

CYL120 Inorganic and Organic Chemistry: Concepts and Applications

4 credits **CYL 120 (INORGANIC)**

Inorganic Chemistry:

**Prof. A. K. Ganguli**

**Organic :  
Prof Nalin Pant  
Minor I & II**

(i) Transition metal complexes: Crystal field theory, basic concepts, crystal field effects in linear (ML2), tetrahedral, square planar (ML4) and octahedral geometry (ML6), pairing energies, weak field and strong field case, crystal field stabilization energy, factors affecting magnitude of  $10Dq$ , high and low spin complexes, evidences for crystal field stabilization, tetragonal distortions from octahedral geometry, electronic spectra and magnetism.

**AKG**

**1 + 7**

(ii) Organometallics: EAN rule, metal carbonyls – synthesis, bonding and structure, metallocenes – synthesis and properties, Homogeneous and heterogeneous catalysis.

**J D Singh**

(iii) Bioinorganic chemistry: Metalloporphyrins, metalloproteins, hemoglobin and myoglobin – structure and function.

(iv) Inorganic solids: Structures and applications. Layered solids, Zeolites, magnetic and electronic properties of inorganic solids.

**AKG 2**

**(all lectures till from September 19 to October 17, 2012)**

**MS-709 , TEL : 1511; email : ashok@chemistry.iitd.ac.in**

**October 18 to Nov 16 : Prof J D Singh**

**Quiz ( october)**

**Major Exam : AKG & JDS (inorganic)**

A K Ganguli (ashok@chemistry.iitd.ac.in), MS-709, Tel :1511

1. Transition metal complexes – **REVISION** of  
Nomenclature, Isomerism and valence bond theory 1
2. **CRYSTAL FIELD Theory** 7  
Magnetic / optical properties of complexes  
Structural distortion in metal complexes
3. **Introduction to Inorganic Solids** 2

## Books Recommended

1. James E. HuHeey

Inorganic chemistry

2. F. A. Cotton, G. Willkinston and P. L. Gaus

Basic Inorganic Chemistry, J. Wiley and sons (1995) – Singapore

3. Shriver and Atkins : Inorganic Chemistry

( my part)

Quiz (10 marks; 30 min)

Major (20 marks; 1 hr)

# Why Study Inorganic Chemistry??

**Intellectual Pursuit**

**Practical Impact**

1. Eight out top ten chemicals are Inorganic. ( $\text{H}_2\text{SO}_4$ ) *max tonnage*

2. Inorganic Materials

(Semi conductors, Light guides on linear optical materials, super conductors) GaAs,  $\text{KTaO}_3$ ,  $\text{LiNbO}_3$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$

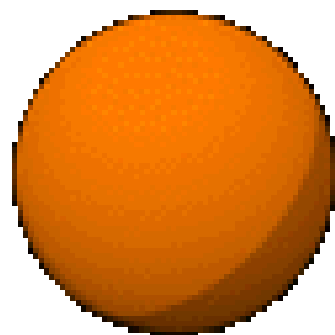
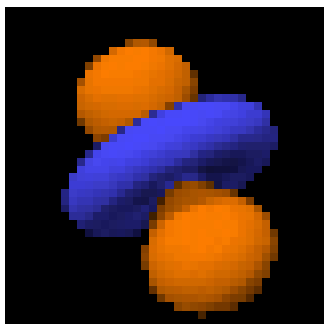
*Dupont, Monsanto, Dow Chemicals, Hercules, Baeyer, Unilever – Top Chemical Companies*

# Periodic Table of the Elements 2006

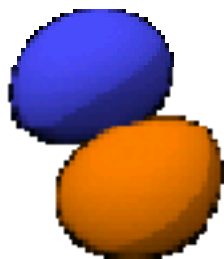
1 H 1.01																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 15.99	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
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)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (270)	109 Mt (268)	110 Ds (281)	111 Rg (272)							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

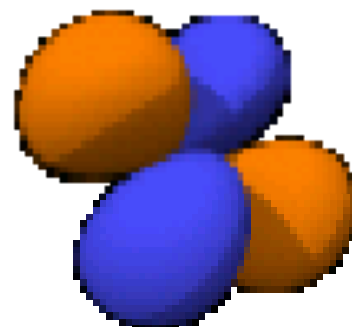
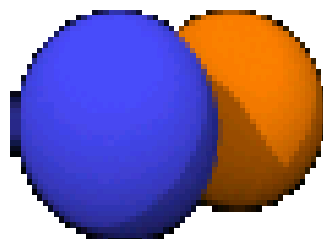
# ATOMIC ORBITALS



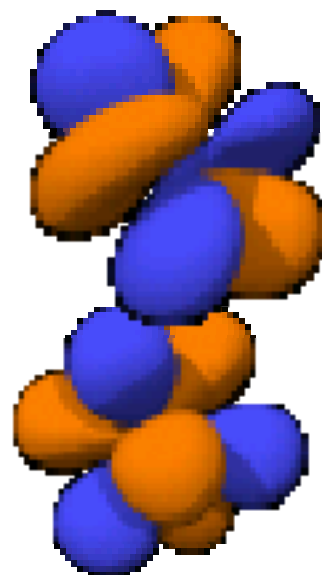
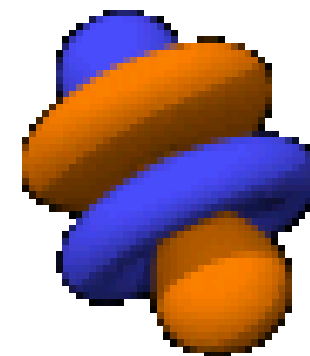
s



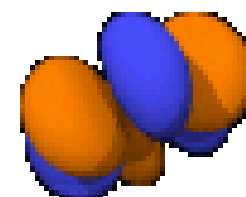
p



d



f



$$H\psi = E \psi$$

Schrodinger,s equation

$$\Psi = R(r) \Theta(\theta, \phi)$$

$$n = 1, 2, 3, \dots$$

$$l = 0 \text{ to } n-1$$

Quantum numbers

For  $n = 1, l = 0$       1s sub shell

For  $n = 2, l = 0, 1$

$l = 0$       2s sub shell

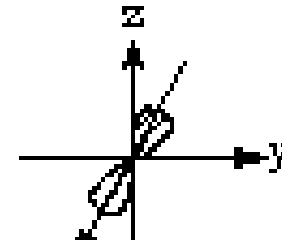
$l = 1$       2p sub shell

$$M_l = -l \text{ to } +l.$$

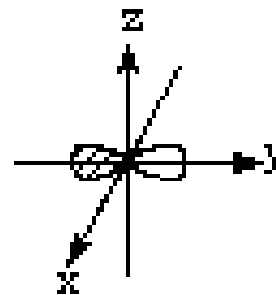
example  $Y_{-1}^1(\theta, \phi) = (1/2)(\sqrt{3}/\sqrt{2\pi})(\sin\theta)e^{-i\phi}.$

$$M_l = -1, l = 1$$

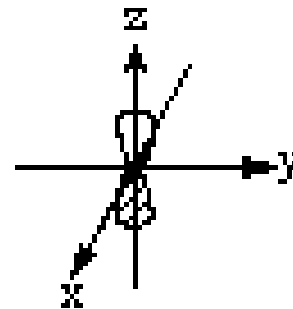
$$\Psi_{p_x}(r) = \frac{x}{r} R'(r)$$



$$\Psi_{p_y}(r) = \frac{y}{r} R'(r)$$



$$\Psi_{p_z}(r) = \frac{z}{r} R'(r)$$





# Transition Metal Complexes

## Transition Metal?

Elements having partial filled 'd' or 'f' shell in any of their commonly occurring oxidation states.

