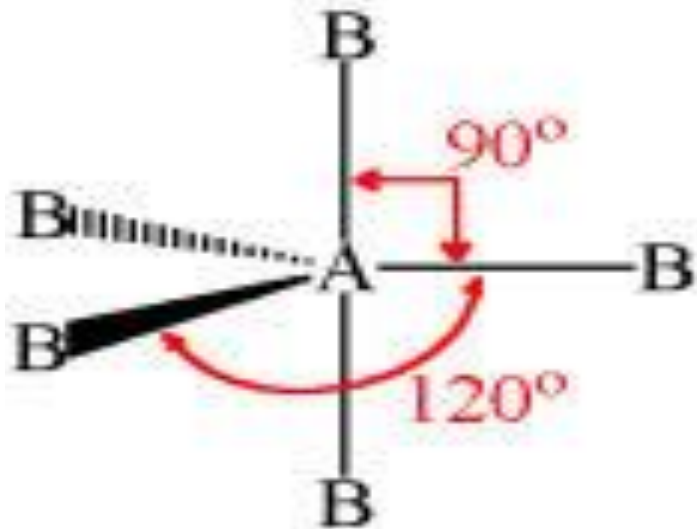


Atom	At. No.	Complex	Elec. Lost	Elec. Gained	EAN
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36 (Kr)
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36 (Kr)
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36 (Kr)
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36 (Kr)
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36 (Kr)
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36 (Kr)
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54 (Xe)
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86(Rn)
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84

EAN violations



- $[\text{Ni}(\text{NH}_3)_6]^{2+}$
- $\text{EAN} = 28 - 2 + 12 = 38 \neq 36$ (Kr)
- If we want 36 to be EAN we have to have penta coordination which leads to an irregular structure

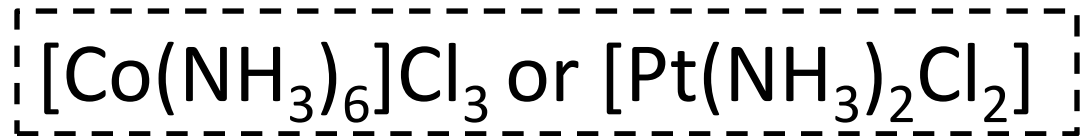
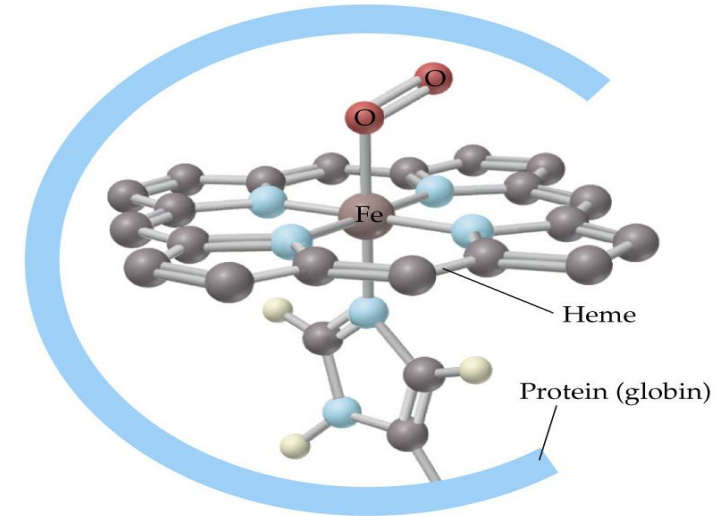
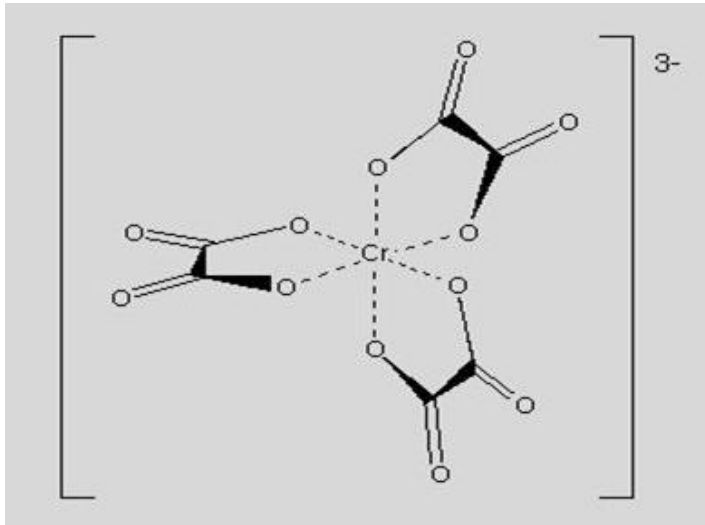


- Which in turn gives less stability
- Whenever higher coordination with a regular structure is possible that is preferred

Definition of Chelate



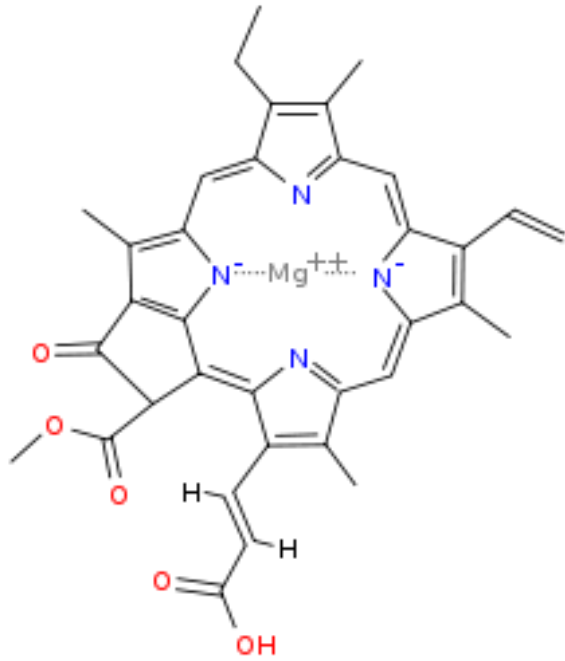
When more than one atom of the ligand is bonded to the central metal atom, ring structures are formed. Such ring structured complexes are called chelates.



