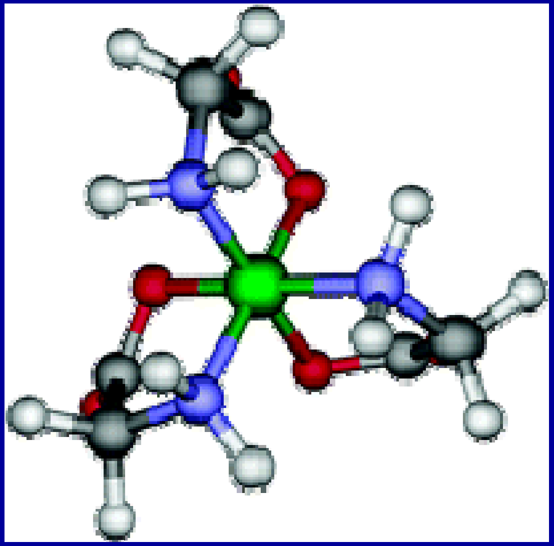
Coordination Chemistry

Alfred Werner
(1866-1919)

NP in Chemistry
1913

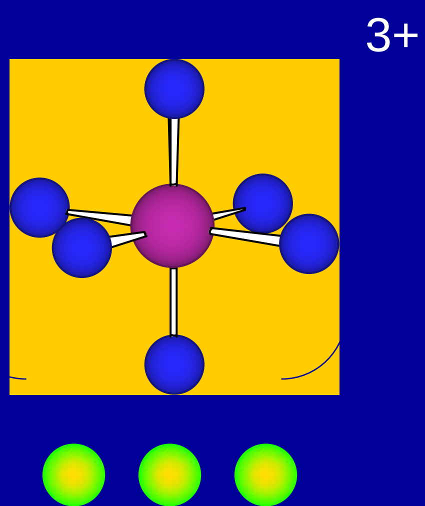
1893 To central atom, more ligands can be bound then is its oxidation number

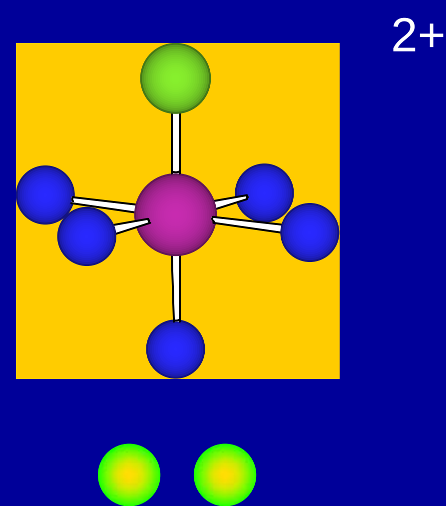


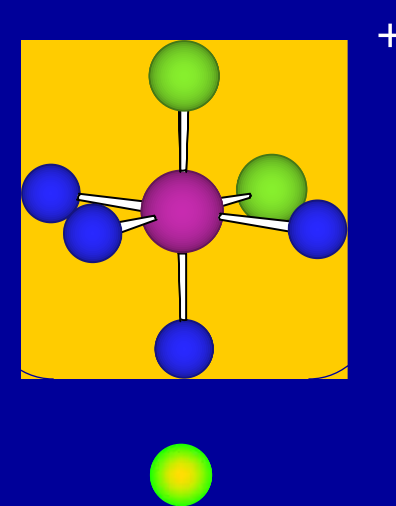
$[Co^{II}(gly)_3]^-$

Coordination Compounds

$[Co(NH_3)_6]Cl_3$ | $[Co(NH_3)_5Cl]Cl_2$ | $[Co(NH_3)_4Cl_2]Cl$

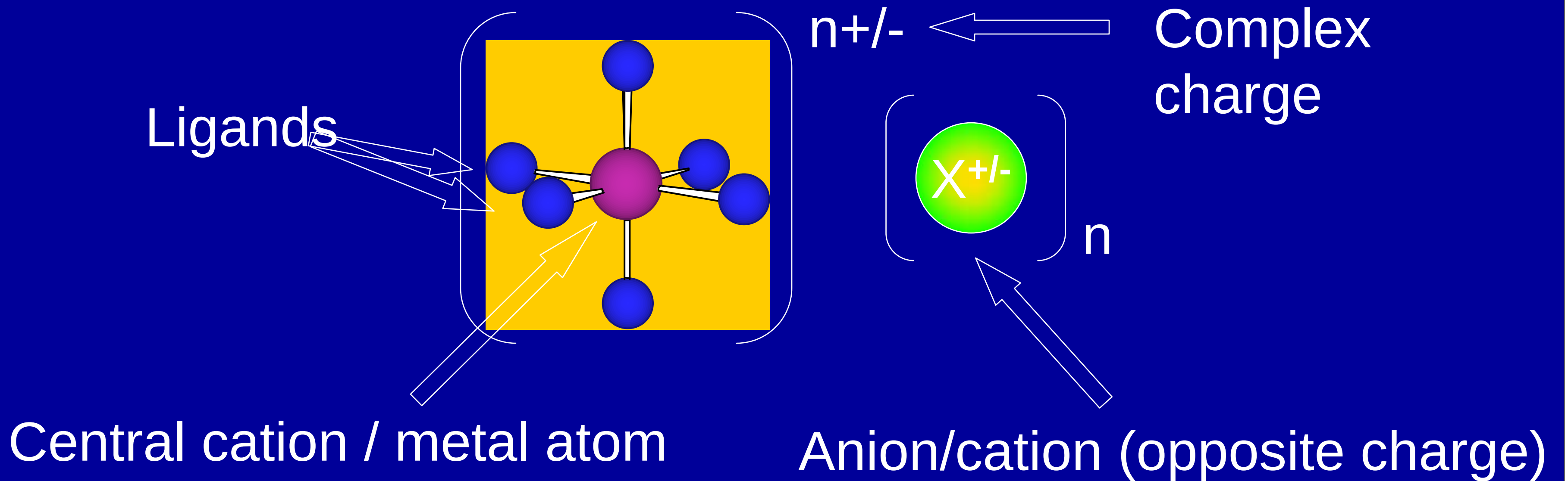






Metal in oxidation state n+ (primary valence)
Complex has coordination number m (secondary valence)
Ligands bound to central atom by donor-acceptor bonds

Coordination Compounds



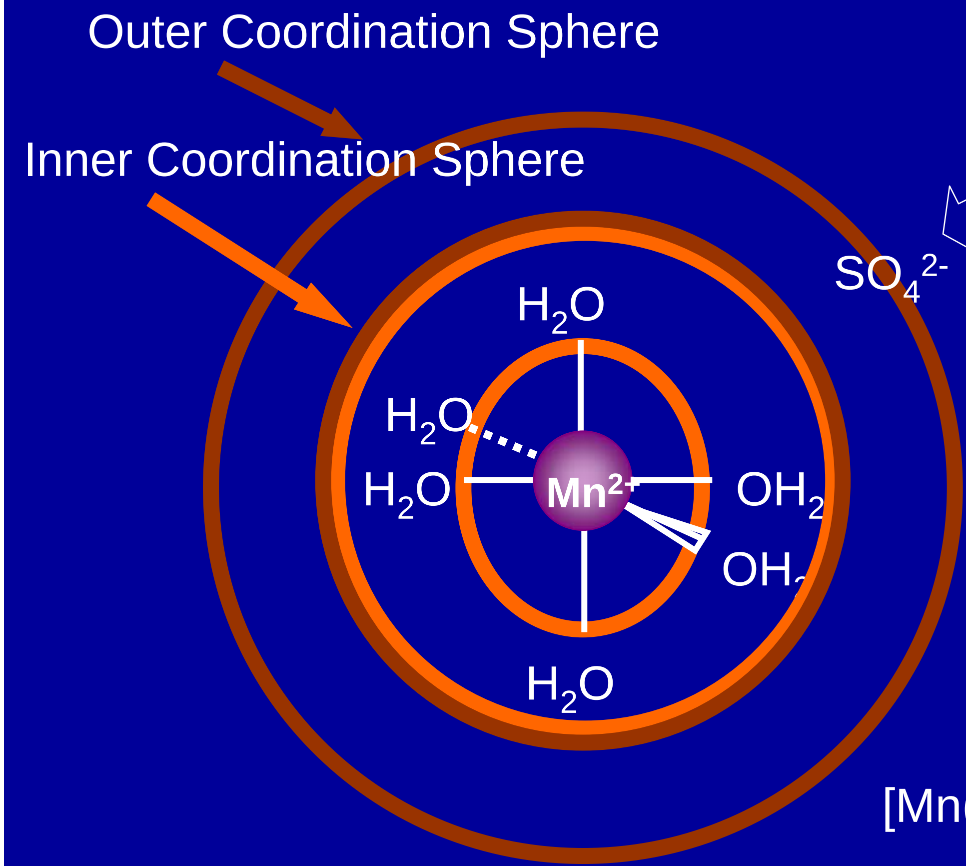
Central metal cation / neutral atom surrounded by a set of ligands. Each ligand provides 2 electrons to empty d-orbitals at metal and forms donor-acceptor bond.