Fe, Co, Ni, Cu, Ag, Au etc

d - block transition metals.

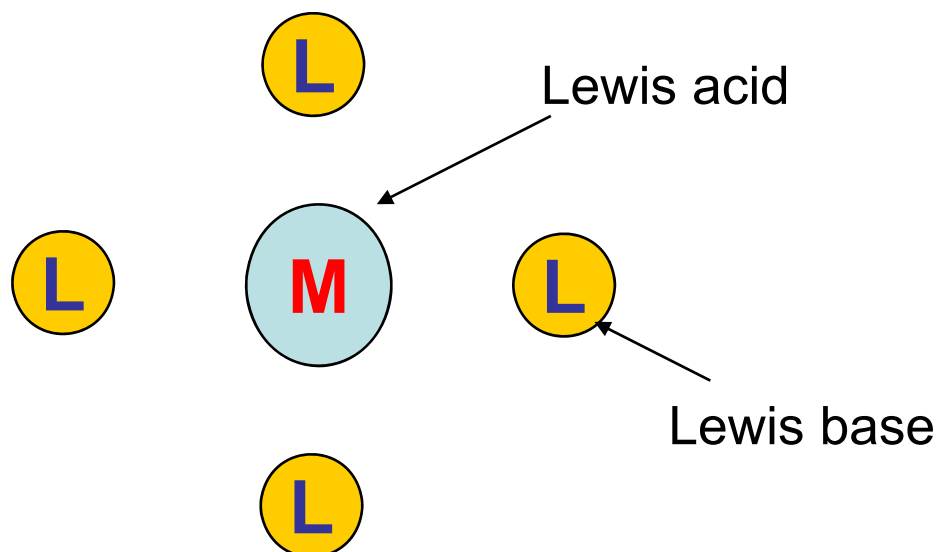
f -block (inner) transition metals (Lanthanides and actinides)

*Metals, variable oxidation states, hard, high melting point*

# Transition metal complexes / Coordination Compounds

A central atom, ion surrounded by anions or neutral molecules, which are Lewis bases and may be monoatomic or polyatomic, neutral or anionic (ligands) are coordination compounds.

**Ligand:** Lewis base bonded (coordinated) to a metal ion in a coordination compound.



Monodentate, bidentate

Coordination compounds on dissolution give rise to complex ions (complexes)

*[Retains the identity in solution]*

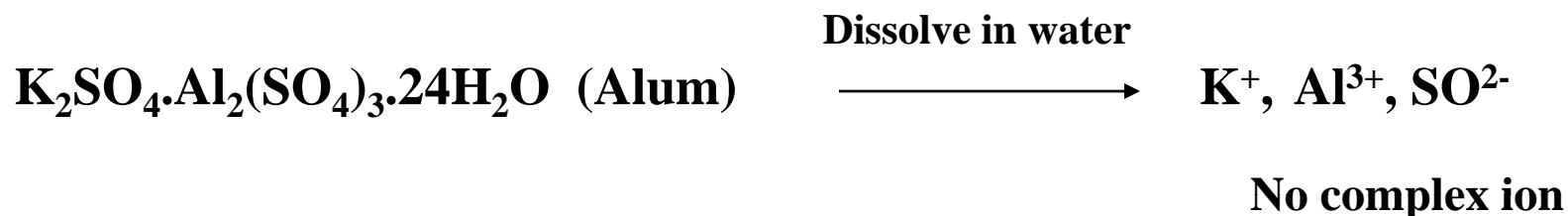


*Coordination compound*

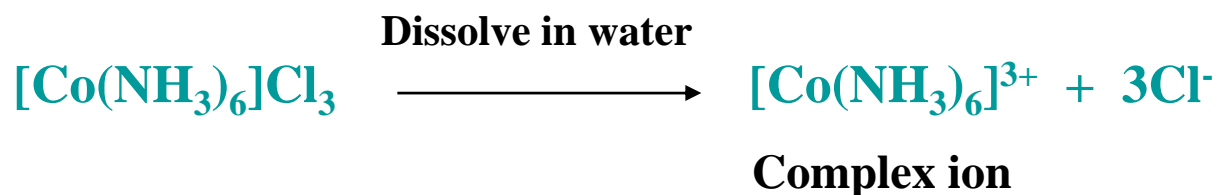
*Complex ion*

## How Complexes differ from Double salts??

**Double salts on dissolution in water lose their identity**



**Complex ions don't lose their identity on dissolution**



S. M. Jorgensen (1837 – 1914) }  
A. Werner (1866 - 1919) }      Synthesized many transition metal complexes

*1<sup>st</sup> Nobel prize in Inorganic chemistry (1913) : Werner*

## CoCl<sub>3</sub> – NH<sub>3</sub> Complexes

compound	Colour	Moles of AgCl	Werner's formula
CoCl <sub>3</sub> · 6NH <sub>3</sub>	Yellow	3	[Co(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub>
CoCl <sub>3</sub> · 5NH <sub>3</sub>	Purple	2	[Co(NH <sub>3</sub> ) <sub>5</sub> Cl]Cl <sub>2</sub>
CoCl <sub>3</sub> · 4NH <sub>3</sub>	Green	1	[Co(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> ]Cl