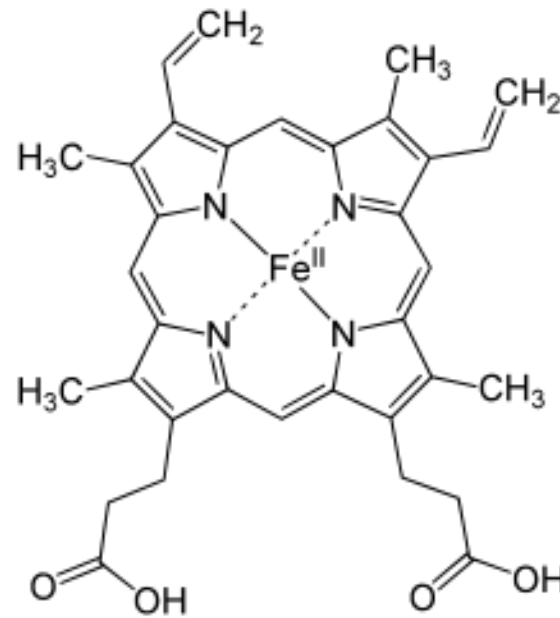
Example of Chelation



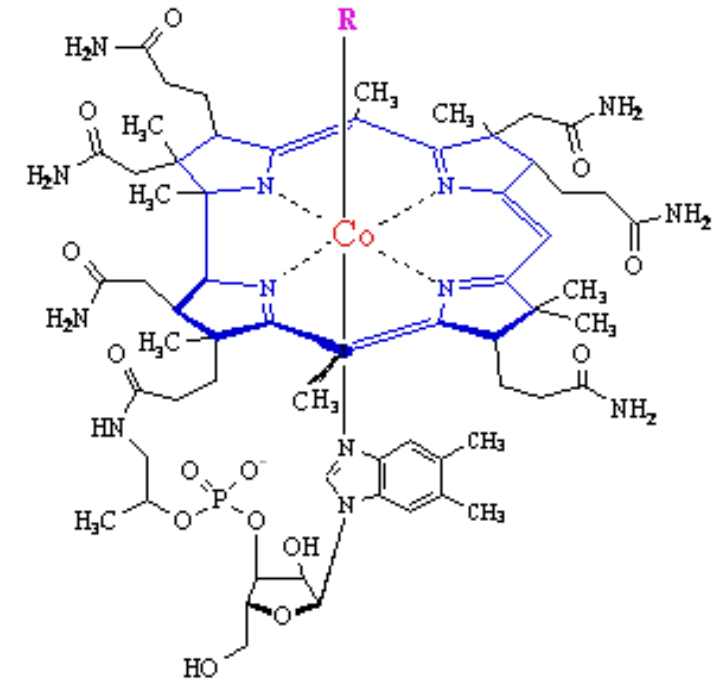
Chlorophyll, hemoglobin, vitamin B₁₂ have porphyrin related structures



chlorophyll



hemoglobin



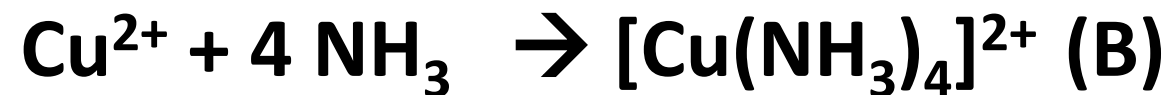
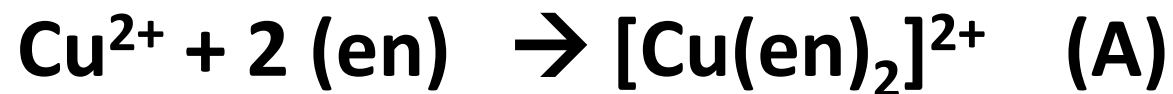
vitamin B₁₂

Stability of Chelates



The chelates are more stable than the normal compounds.

Consider the following square planar complexes

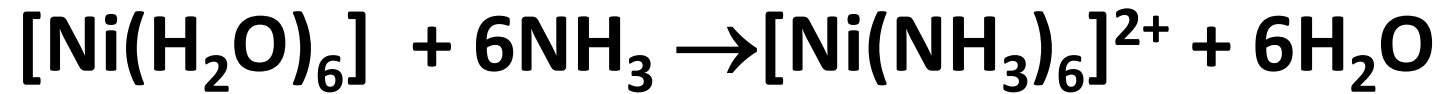
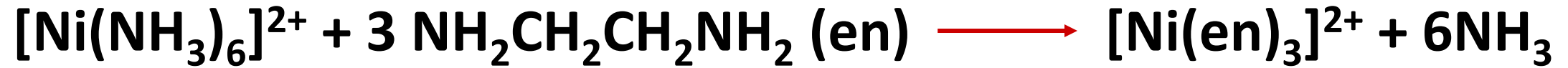