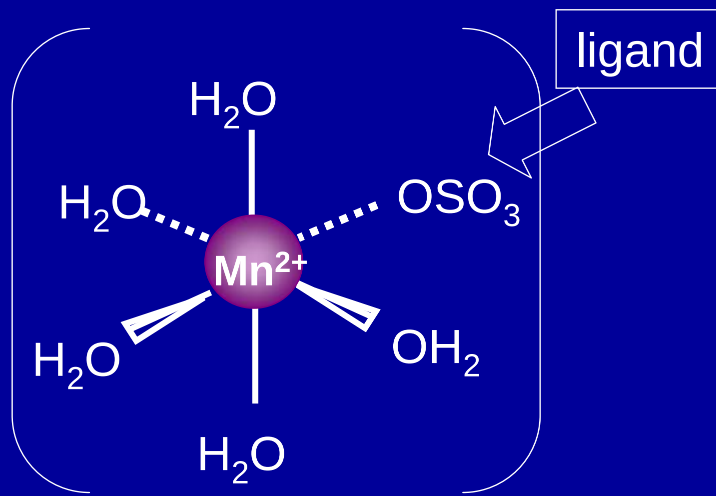
Number of ligands = Coordination number

Inner and Outer Coordination Sphere

Inner Coordination Sphere = ligands driectly bound to the central atom

Outer Coordination Sphere = ions asociated with a complex, not bound



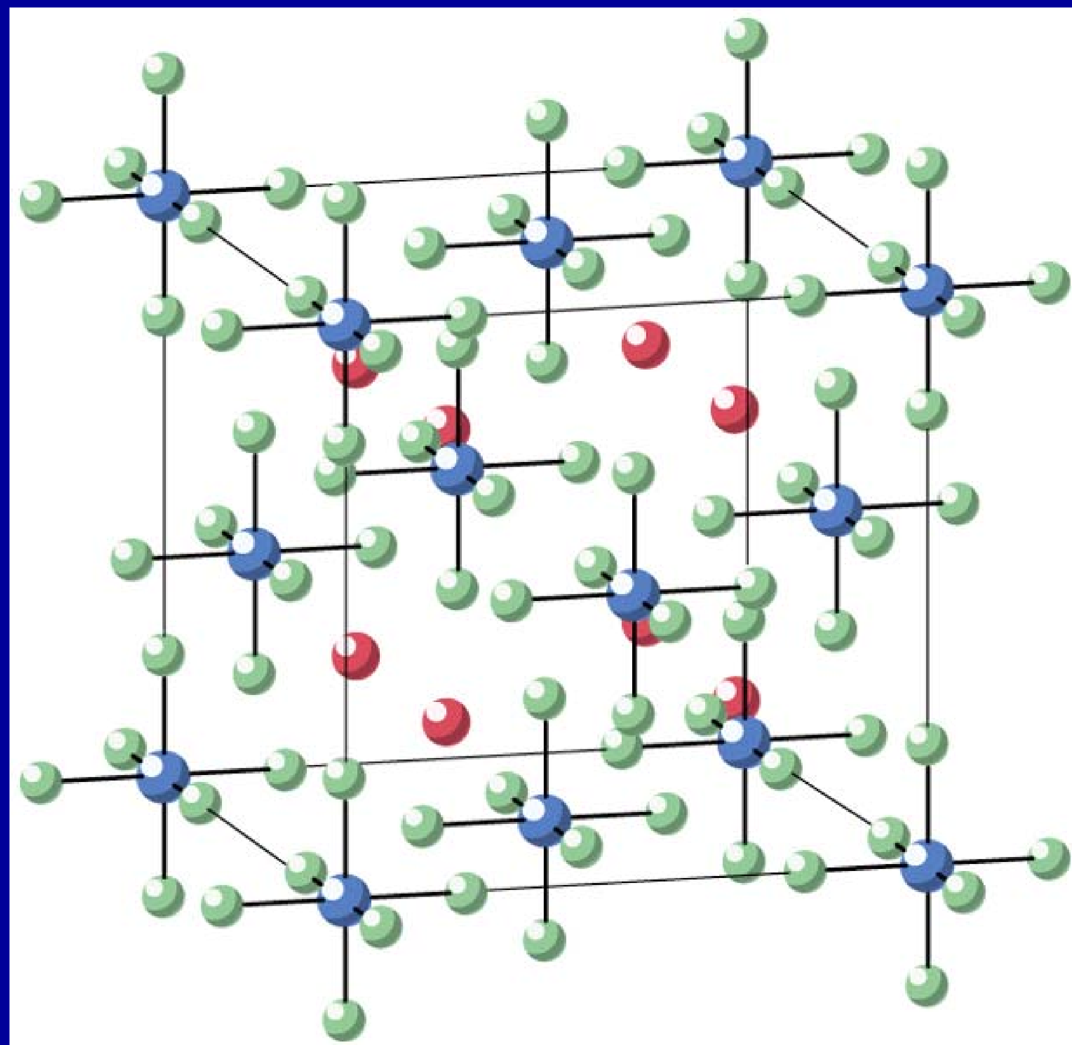


$[Mn(OH_2)_5(SO_4)_5]$: Inner Coordination of SO_4^{2-}

$[Mn(OH_2)_6][SO_4]$: outer coordination of SO_4^{2-}

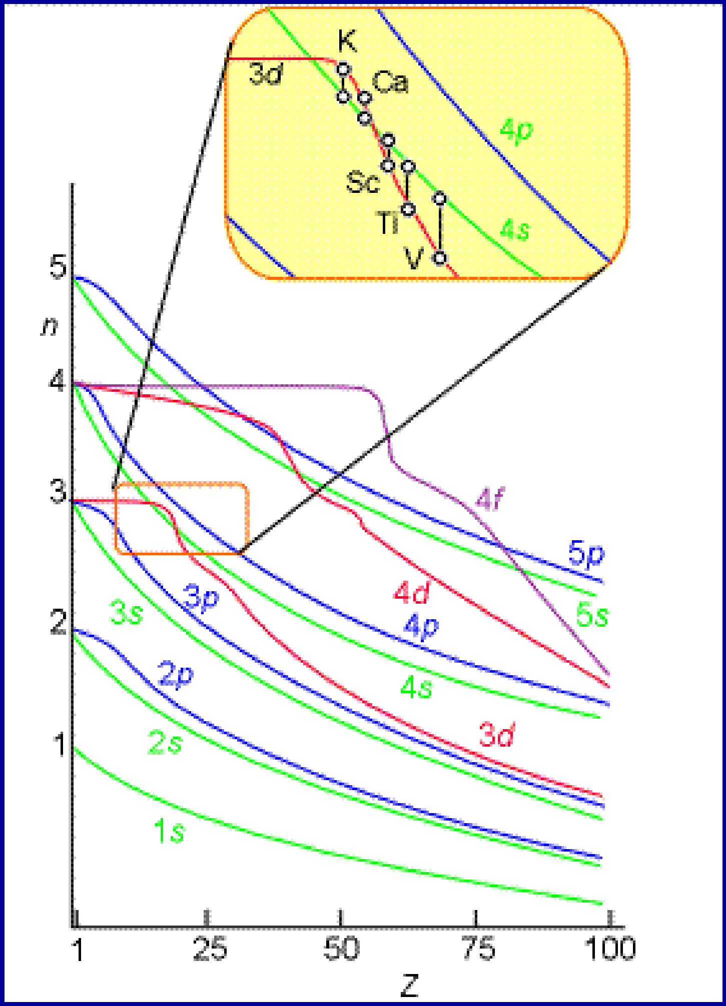
Coordination Compounds

$K_2[PtCl_6]$

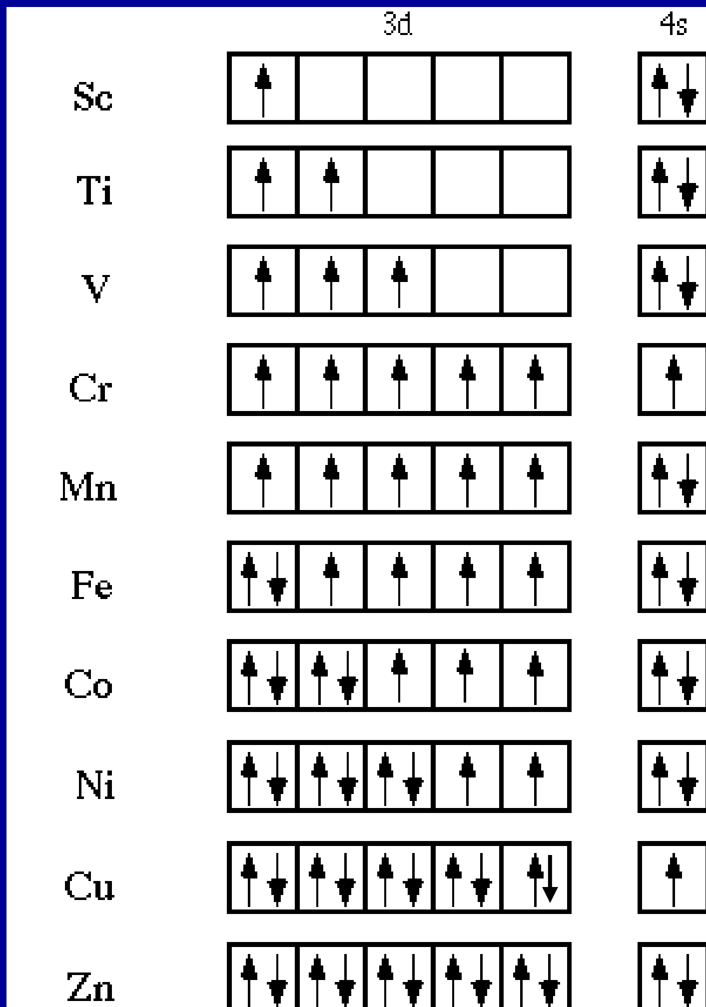


Energy Level Ordering

Ar	[Ne] $3s^2$ $3p^6$ ($4s^0$)
K	[Ar] $4s^1$ ($3d^0$ $4p^0$)
Ca	[Ar] $4s^2$ ($3d^0$ $4p^0$)
Sc	[Ar] $3d^1$ $4s^2$ ($4p^0$)
Ti	[Ar] $3d^2$ $4s^2$ ($4p^0$)



Stability of Half- / Filled d-Orbitals



Cr [Ar] $3d^5\,4s^1\,(4p^0)$

Cu [Ar] $3d^{10}\,4s^1\,(4p^0)$

Oxidation States of TMs

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
3	2,3 4	1,2,3 4,5	1,2, 3,4, 5,6	1,2, 3,4, 5,6,7	2,3, 4,5,6	1,2,3 ,4	1,2 3,4	1,2	2

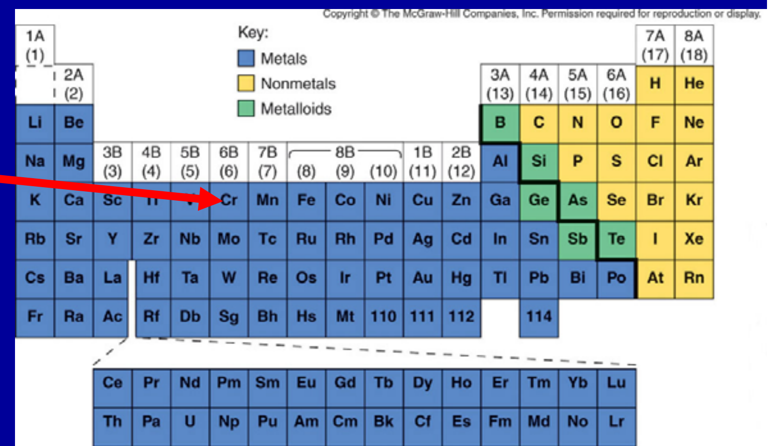
First Ionization Energies of the Transition Elements (kJ/mol)