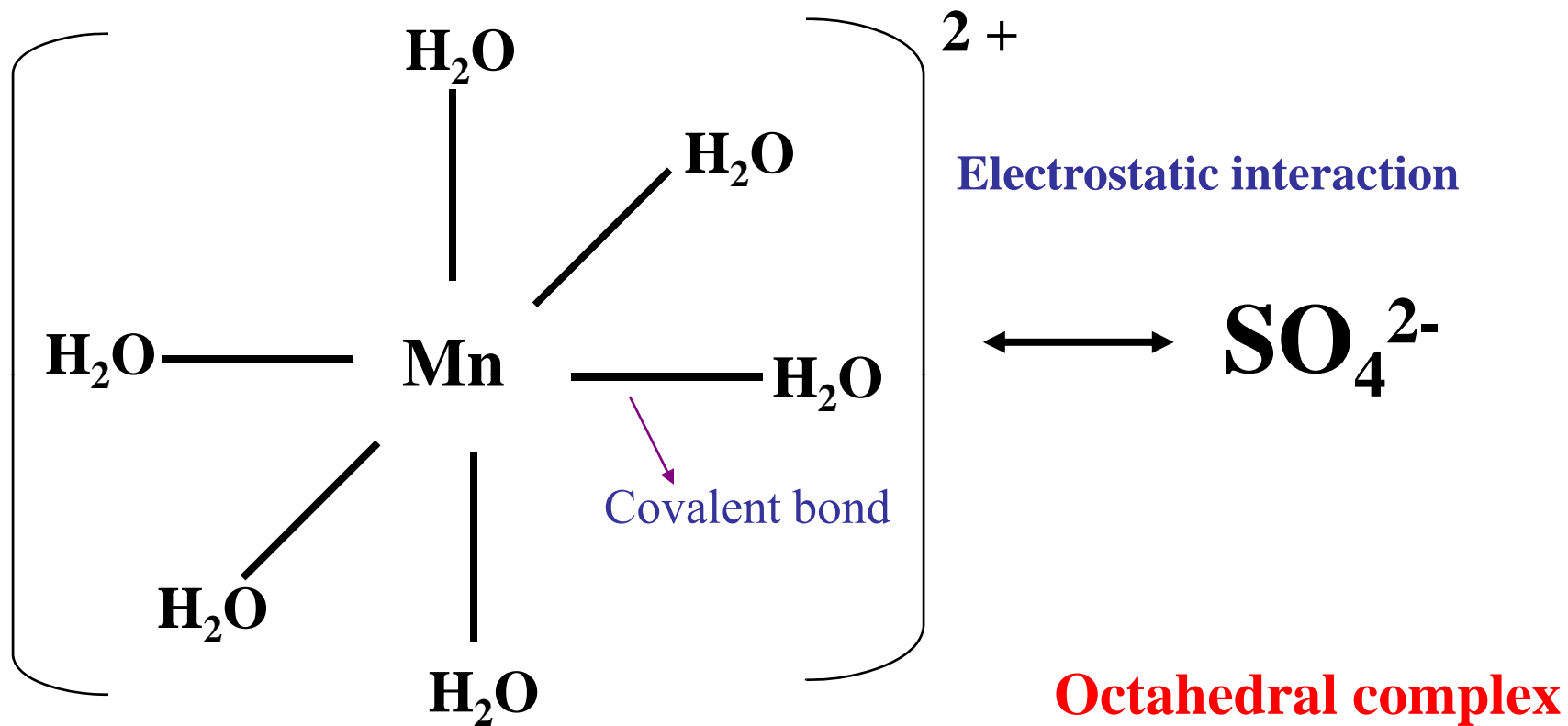
### Werner's main Study

#### Primary Valencies



#### Secondary Valencies

Normally fixed for a particular ion and oxidation state.



Coordination number is 6 (secondary valency)

Mn<sup>2+</sup>      —————      Central metal ion (Lewis acid)

H<sub>2</sub>O      —————      Ligand (Lewis base)

# Types of Ligands

## Monodentate ligands

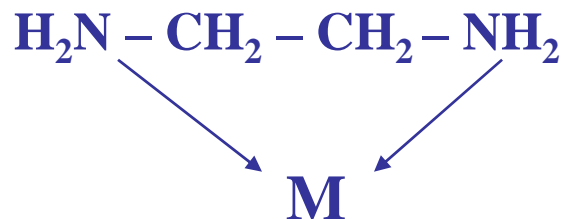
Donate one pair of electrons to a central metal ion.

e.g.  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$

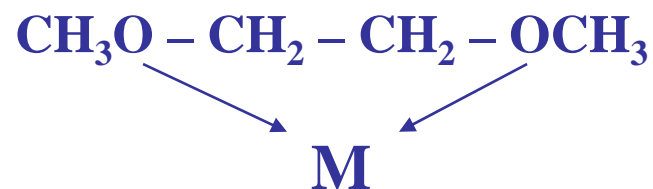
## Bidentate ligands

They have two donor atoms

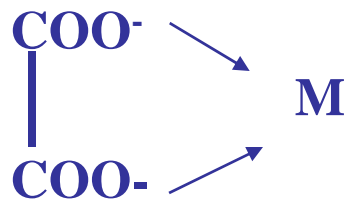
Ethylenediamine (en)



Dimethyl glycol (glyme)



Oxalate ion (oxalato)



## More Examples

Glycinato (gly)



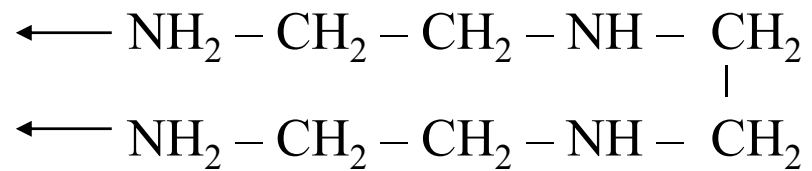
**bidentate**

Iminodiacetato (imda)



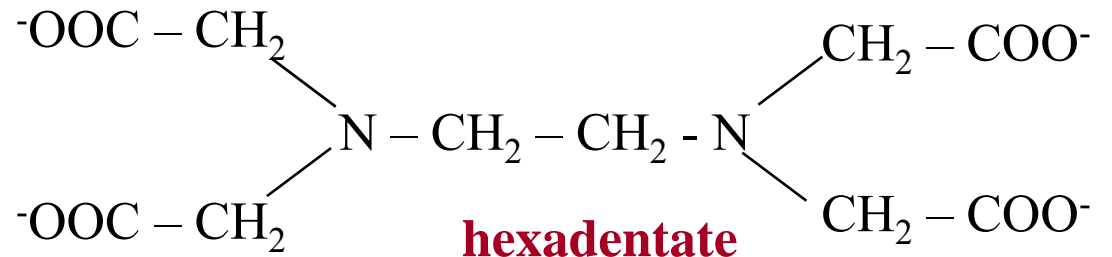
**tridentate**

Triethylenetetramine (tren)



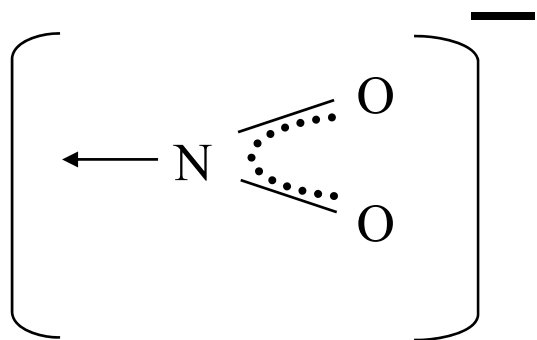
**tetradentate**

Ethylenediamine  
tetraacetate (edta)

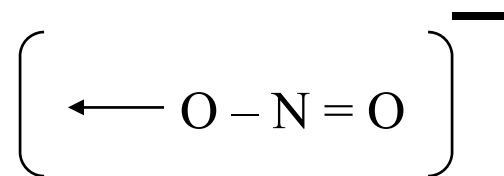


**hexadentate**

## Ambidentate Ligands



Nitro



nitrito



SCN<sup>-</sup>

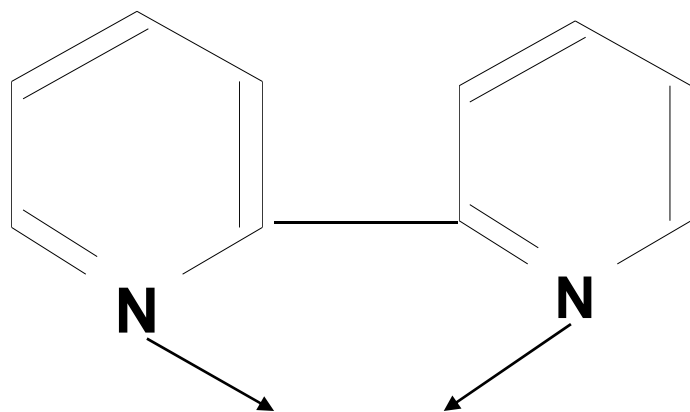
thiocyanato



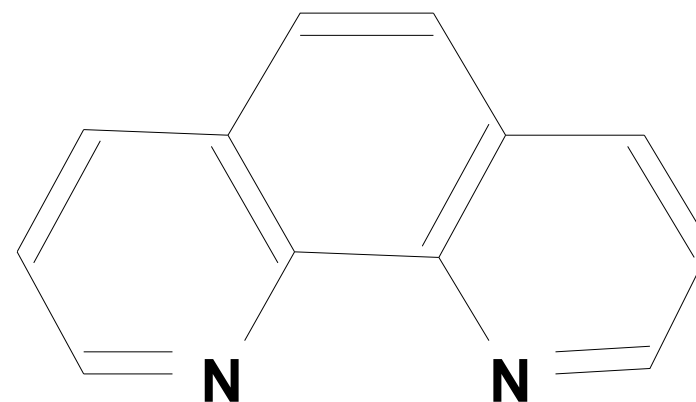
NCS

isothiocyanato

## Organic Ligands



2, 2'-Bipyridine (bpy)