- A and B have same 4 Cu-N bonds

The higher stability of A is due to

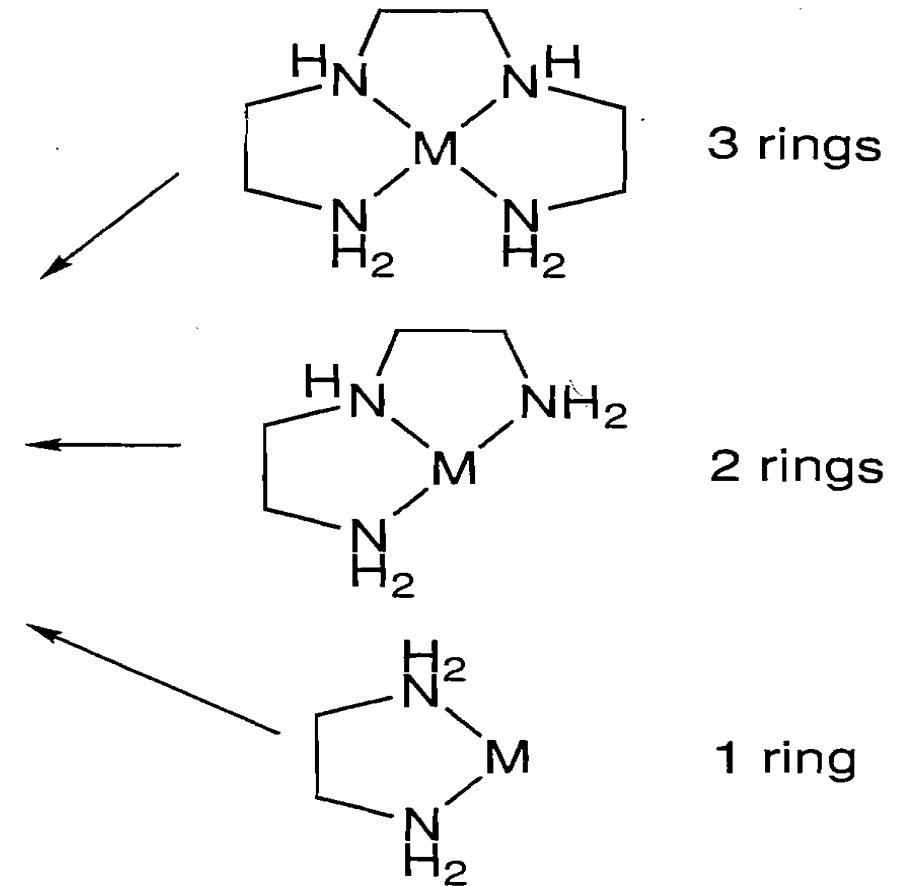
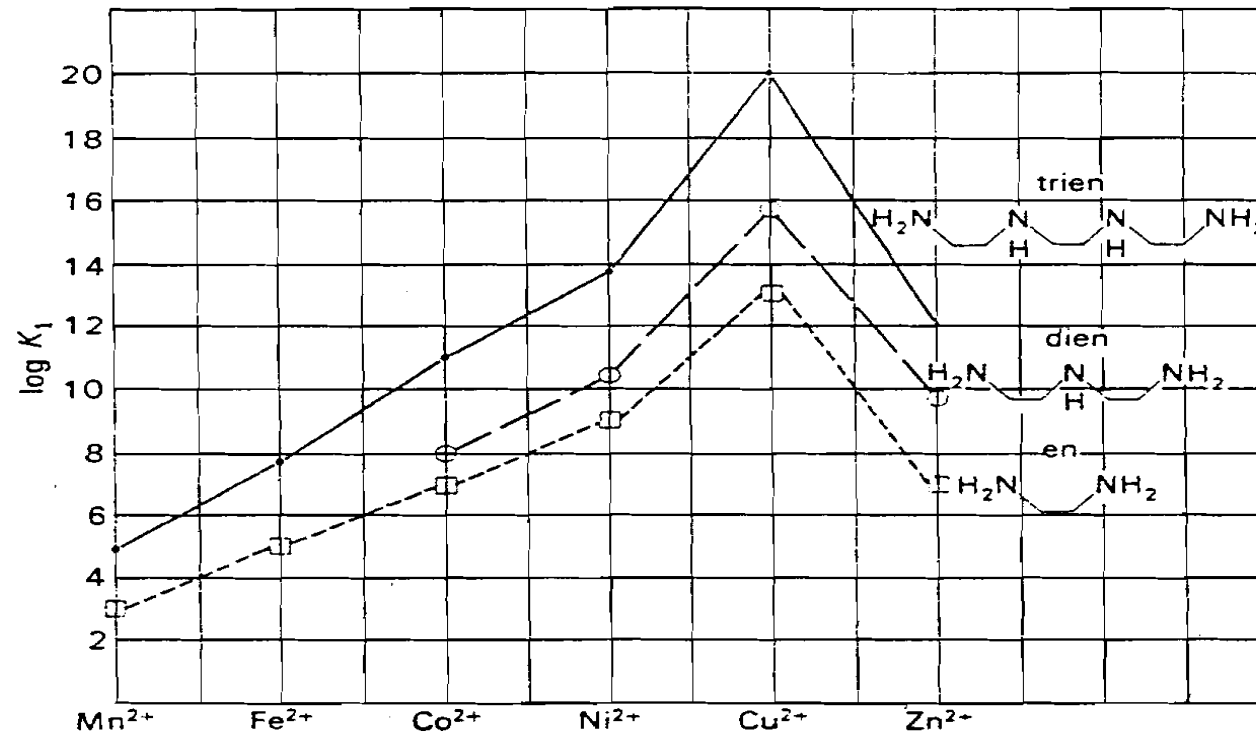
- Two bonds have to be simultaneously broken to detach the ring. More the rings are formed more will be the stability.
- Entropy factors (consider the backward reactions of the reactions given above).