Period										
Fourth	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	631	658	650	652	717	759	758	737	745	906
Fifth	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	616	660	664	685	702	711	720	805	731	868
Sixth	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	538	680	761	770	760	840	880	870	890	1007

d-Electron Count

Number of electrons in valence level

Cr [Ar] $3d^5\,4s^1\,(4p^0)$



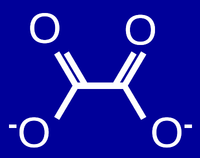
Number of electrons removed during cationt formation: electrons of s-orbital are removed first

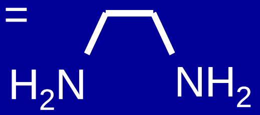
Cr^{3+}

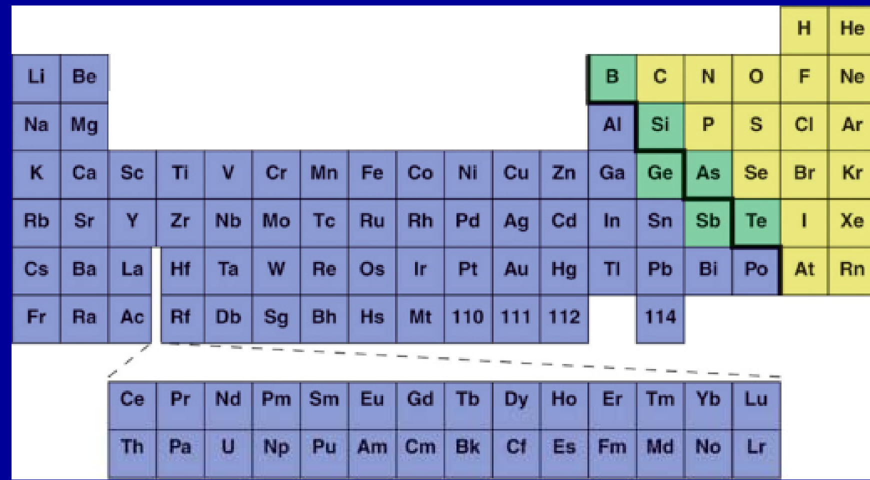
Number of electrons remaining in d-orbitals

Cr^{3+} [Ar] $3d^3\,4s^0\,(4p^0)$

Cr^{3+} is a d^3 cation

ox = 

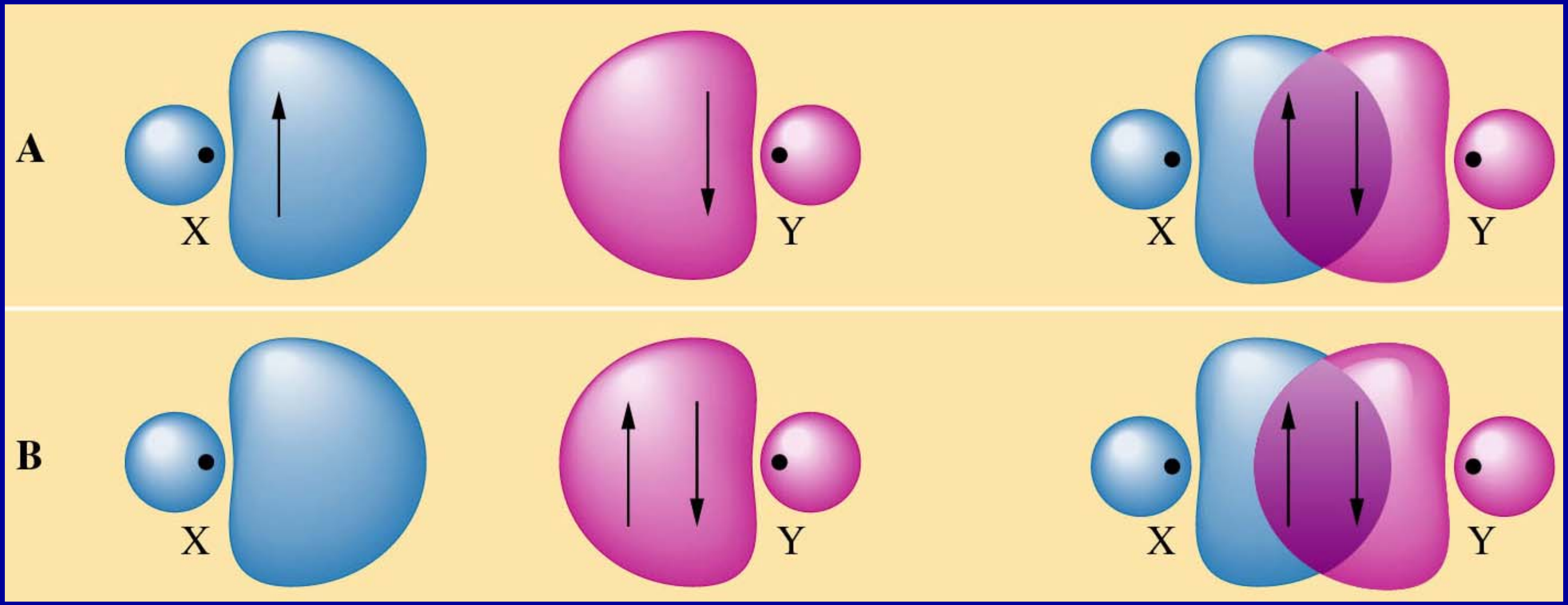
en = 



Complex	Ox.No. (Ligand)	Ox.No. (M)	No. d-electrons
$[Cr_2O_7]^{2-}$	-2	+6	d^0
$[MnO_4]^-$	-2	+7	d^0
$[Ag(NH_3)_2]^+$	0	+1	d^{10}
$[Ti(H_2O)_6]^{3+}$	0	+3	d^1
$[Co(en)_3]^{3+}$	0	+3	d^6
$[PtCl_2(NH_3)_2]$	-1, 0	+2	d^8
$[V(CN)_6]^{4-}$	-1	+2	d^3
$[Fe(ox)_3]^{3-}$	-2	+3	d^5

Donor-Acceptor Bond

donor-acceptor bond is equivalent to a covalent bond



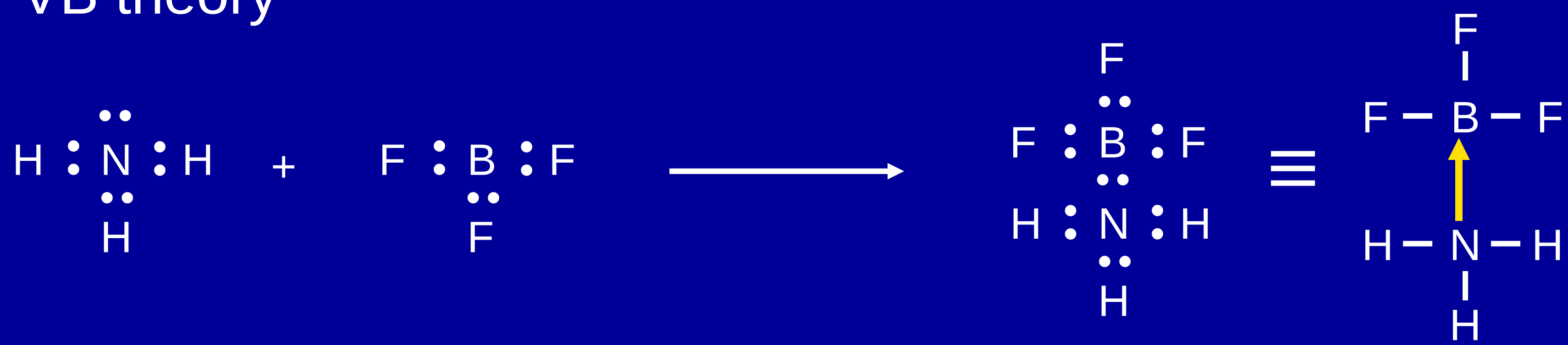
Acceptor
Empty orbital

Donor
Free e pair

Covalent Bond

Donor-Acceptor Bond

VB theory



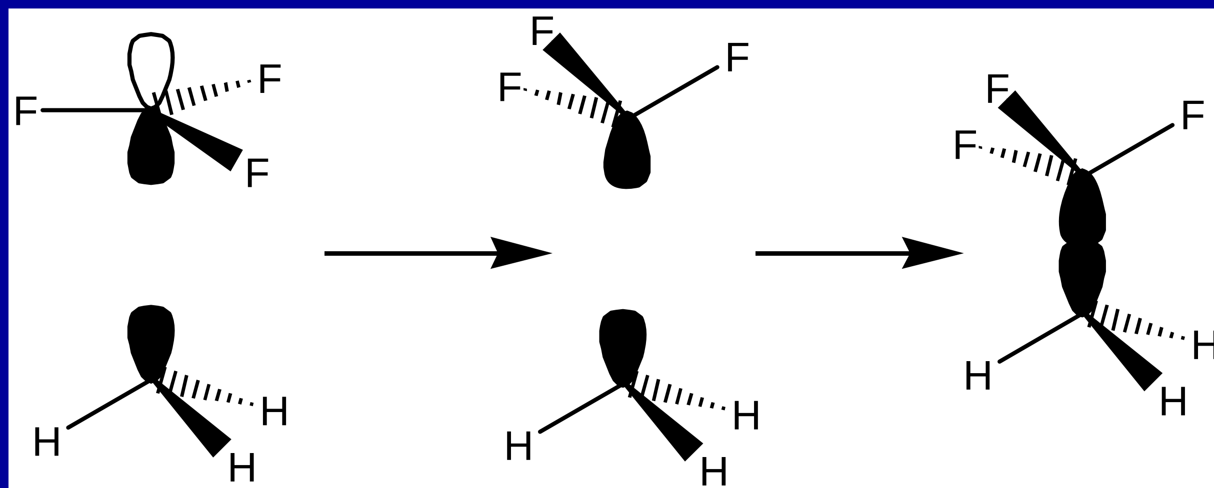
$$NH_3 + BF_3 \longrightarrow H_3N \rightarrow BF_3$$