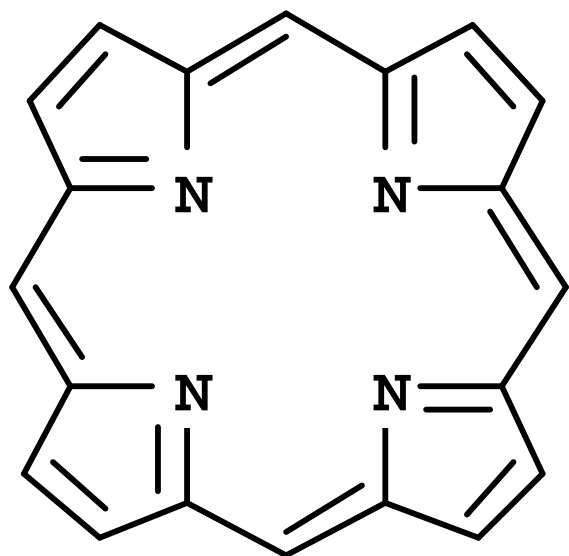
1,10 – Phenanthroline (phen)



## Alkyl groups as ligands

$\text{CH}_3$  (methyl),  $\text{CH}_3\text{CH}_2$  (ethyl),  $\text{C}_6\text{H}_5$  (Phenyl)

## Macrocyclic ligands



Porphyrin

tetradentate

# Nomenclature of Transition metal Compounds

## A. Writing the name of the complex compound

### 1. Designation of ligands

#### (a) Anionic ligands end with 'o'

$\text{NO}_2^-$	nitro,	$\text{CN}^-$	cyano
$\text{Cl}^-$	chloro,	$\text{NO}_3^-$	nitrato

#### (b) Organic ligands retained their names

Pyridine (py) or ethylenediamine (en)  
alkyl groups: methyl, phenyl

#### (c) Special names

$\text{H}_2\text{O}$  (aqua),  $\text{NO}$  (nitrosyl),  $\text{CO}$  (carbonyl),  $\text{NH}_3$  (ammine)

## 2. Designation of metal

(a) Cationic and neutral complexes end in the english name followed by the oxidation state of the metal in brackets.

e.g. nickel(II) or iron(II).

(b) Anionic complexes have the latin name of the metal

ferrate( ), Stannate ( )

Cuprate ( ), Argentate ( )

## 3. Numerical prefixes

(a) For two similar ligands di or bis

(b) three similar ligands tri or tris

(c) four similar ligands tetra or tetrakis etc.

### 3. Order of listing

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



dichlorotetraamminecobalt(III) chloride. *wrong*

tetraamminedichlorocobalt(III) chloride. *right*

### A. Writing the formulae of the complex compound

1. First central metal atom, then anionic ligands and then neutral ligands (Cl<sup>-</sup>, NH<sub>3</sub>)



## Examples



hexanitro cobalt (III) chloride



tetra amminecopper(II)sulphate



bis pyrridinedichlorocopper(II)

dichloro dipyridine copper (II)

dichloro bis (pyridine) copper (II)

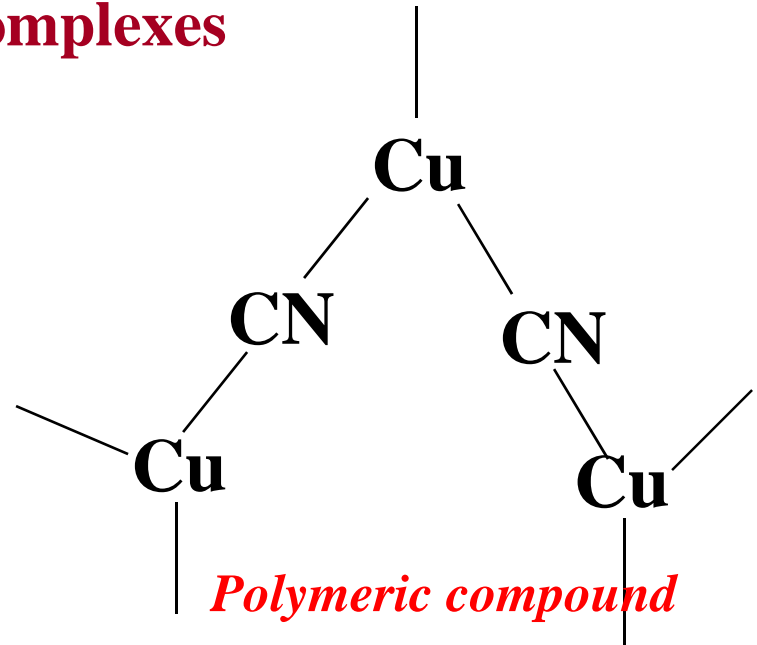


*cis*-diamminedichloroplatinum(II)

# Geometry of complexes

Coordination No.2

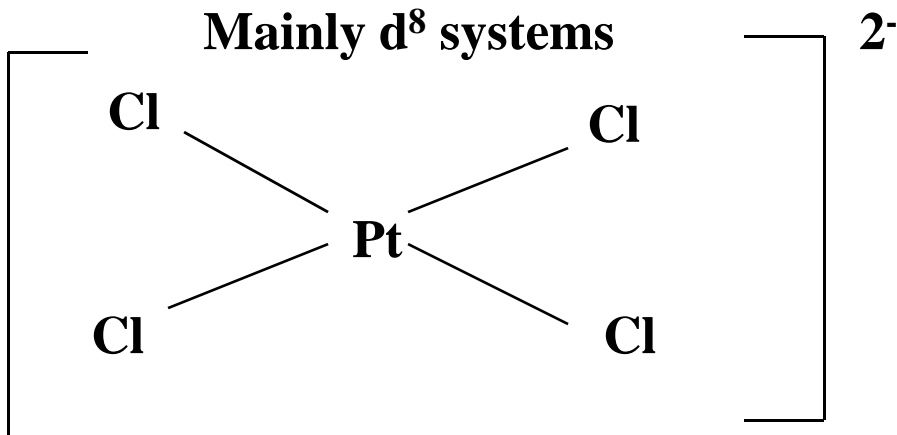
(linear)



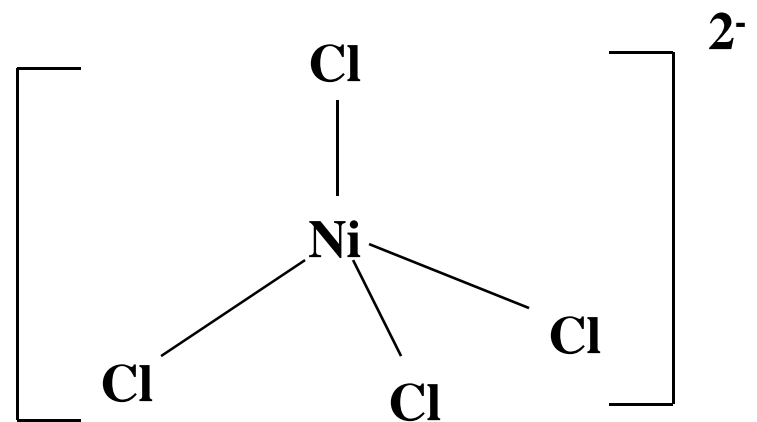
Coordination no. 4 (large ligands)