Chelate formation: Major factor



- en and NH_3 have similar N-donor environment
- en is bidentate and *chelating* ligand
- reaction proceeds towards right, ΔG negative
- $\Delta G = \Delta H - T\Delta S$ (ΔH -ve, ΔS ++ve)
- reaction proceeds due to entropy gain
- ΔS ++ve is the major factor behind chelate effect

No. of Chelate Ring



Stability increases because enthalpy becomes increasingly negative (increased number of M–N bonds) & entropy increases

Chelating ligands

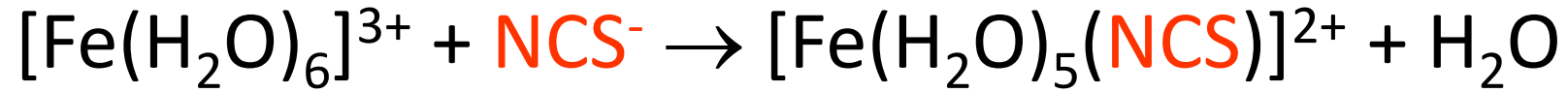


- Chelating ligands give much larger values of formation constants



- Sequestering agent are chelating agents that are used to remove unwanted metal ions
- In medicine, sequestering agent are used to selectively remove toxic metal ions (e.g., Hg^{2+} or Pb^{2+}), while leaving biologically important metal ions

Stability of complexes



$$K_f = [\text{Fe}(\text{H}_2\text{O})_5(\text{NCS})]^{2+} / [\text{Fe}(\text{H}_2\text{O})_6]^{3+} [\text{NCS}^-]$$

Equilibrium constant $K_f \Rightarrow$ formation constant

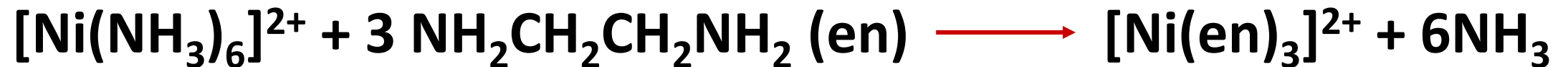


Stability of complexes



- $K_1, K_2, \dots \Rightarrow$ Stepwise formation constant.
- To calculate concentration of the final product, use **overall formation constant β_n** :

$$\beta_n = K_f = [ML_n]/[M][L]^n = K_1 \times K_2 \times K_3 \times \dots \times K_n$$



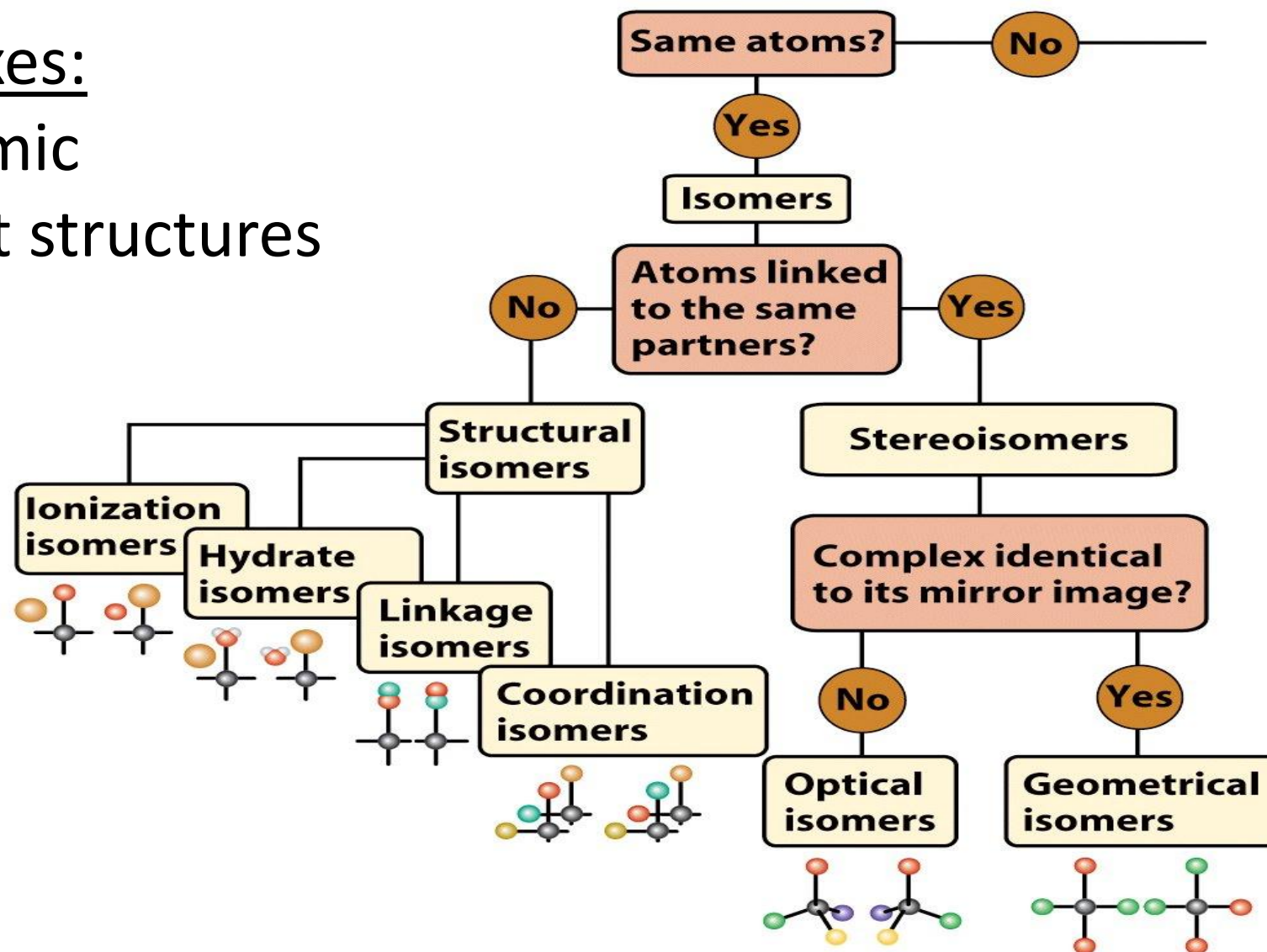
Isomerism

innovate

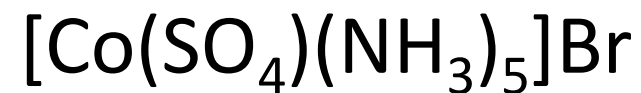
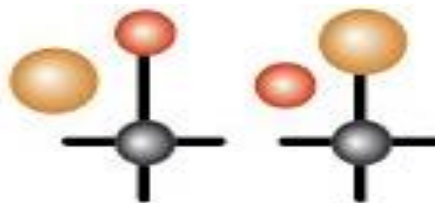
achieve