→ Donor-Acceptor Bond

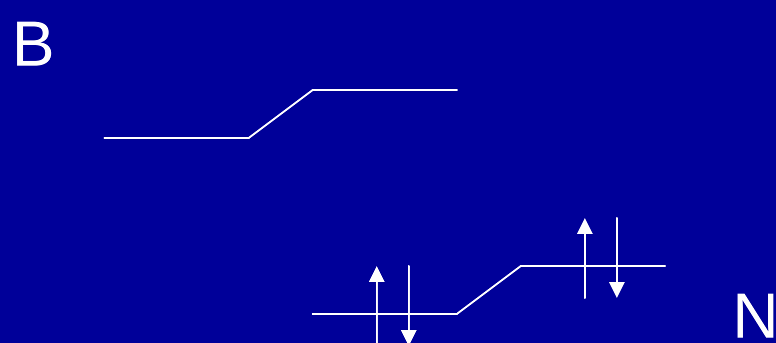
Donor-Acceptor Bond

NH_3 + BF_3 ⟶ H_3N —> BF_3

VB theory



MO theory

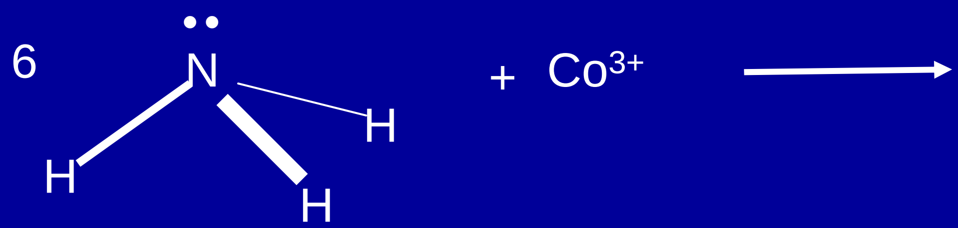


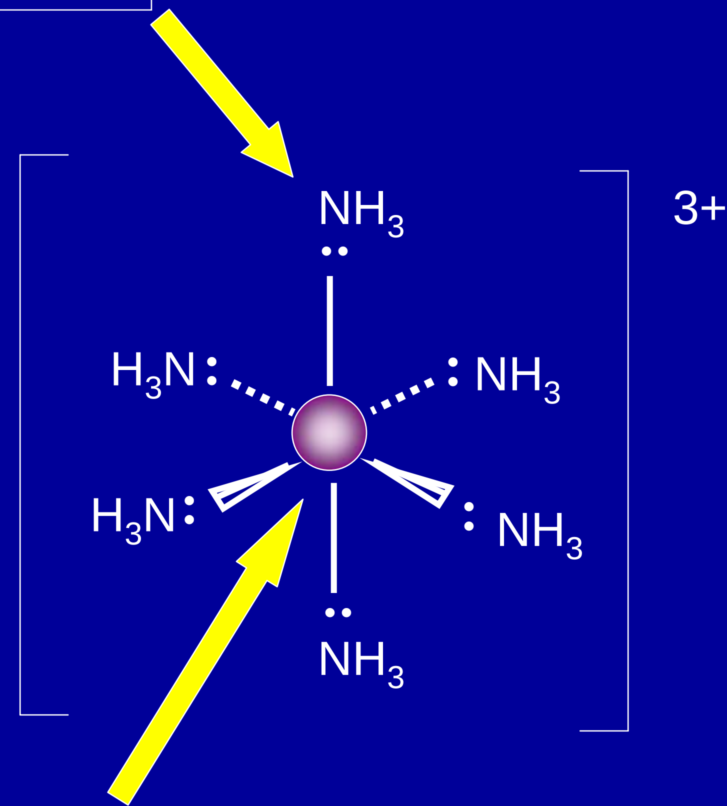
Donor-Acceptor Bond

VB theory

$[Co(NH_3)_6]^{3+}$

"Lewis Base"



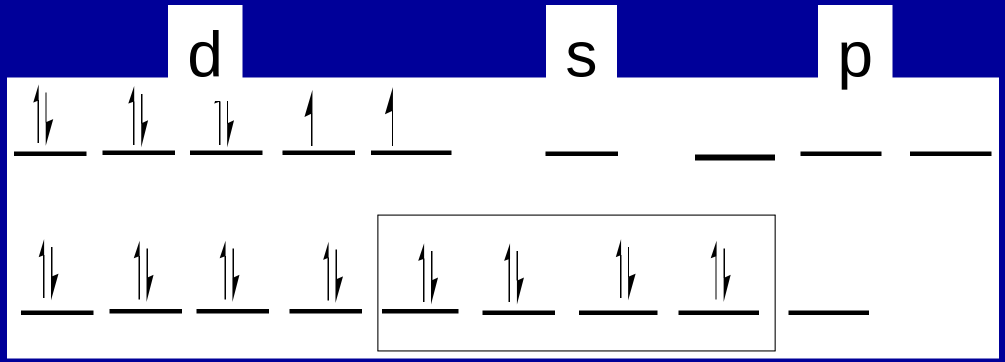


Each ligand provides 2 electrons

"Lewis Acid"