(a) Square planar

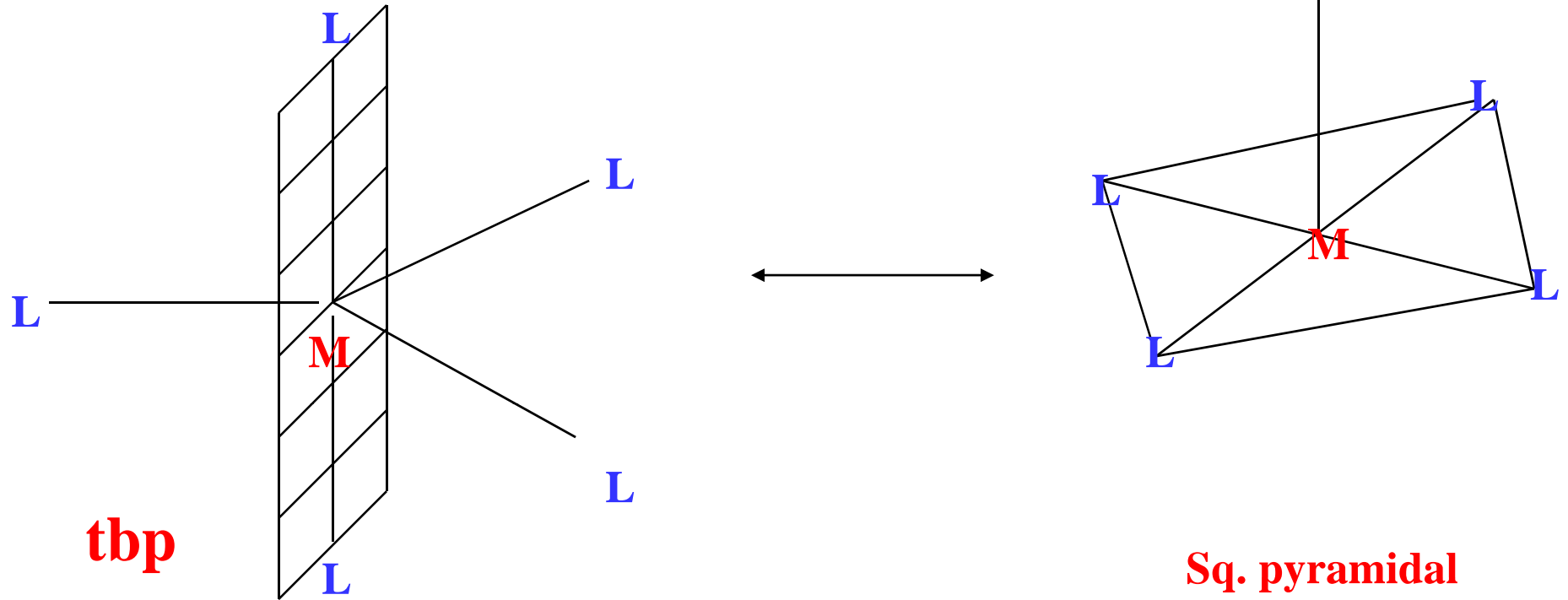
Mainly  $d^8$  systems



(b) Tetra hedral



**Coordination no. 5**



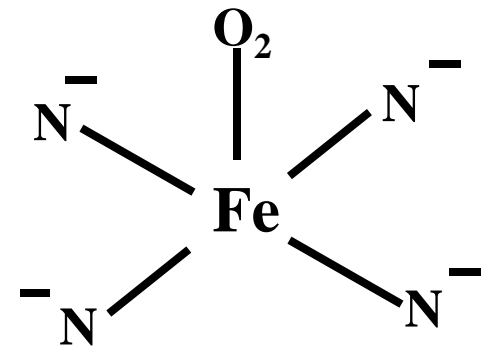
$[\text{Ni}(\text{CN})_5]^{2-}$  shows both structures (little energy difference)

$[\text{CuCl}_5]^{3+}$       **TBP structure**

$\text{NbCl}_5$       **TBP structure**

**Biologically important molecules**

Haemoglobin,      Oxomyoglobin

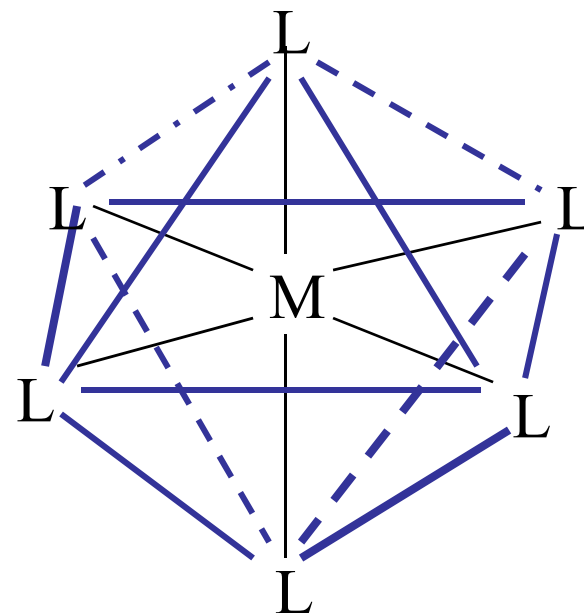


## Coordination no. 6

**ML<sub>6</sub> octahedral complex**

Most important from d<sup>1</sup> to d<sup>9</sup>

e. g. [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, [Fe(CN)<sub>6</sub>]<sup>3-</sup>



Higher coordination possible with large cations and small anions

e.g. [ZrF<sub>7</sub>]<sup>3-</sup>, TaCl<sub>4</sub>(PR<sub>3</sub>)<sub>3</sub>