lead

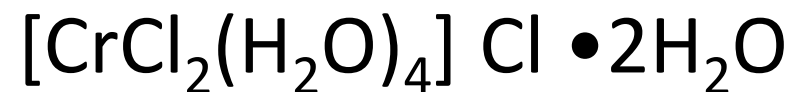
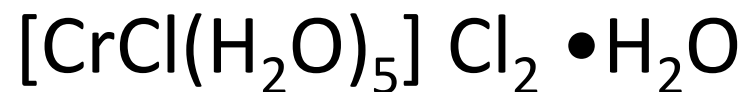
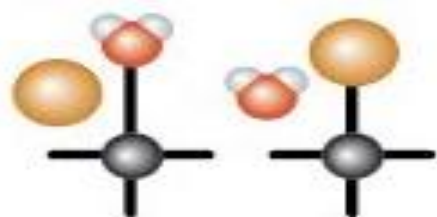
Coordination complexes:
Isomerism: Same atomic composition, different structures



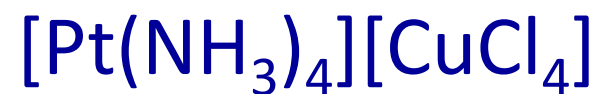
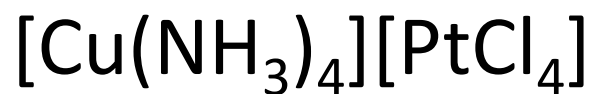
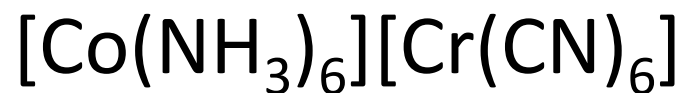
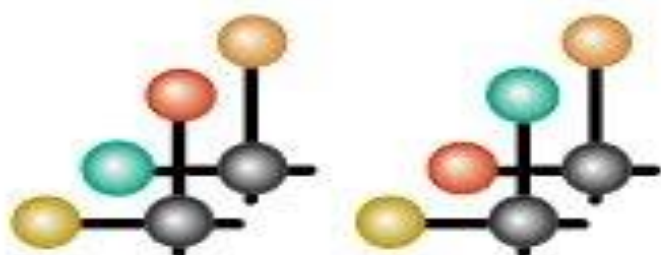
Structural isomer



Ionization Isomers

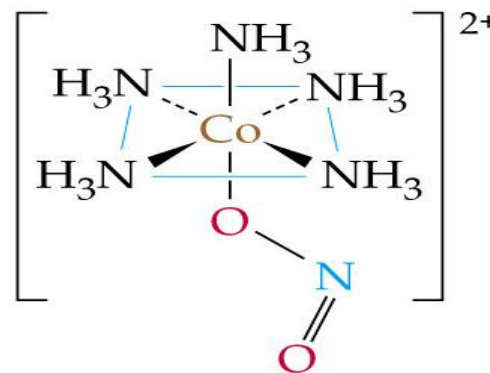
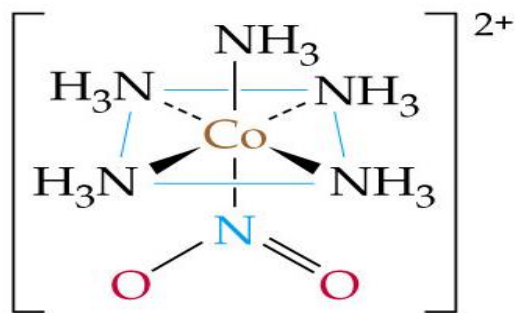
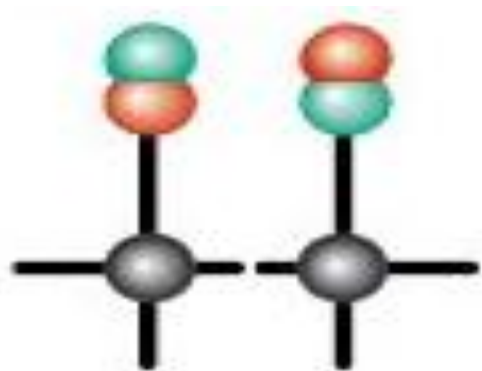


Hydrate Isomers

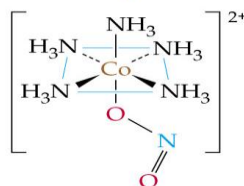
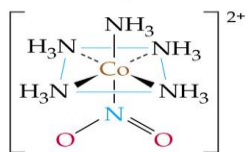


Coordination Isomers

Structural isomer



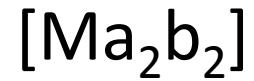
Linkage Isomers



Ambidentate ligands

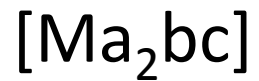
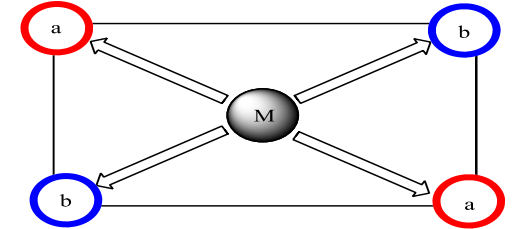
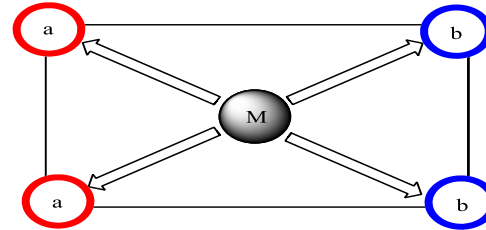
CN^- through C or N;
 SCN^- through S or N;
 $\text{S}_2\text{O}_3^{2-}$ through S or O.

Stereoisomers of square planar com.