Pt^{2+} [Xe] $4f^{14}\,5d^{8}\,4s^{0}$

$PtCl_4^{2-}$

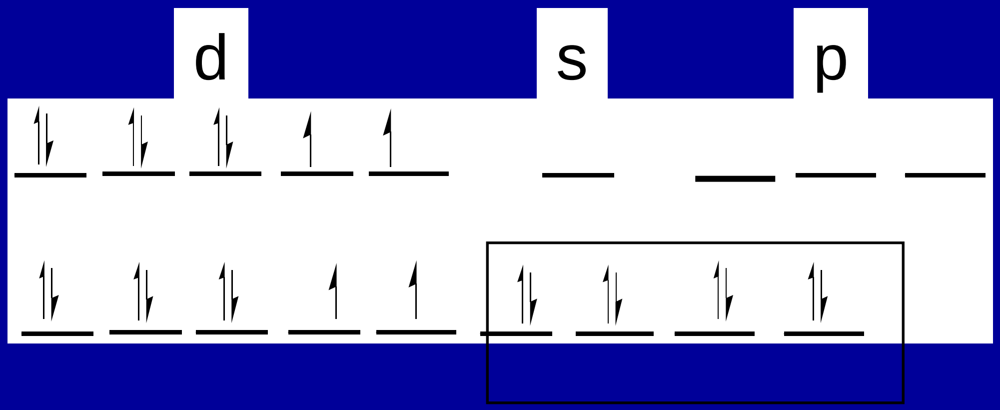


dsp^2 hybrid orbitals

Electrons from Cl^-, square planar

Ni^{2+} [Ar] $3d^{8}4s^{0}$

$NiCl_4^{2-}$

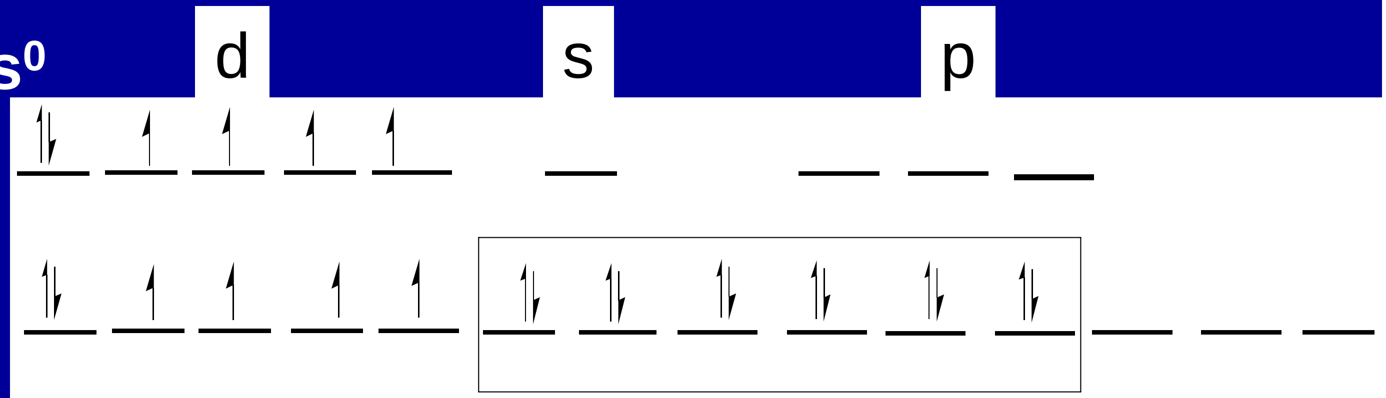


sp^3 hybrid orbitals

Electrons from Cl^-, tetrahedral

Co^{3+} [Ar] $3d^6 4s^0$

CoF_6^{3-}

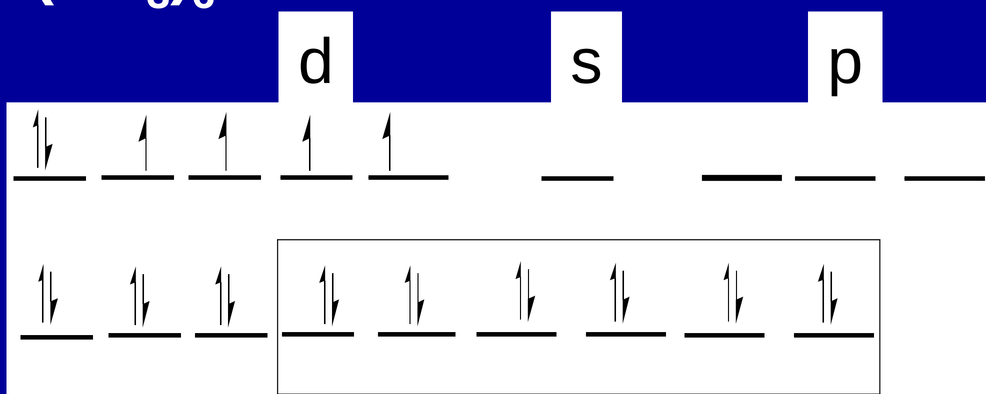


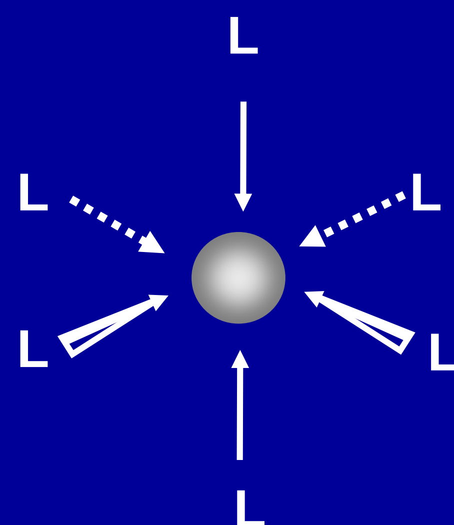
sp^3d^2 hybrid orbitals

Electrons from F^-, octahedral

Co^{3+} [Ar] $3d^6 4s^0$

$Co(NH_3)_6^{3+}$



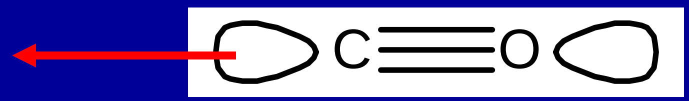


d^2sp^3 hybrid orbitals

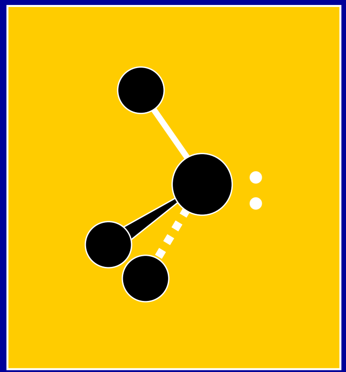
Electrons from NH_3, octahedral

Monodentate Ligands

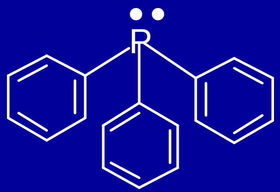
CO
Carbon dioxide

Cr 

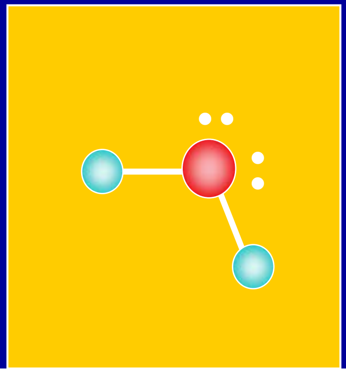
$Ni(CO)_4$, $Fe(CO)_5$, $Mo(CO)_6$



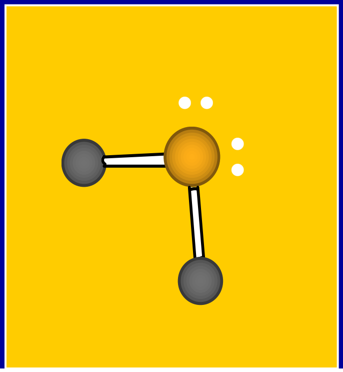
NH_3
ammonia



PPh_3
phosphane



H_2O
water



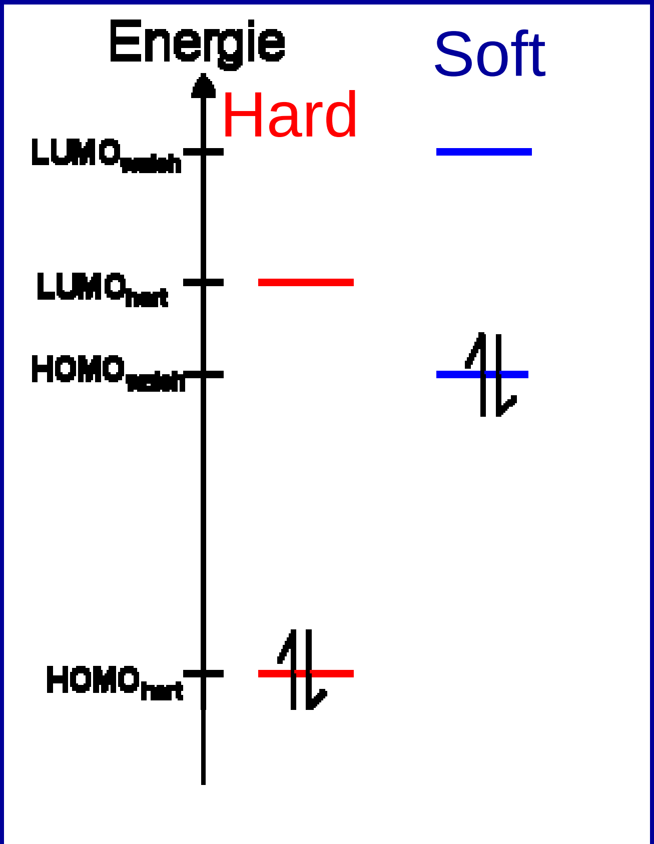
SR_2
thioether

HSAB = Hard and Soft Acids and Bases

R. Pearson 1963

High oxidation states of central atoms are stabilised by F^-, O^{2-}

Low oxidation states are stabilised by CO, CN^-



Acid

Base

HSAB

HARD donor atoms

NH_3, F^-, H_2O, OH^-, CO_3^{2-}

Small donor atoms

High electronegativity

Difficult to polarize

Stabile complexes

Hard metals

Fe(III), Mg(II), Cr(III), Al(III)

Small atoms (1st trans. row)

Large charge

Weak complexes

SOFT donor atoms

CO, PPh_3, I^-, C_2H_4, SRH, CN^-, SCN^-

Large donor atoms

Low electronegativity

Easily polarized

Stabile complexes

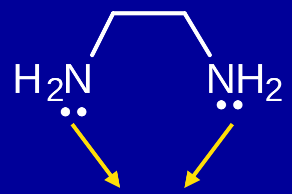
Soft metals

Ag(I), Cu(I), Hg(II), Au(I)

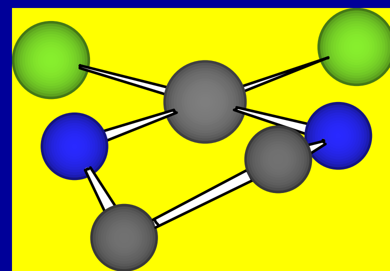
Large atoms (2nd and 3rd transition row)