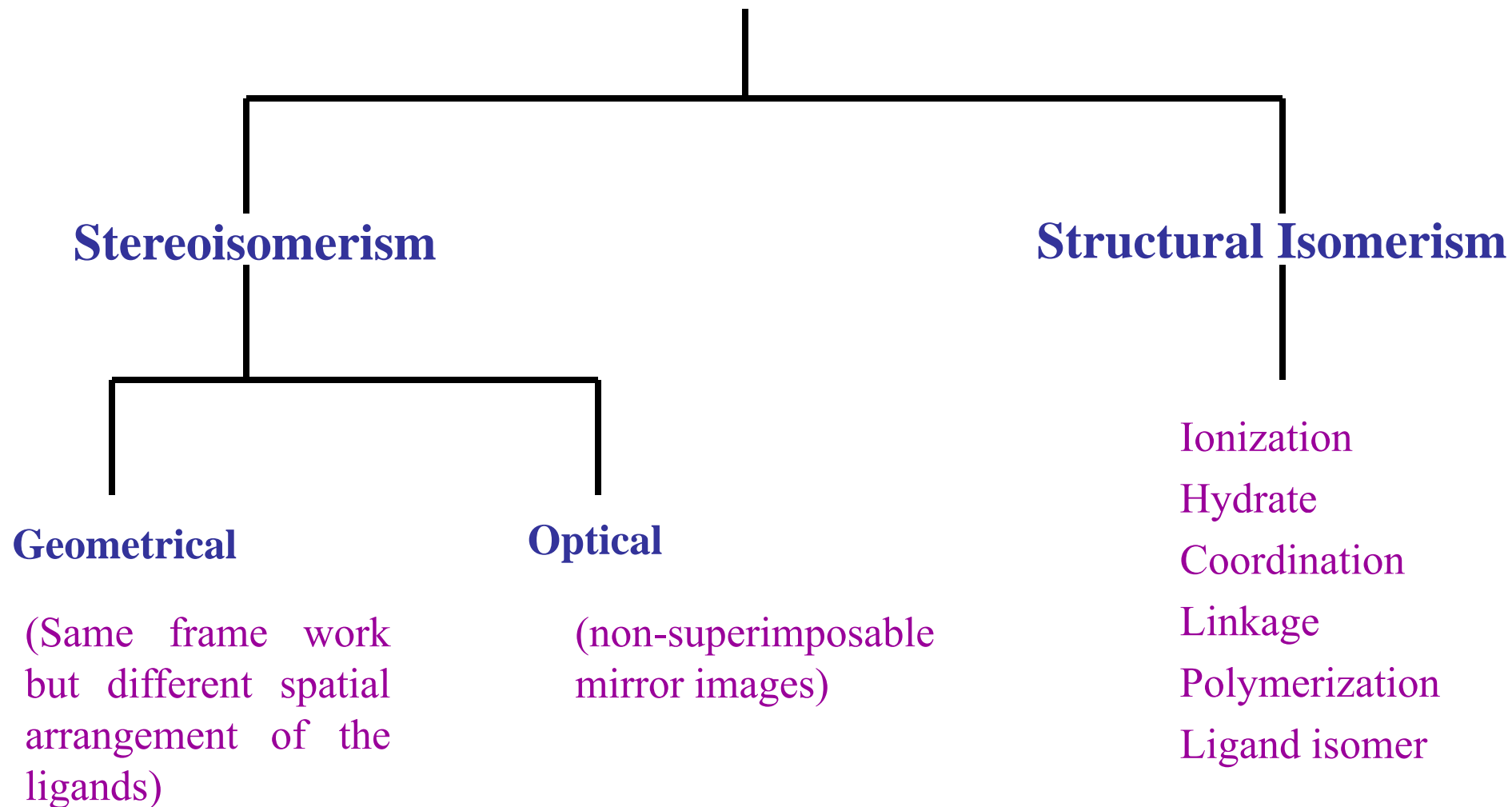
*Square antiprism*

[Nd(OH<sub>2</sub>)<sub>9</sub>]<sup>3+</sup>, [ReH<sub>9</sub>]<sup>2-</sup>, [Ce(NO<sub>3</sub>)<sub>6</sub>]<sup>2-</sup>

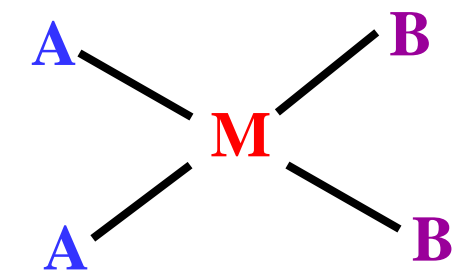
*icosahedron*



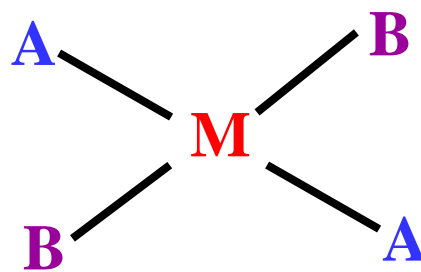
# Isomerism



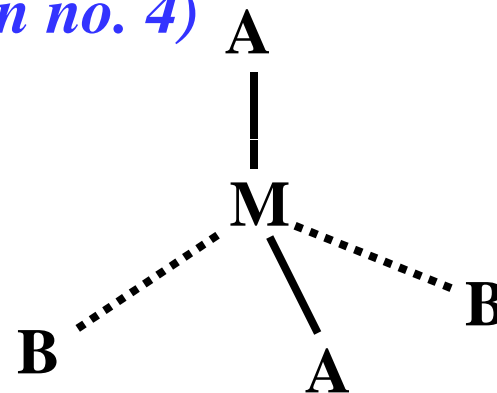
## Geometrical Isomers (*coordination no. 4*)



cis



trans

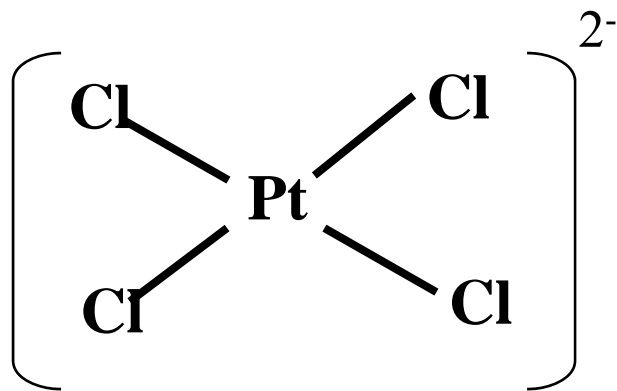


tetrahedral

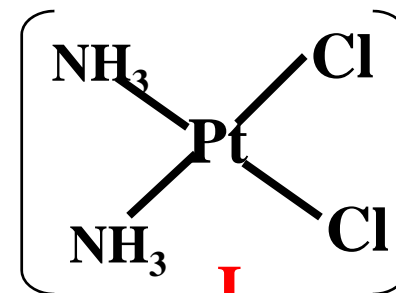
Square planar

All are optically inactive

Cis/ trans isomers can be isolated

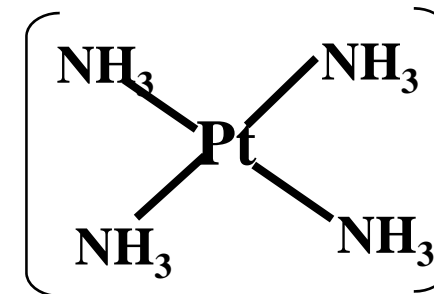


NH<sub>3</sub>



I

Excess NH<sub>3</sub>

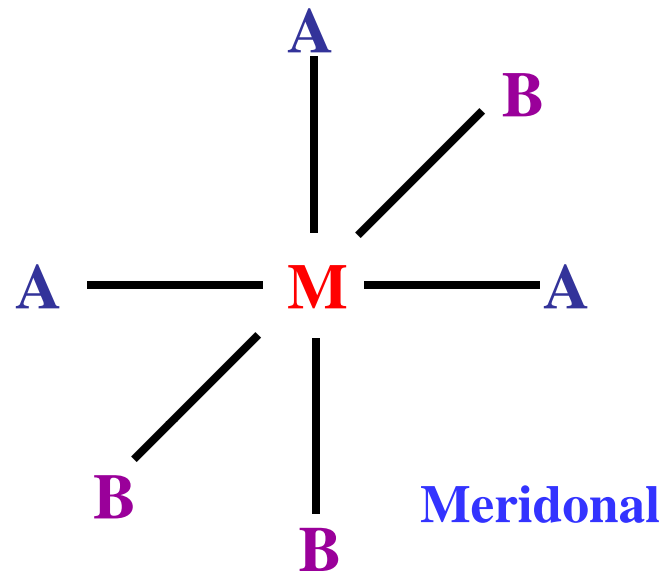
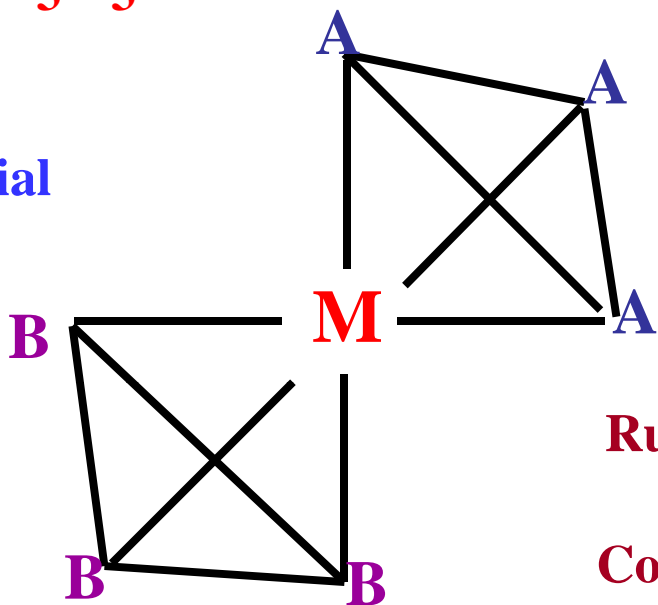