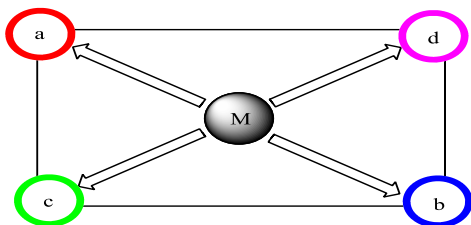
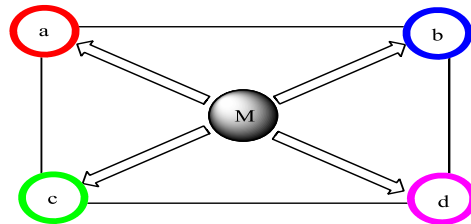
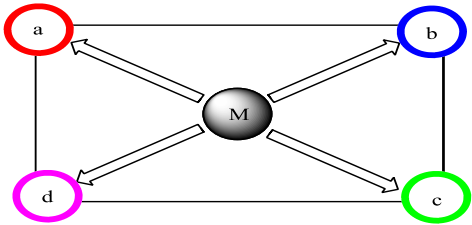
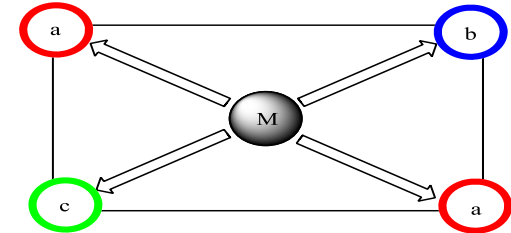
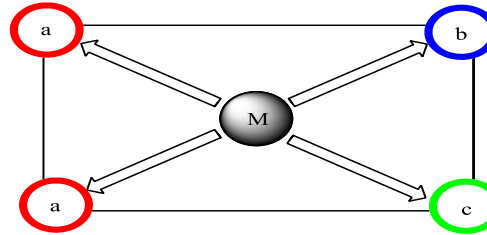
M=Metal centre;

a and b are monodentate ligands



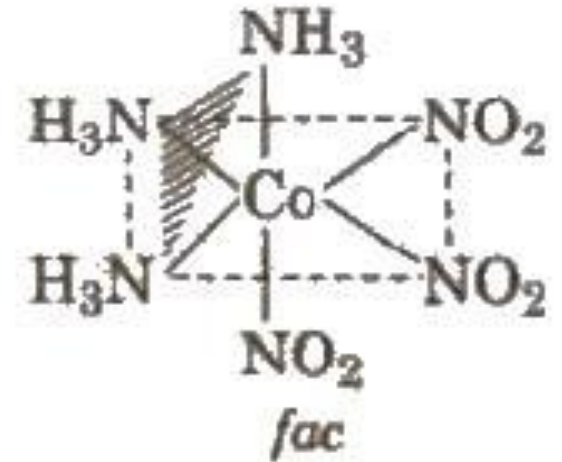
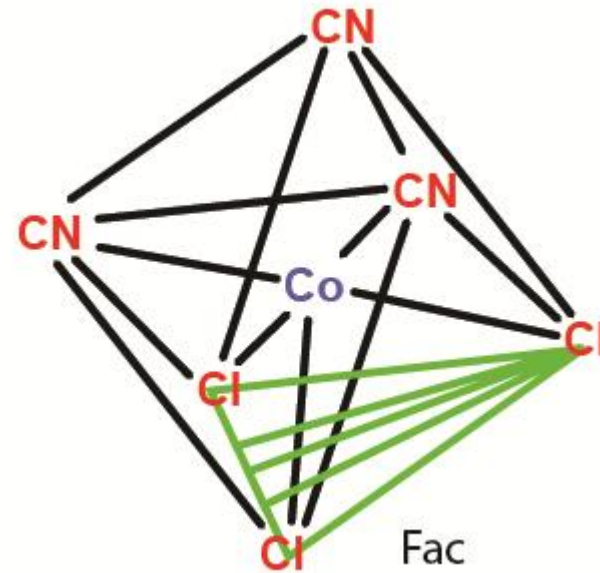
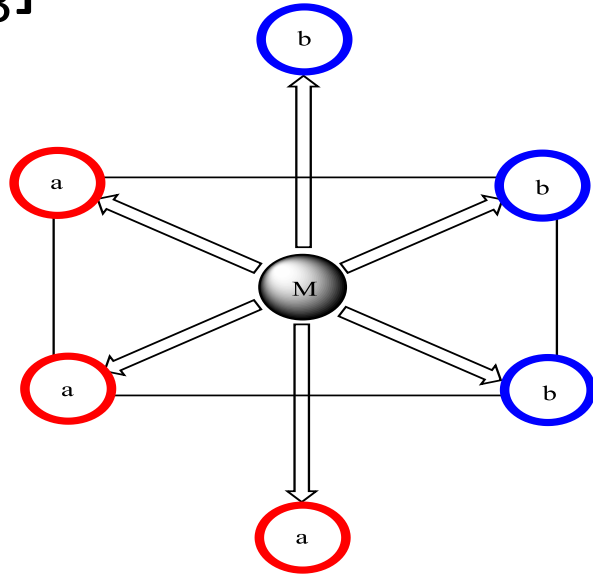
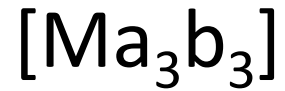
M=Metal centre;