Small charge

Neutral Bidentate Ligands



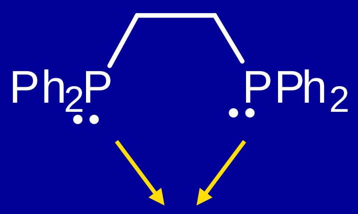
$[PtCl_2(en)]$



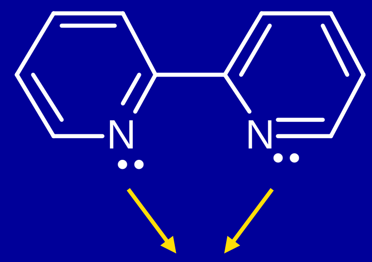
Five-membered chelate cycl

square planar complex

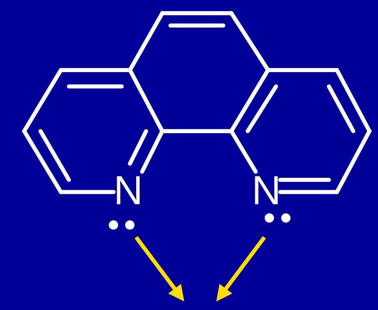
1,2-diaminoethane = ethylendiamine = en



1,2-difenylphosphinoethane
dppe

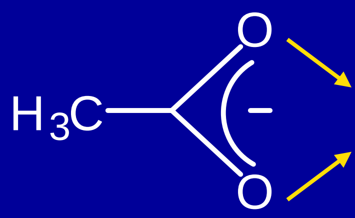


2,2'-bipyridine
bipy

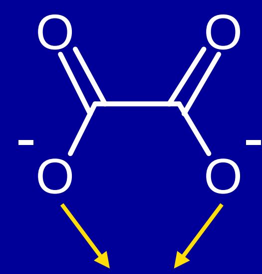


1,10-phenanthroline
phen

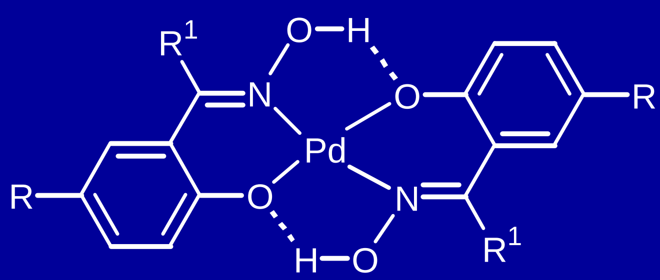
Anionic Bidentate Ligands



acetate = ac^-

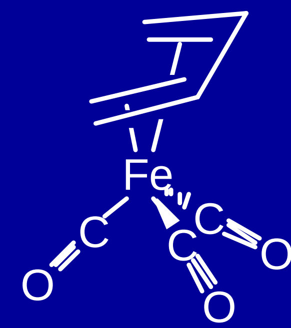


oxalate = ox^{2-}



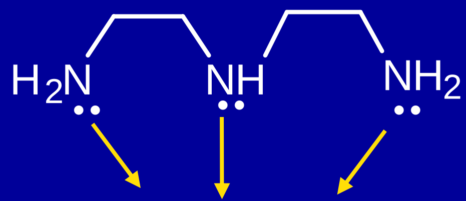
complex Pd(II)-oxim

π-donor bidentate ligand



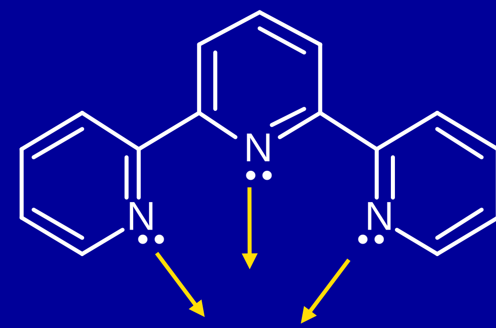
$[Fe(CO)_3(h^4\text{-}C_4H_6)]$

Tridentate Ligands



diethylentriamine

dien

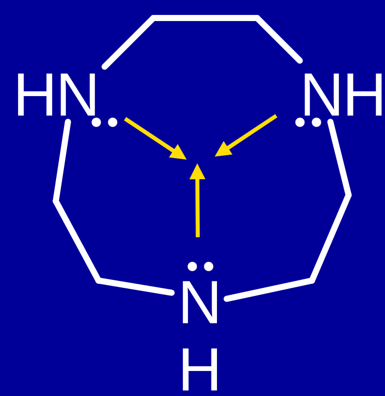


2,2':6',2"-terpyridine

tpy

1,2,4-triazacyclononane

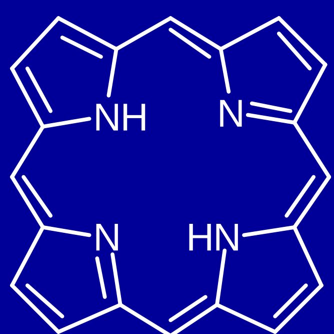
Macrocyclic ligand



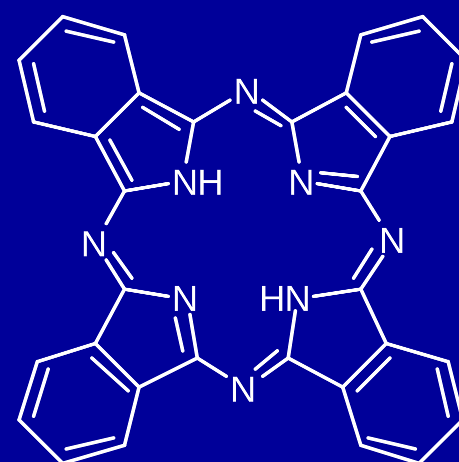
Tetradentate Ligands

tris(2-aminoethyl)amine

tren



porfyrine

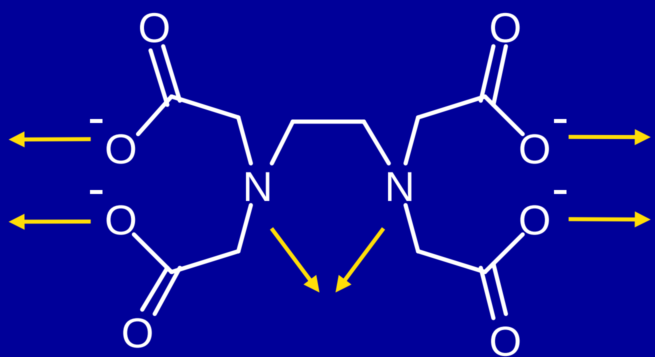


ftalocyanine

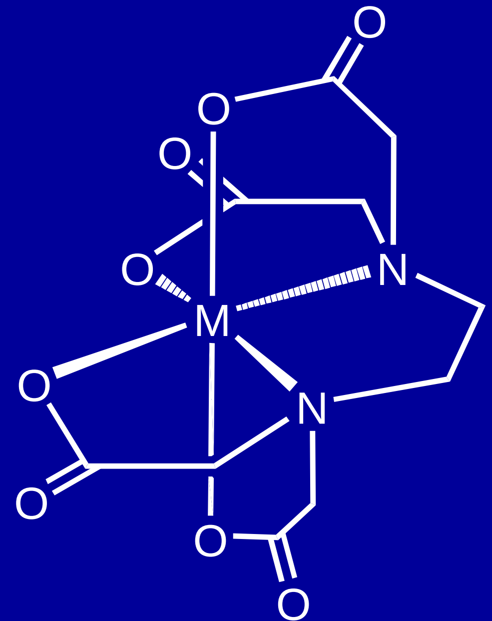
Multidentate Ligands

tetraanion of ethylendiamintetraacetic acid

EDTA



Hexadentate



Nomenclature of Coordination Complexes

H_2O-Aqua
NH_3-Ammine
CO-Carbonyl
NO-Nitrosyl
CH_3NH_2-Methylamine
C_5H_5N-Pyridine
F^--Fluoro
Cl^--Chloro
Br--Bromo
I^--Iodo

O^{2-}-Oxo
OH^--Hydroxo
CN^--Cyano
SO_4^{2-}-Sulfato
$S_2O_3^{2-}$-Thiosulfato
NO_2^--Nitrito-N-
ONO^--Nitrito-O-
SCN^--Thiocyanato-S-
NCS^--Thiocyanato-N-

Stability of Complexes

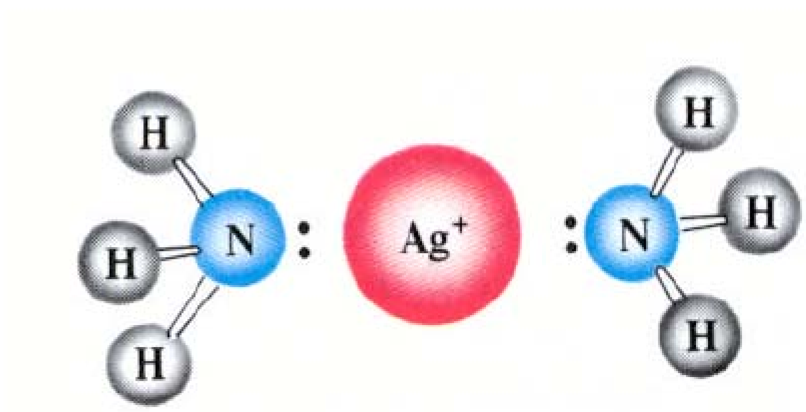
Stability constant of a complex

= equilibrium constant of its formation

High value of K = stabile complex

$$Ag^{+} + NH_3 = [Ag(NH_3)]^{+}$$

$$[Ag(NH_3)]^{+} + NH_3 = [Ag(NH_3)_2]^{+}$$



$$K_1 = \frac{[AgNH_3^{+}]}{[Ag^{+}][NH_3]}$$

$$K_2 = \frac{[Ag(NH_3)_2^{+}]}{[AgNH_3^{+}][NH_3]}$$

Stability of Complexes

Stability constant of a complex ML_n

$$\mathrm{Me} + \mathrm{L} \rightleftharpoons \mathrm{MeL} \qquad K_1 = \frac{c_{\mathrm{MeL}}}{c_{\mathrm{Me}} \cdot c_{\mathrm{L}}}$$

$$\mathrm{MeL} + \mathrm{L} \rightleftharpoons \mathrm{MeL_2} \qquad K_2 = \frac{c_{\mathrm{MeL_2}}}{c_{\mathrm{MeL}} \cdot c_{\mathrm{L}}}$$

$$\mathrm{MeL_2} + \mathrm{L} \rightleftharpoons \mathrm{MeL_3} \qquad K_3 = \frac{c_{\mathrm{MeL_3}}}{c_{\mathrm{MeL_2}} \cdot c_{\mathrm{L}}}$$

$$\mathrm{MeL_3} + \mathrm{L} \rightleftharpoons \mathrm{MeL_4} \qquad K_4 = \frac{c_{\mathrm{MeL_4}}}{c_{\mathrm{MeL_3}} \cdot c_{\mathrm{L}}}$$

$$K_1 > K_2 > K_3 \ldots > K_n$$

Stability of Complexes

Total stability constant of a complex ML_n

$$Me + L \rightleftharpoons MeL \qquad K_1 = \frac{c_{MeL}}{c_{Me} \cdot c_L}$$

$$MeL + L \rightleftharpoons MeL_2 \qquad K_2 = \frac{c_{MeL_2}}{c_{MeL} \cdot c_L}$$

$$MeL_2 + L \rightleftharpoons MeL_3 \qquad K_3 = \frac{c_{MeL_3}}{c_{MeL_2} \cdot c_L}$$

$$MeL_3 + L \rightleftharpoons MeL_4 \qquad K_4 = \frac{c_{MeL_4}}{c_{MeL_3} \cdot c_L}$$

$$Me + L \rightleftharpoons MeL \qquad \beta_1 = \frac{c_{MeL}}{c_{Me} \cdot c_L}$$

$$Me + 2L \rightleftharpoons MeL_2 \qquad \beta_2 = \frac{c_{MeL_2}}{c_{Me} \cdot c_L^2}$$

$$Me + 3L \rightleftharpoons MeL_3 \qquad \beta_3 = \frac{c_{MeL_3}}{c_{Me} \cdot c_L^3}$$

$$Me + 4L \rightleftharpoons MeL_4 \qquad \beta_4 = \frac{c_{MeL_4}}{c_{Me} \cdot c_L^4}$$

$$\beta_n = K_1 \cdot K_2 \ldots K_n$$

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$

Chelate Effect

logK = 8.61

$$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6\ H_2O$$

logK = 18.28

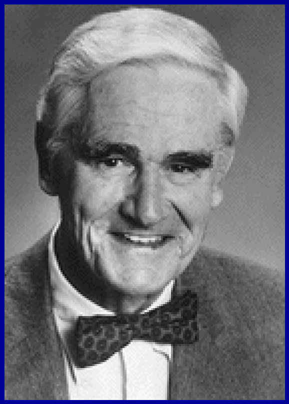
$$[Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6\ H_2O$$

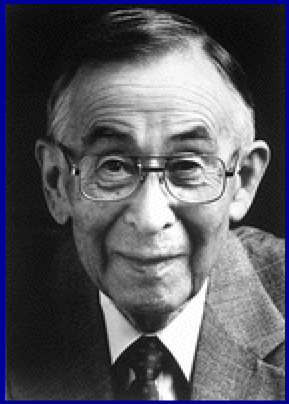
$\Delta G = -RT \ln K = \Delta H - T\Delta S$

ΔH same for both reactions (Ni-O $\rightarrow$ Ni-N)
ΔS high for chelate, more product particles

Chelates, Macrocycles, Cryptates

NP in Chemistry 1987



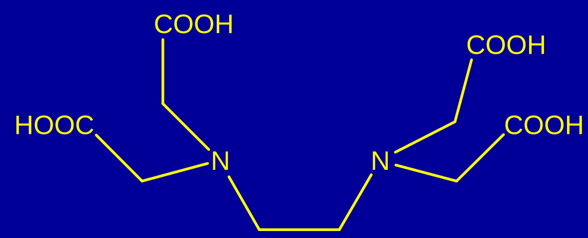


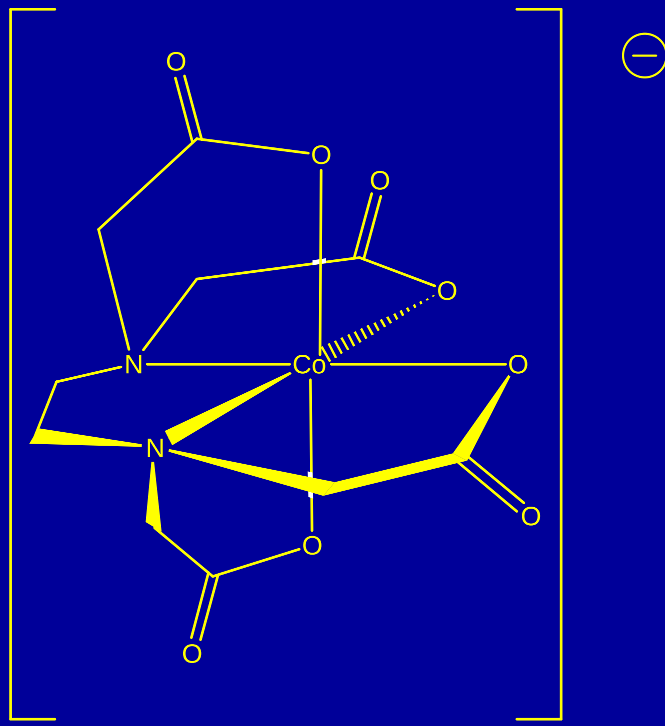
Donald J. Cram **Jean-Marie Lehn** **Charles J. Pedersen**