II

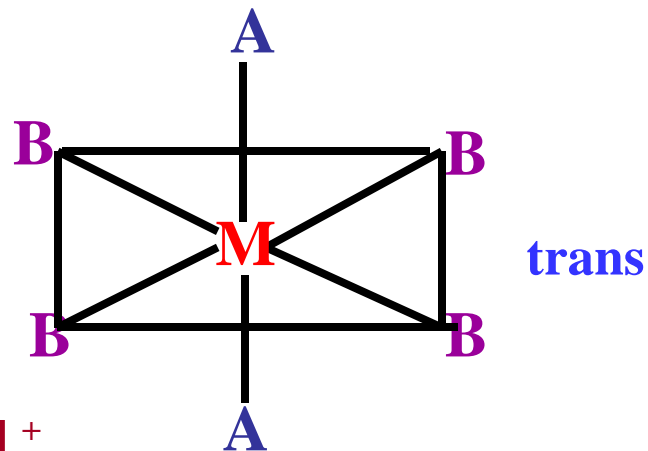
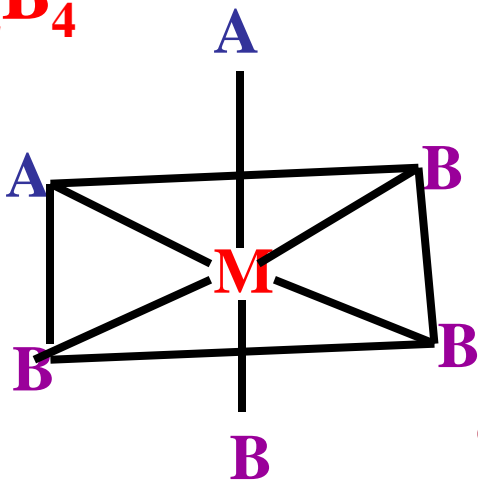
# Geometrical Isomerism in Octahedral complexes



Facial

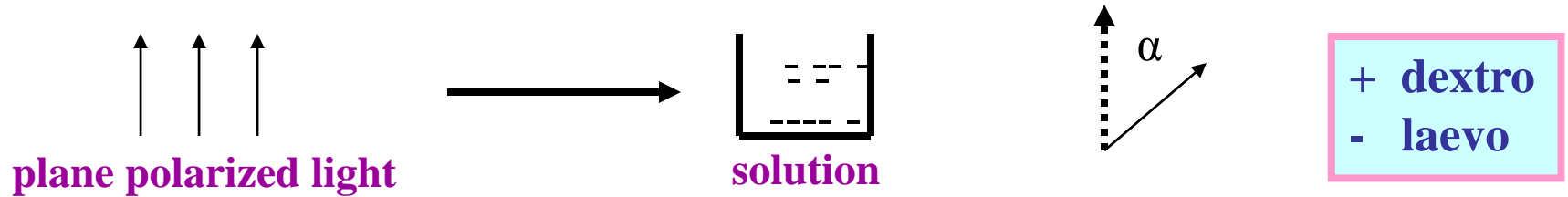


cis



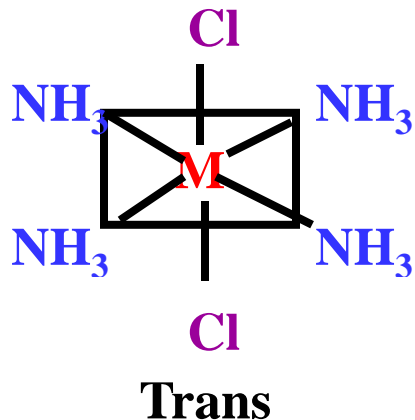
# Optical isomerism

Optical isomers differ only in the direction in which they rotate the plane of the plane polarized light (enantiomers).

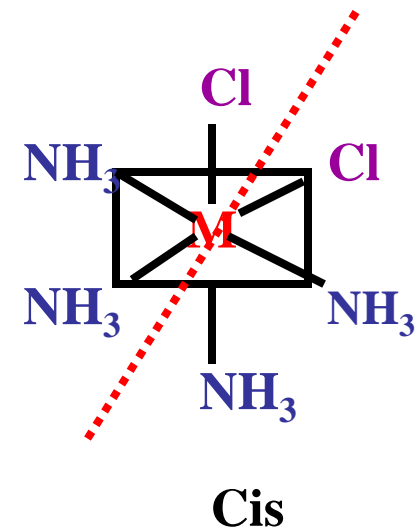


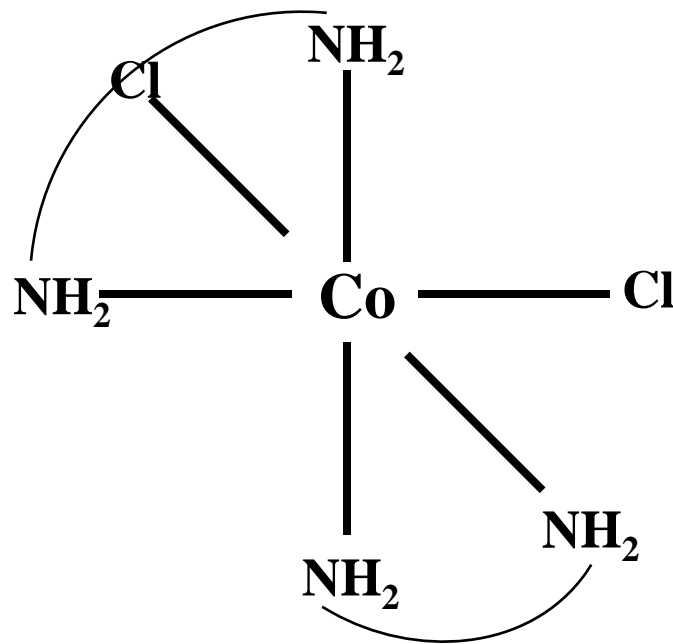
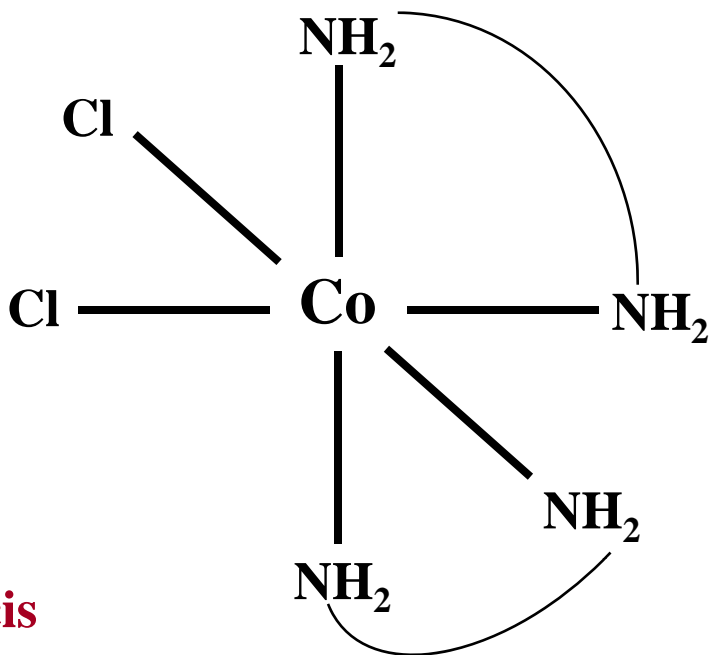
## Absence of optical activity (superimposable mirror images)