a, b and c are monodentate ligands



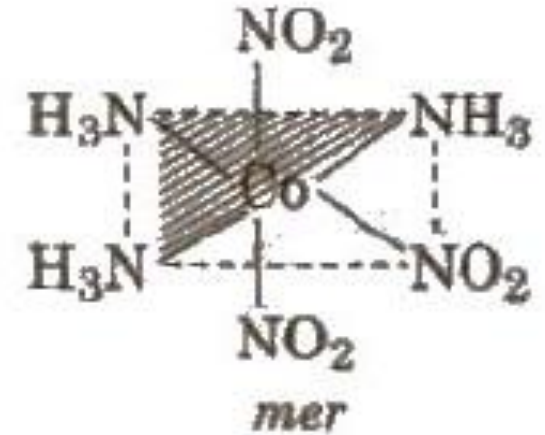
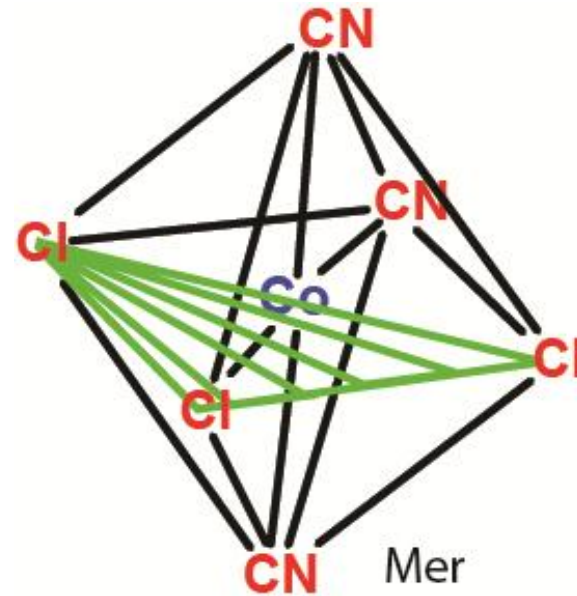
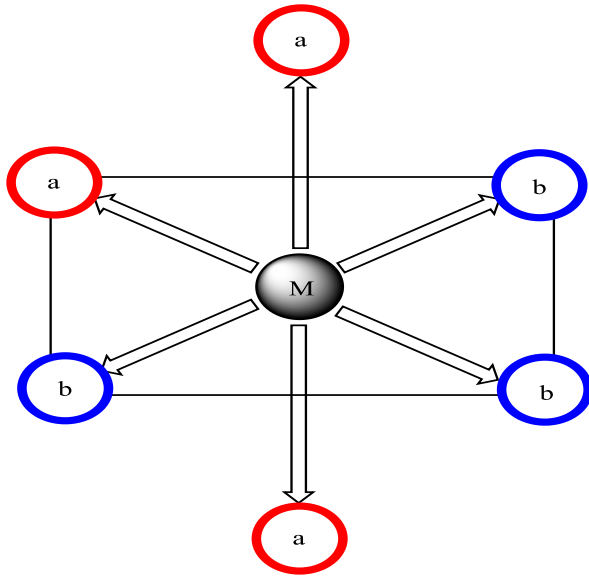
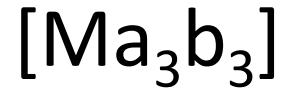
M=Metal centre; a, b, c and d are monodentate ligands

Stereoisomers of Octahedral com.



Facial isomer (*fac*) in which each set of three identical ligands occupies one face of the octahedron surrounding the metal atom, so that any two of these three ligands are mutually cis

Stereoisomers of Octahedral com.

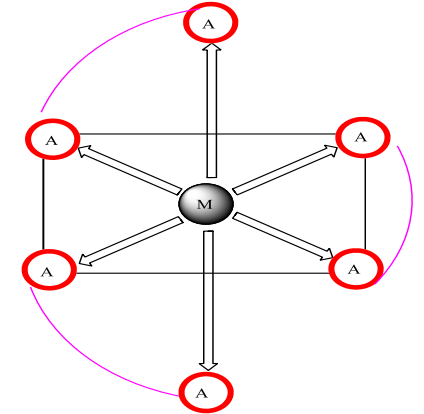
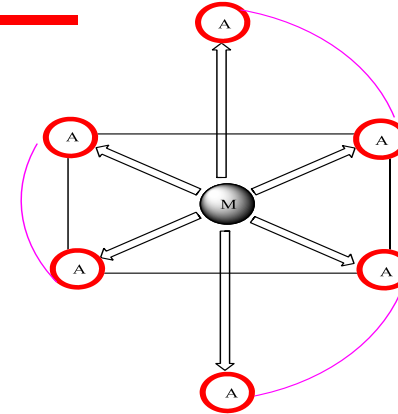


Meridional isomer (*mer*) in which each set of three identical ligands occupies a plane passing through the metal atom (the positions are around the meridian of the octahedron)

Stereoisomers of Octahedral com.



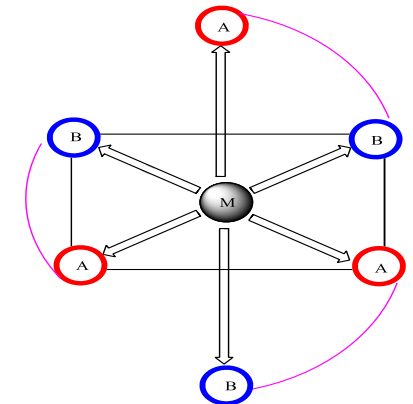
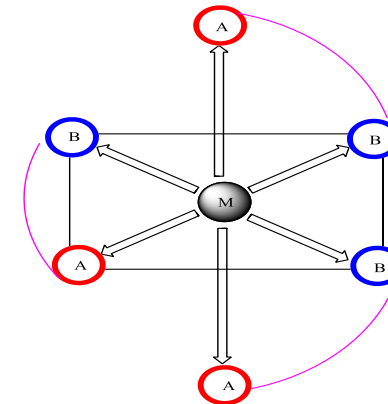
M=Metal centre; AA is a symmetrical bidentate ligand in which the two letters A and A are indicating the two similar coordinating atoms



Two Optical Isomers



M=Metal centre; AB is an unsymmetrical bidentate ligand in which the two letters A and B are indicating the two different coordinating atoms



And their mirror images
Total = 4 isomers

Discussed topics.....



- Double salt and coordination compound
- Werner's work
- Identification of structure by isomer counting
- Effective atomic number
- Chelates and isomerism

Next class.....