Chelates, Macrocycles, Cryptates

EDTA

tetraanion of ethylendiamintetraacetic acid





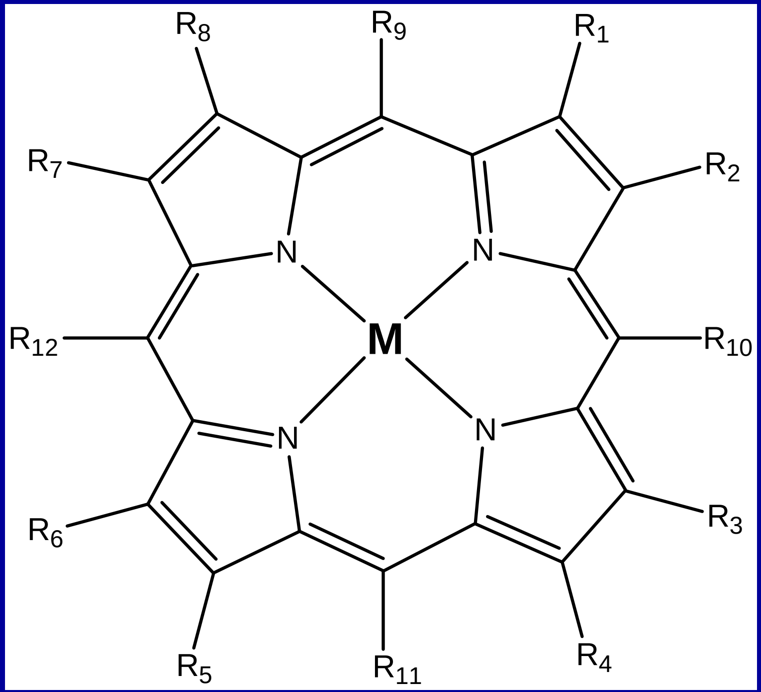
Chelatation therapy of Pb poisoning

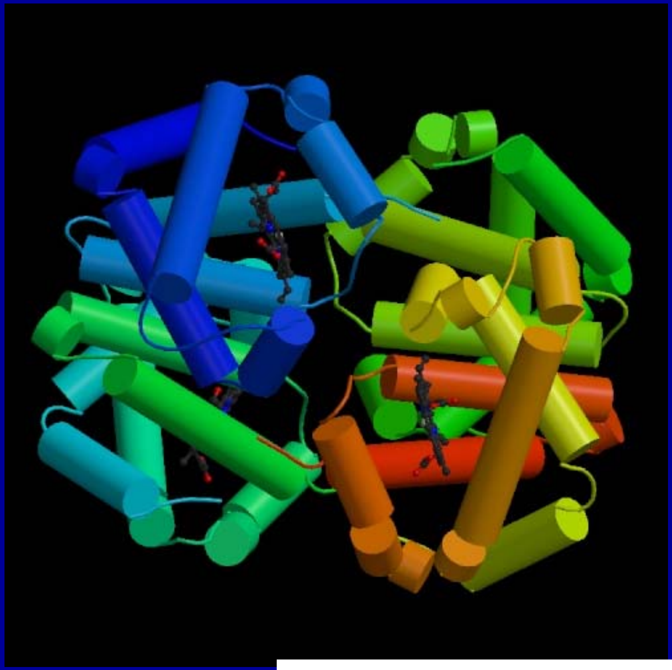
Chelatometry

Dissolves $CaCO_3$

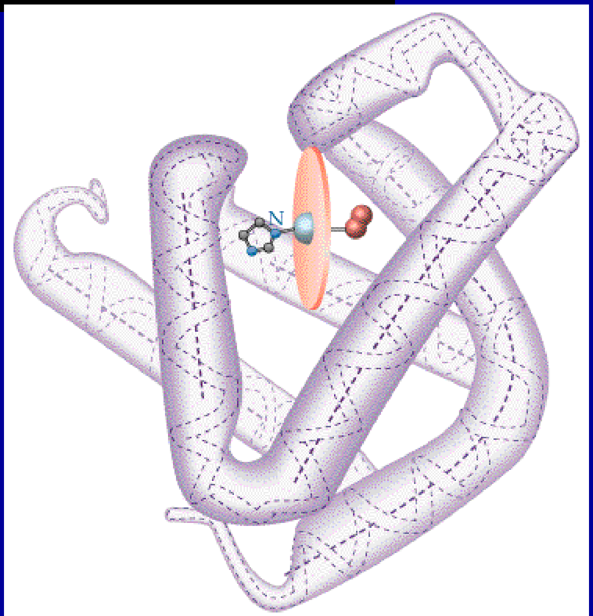
Chelates, Macrocycles, Cryptates

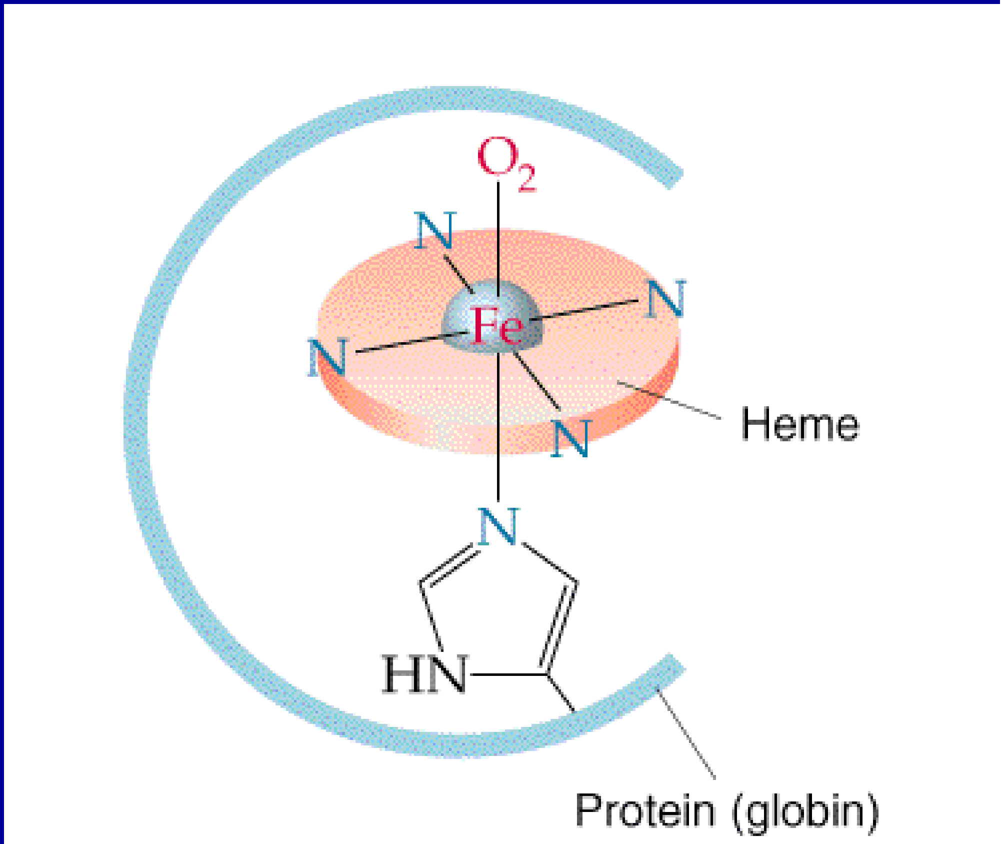
Metalloporphyrins: M = Fe (hem, cytochrom c), Mg (chlorophyl), Co (B_{12})