1. Presence of a mirror plane.
2. Presence of a centre of symmetry.



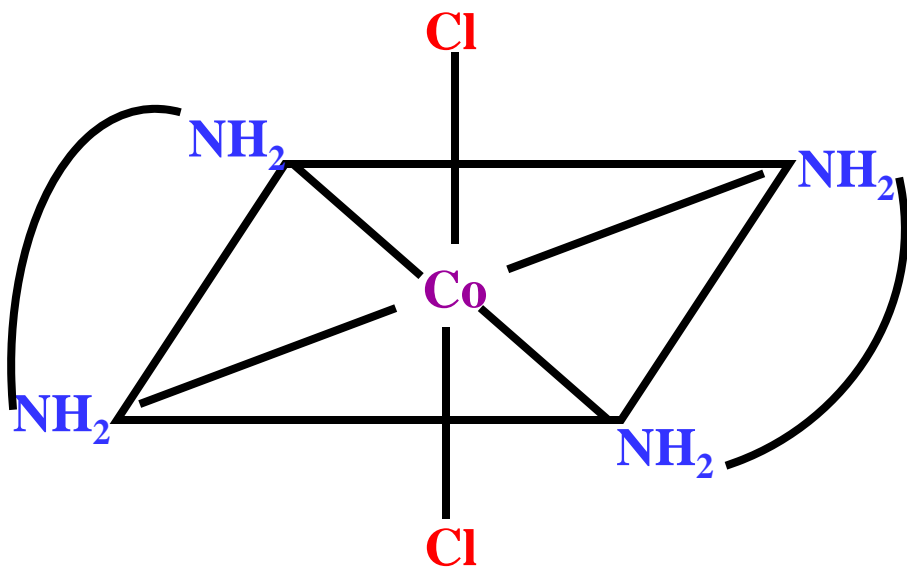
$[\text{CoCl}_2(\text{NH}_3)_4]^+$   
Optically inactive





Non superimposable mirror images.

**(Optically active)**



**trans**

**Not optically active**

# Bonding Concept *(Rationalise structure)*

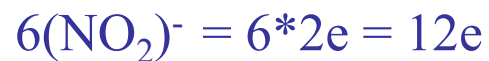
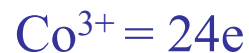
## Bonding in coordination compounds

Sidgwick (1927)

- Extended the Lewis theory
- Sharing of 'e' pair donated by an atom (donor).

## Effective atomic Number (EAN)

M accepts electron pairs and converted into inert gas configuration.



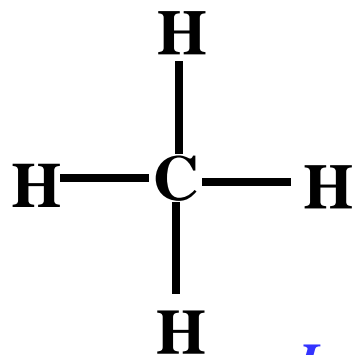
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TOTAL = 36e    Atomic no. of Krypton (Kr)

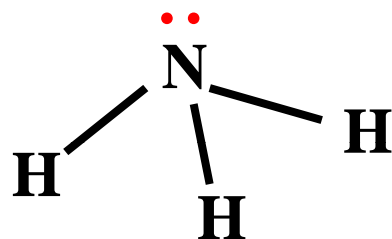
# Chemical Bonding

**G. N. Lewis (1916)**

Bonding between atoms  $\longrightarrow$  Sharing of e<sup>-</sup>s



*Lewis diagram*



*Structure ??*

*Bond angles ??*

Concept of hybridization

**Valence bond Theory**

(Pauling – Slater, 1930's)

Linus Pauling – N.L. (twice)

*“Nature of the chemical bond”*

# Valence bond Theory

(Pauling) — Complexes

1. Metal ion must make available a number of orbitals equal to the coordination number for accommodating the electrons from the ligands.
2. Use of the hybrid orbitals by the metal ion.
  - Maximum & fruitful overlap with ligand orbitals
  - Directionality

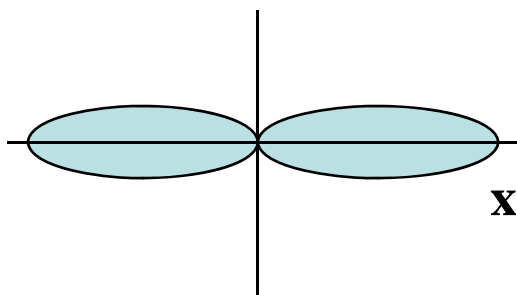
*Note: Hybrid orbitals are not s, p or d orbitals but have a mixed character.*



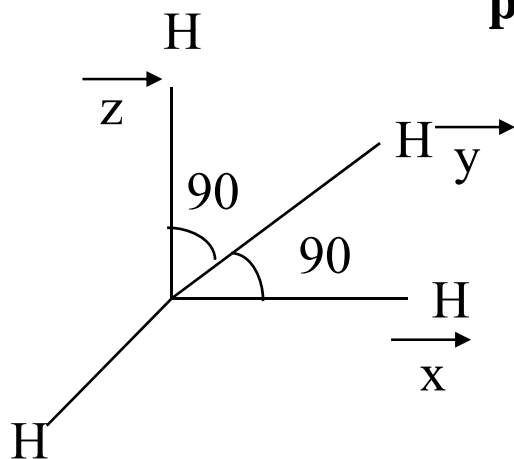
## Why Hybridisation?

CH<sub>4</sub>

Four bonds



p<sub>x</sub>



C 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>2</sup>



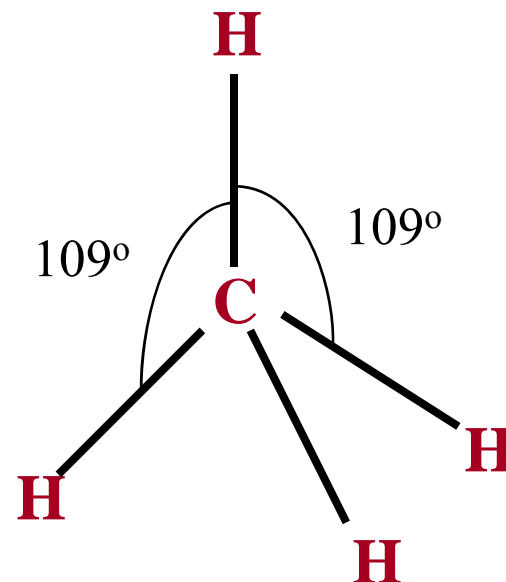
*Promotion of  
one s electron*

1s<sup>2</sup> 2s<sup>2</sup> 2p<sub>x</sub><sup>1</sup> 2p<sub>y</sub><sup>1</sup> 2p<sub>z</sub><sup>1</sup>

Results in three mutually perpendicular bonds.

But

CH<sub>4</sub> is Tetrahedral



All  $\angle$ HCH are equal

## Successes of V. B. T.

1. Simple structure and Magnetic properties are nicely explained.
2. Accounts for low spin square planer and high tetrahedral complex.
3. Low spin inner – orbital and high spin orbital complexes.

## Failures

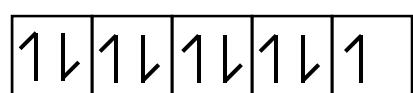
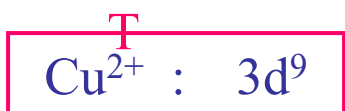
1. Cannot predict 4 – coordination



— square planer or tetrahedral



VB  $\longrightarrow$  both to be tetrahedral



3d



4s 4p  
sp<sup>3</sup>



3d 4s 4p  
dsp<sup>2</sup>

But by experiments there is no evidence of unpaired e<sup>-</sup> in orbital: e. s. r spectroscopy

2. VBT does not predict any distortion in the symmetrical complexes. [ideal — octahedra, tetrahedra]

Au, Cu(II), Ti(III) complexes are distorted among many more.

3. VBT neglects the excited states of the complexes.

—no thermodynamic properties can be predicted

4. It does not explain the colour (spectra) of complexes.

5. Does not explain the temperature variation of magnetic properties of complexes.