- ✓ Crystal field theory
- ✓ Shapes of d orbitals
- ✓ Nature of ligand
- ✓ Spectrochemical series

Classification of Ligands (Supporting Slide)



(A) Charge (formal charge)

- Neutral (e.g. :CO, :PR₃, :NH₃)
- Anionic (e.g. Cl⁻, O²⁻, CH₃⁻)
- Cationic (rare!) (e.g. NO⁺, C₇H₇⁺)

(B) Hard/Soft properties

Hard : period 1 donor (NH₃, OH₂)

Soft : carbon (CO, CH₃⁻, CH₂=CH₂) & period 2 donors
(PR₃, SR₂)

Stability of Chelates (supporting slide)

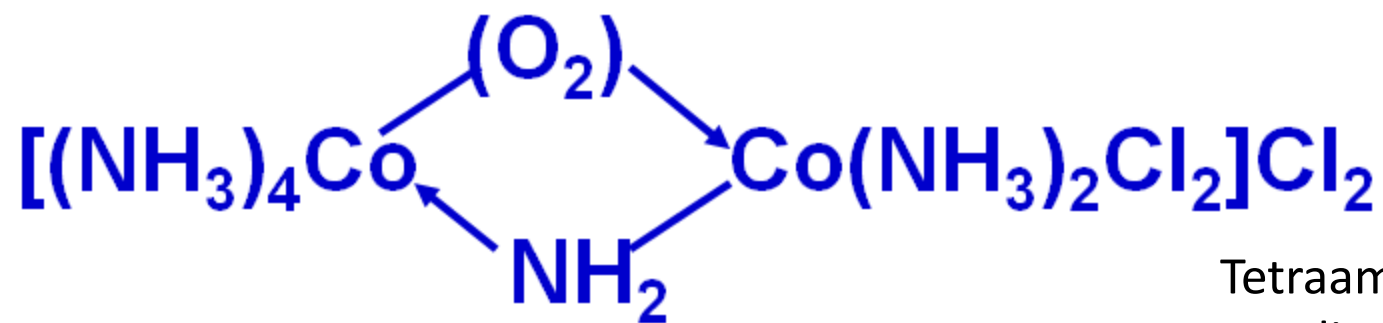


- ❖ Among the ring structures five and six membered rings are more stable
- ❖ For smaller and larger ring sizes the steric factors dominate; i.e. the rings are strained
- ❖ Alternate single and double bonds gives further stability; i.e. conjugation brings delocalization of electrons

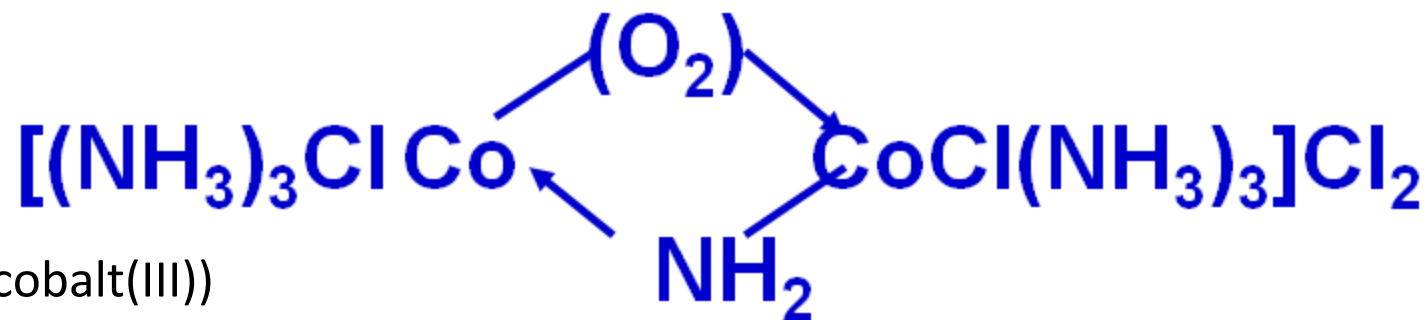
Coordination position isomer



In polynuclear complexes an interchange of ligands between the different metal nuclei gives rise to positional isomerism.



Tetraamminecobalt(III)-μ-amido-μ-superoxo
diamminedichlorocobalt(III) chloride

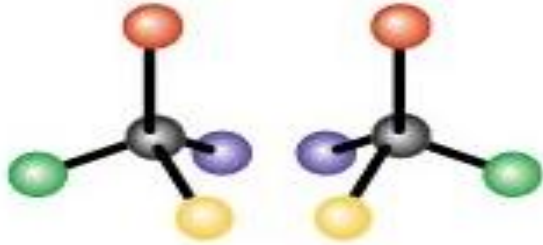


μ-amido-μ-superoxobis(triamminechlorocobalt(III))
chloride

Stereoisomer (supporting slide)



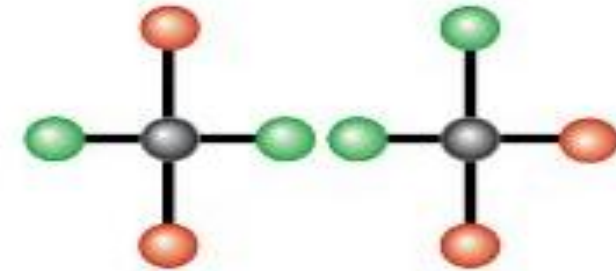
Four-coordinate complexes:



Tetrahedral Complexes

Geometrical complexes cannot arise in tetrahedral complexes. Why?

A tetrahedral complex of the form $[Mabcd]$, where M=Metal centre; a, b, c and d are monodentate ligands occurs in **two optical isomers**.



- Square-planar complexes may have *cis* and *trans* isomers (DIASTEROMERS). No chiral isomers (enantiomers) are possible when the molecule has a mirror plane.
- *cis*- and *trans*-isomers of square planar complex of platinum

Optical isomer (supporting slide)