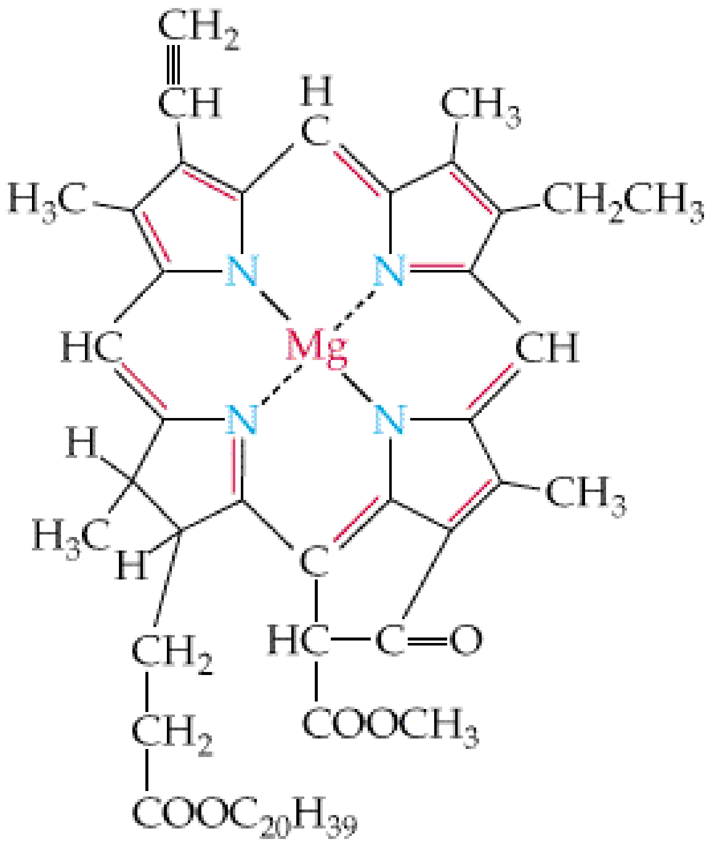




Hemoglobine

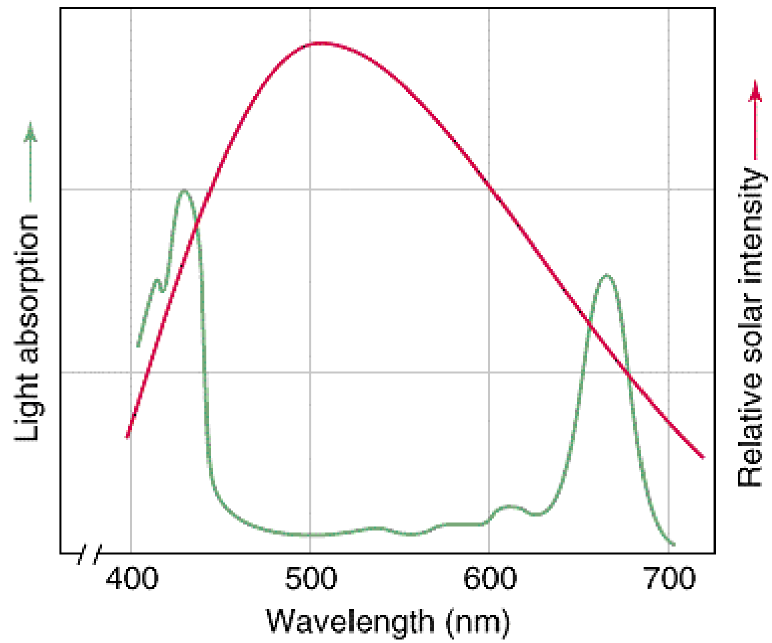






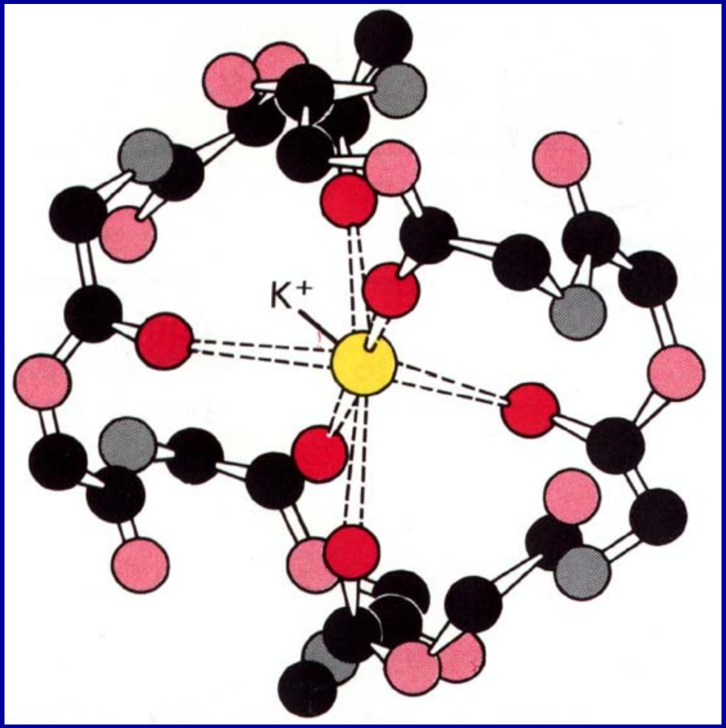
$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

Mg chlorophyl



Chelates, Macrocycles, Cryptates

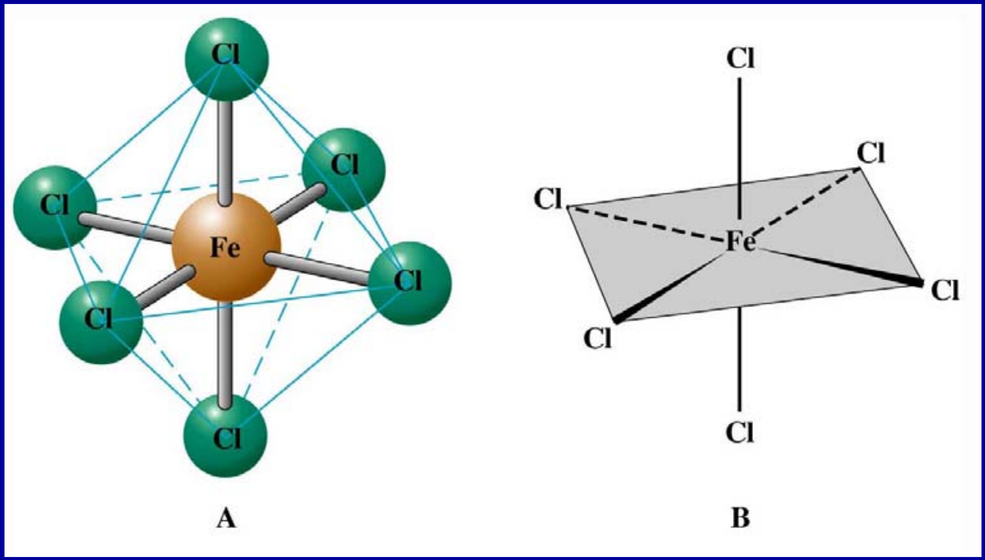
Valinomycine



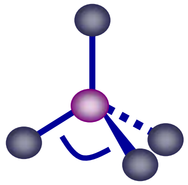
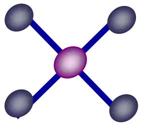
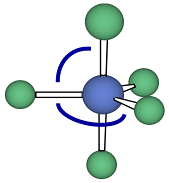
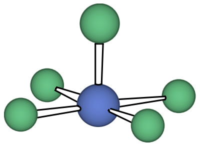
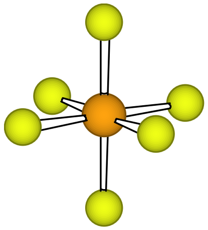
Geometry of Complexes

Octahedral complexes O_h

Tetrahedral complexs T_d



Geometry of Complexes

Tetrahedral	109° 28'	C.N. 4	
Square planar	90°	C.N. 4	
Trigonal bipyramidal	120° + 90°	C.N. 5	
Square pyramidal	90°	C.N. 5	
Octahedral	90°	C.N. 6	

Isomers of Complexes

Structural isomers

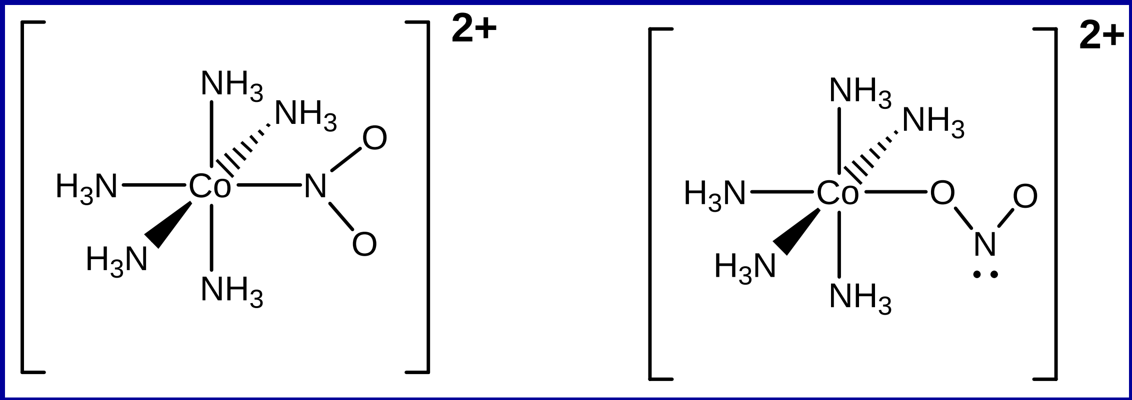
Bonding
Coordination
Ionization

Stereo isomers

Geometric
Optical

Structural Isomers

Bonding : SCN^-, NO_2^-, OCN^-



nitro-

nitrito-

Structural Isomers

Coordination

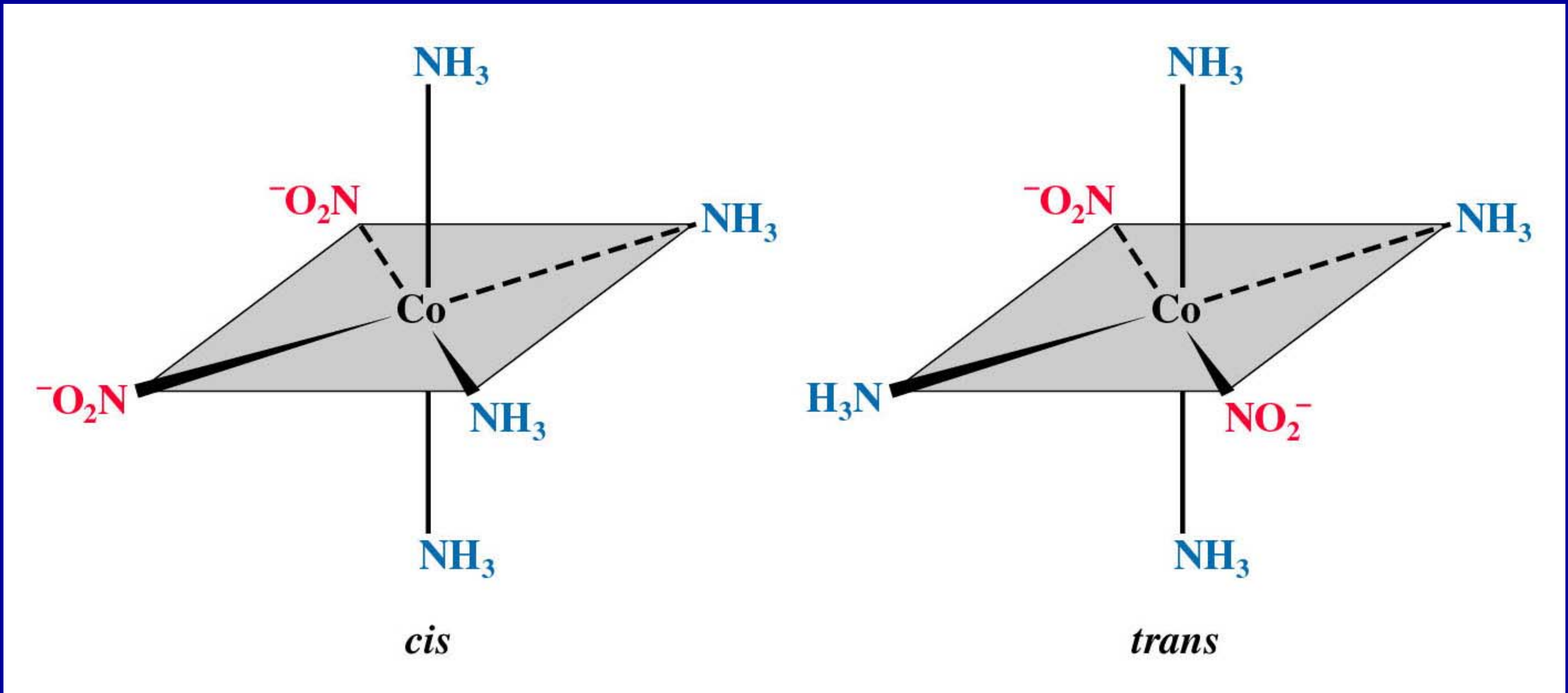
$[Pt(NH_3)_4][CuCl_4]$ $[Cu(NH_3)_4][PtCl_4]$

Ionization

$[Co(NH_3)_5SO_4]Br$ $[Co(NH_3)_5Br]SO_4$

Stereo Isomers

Geometric: cis-trans, diastereomers

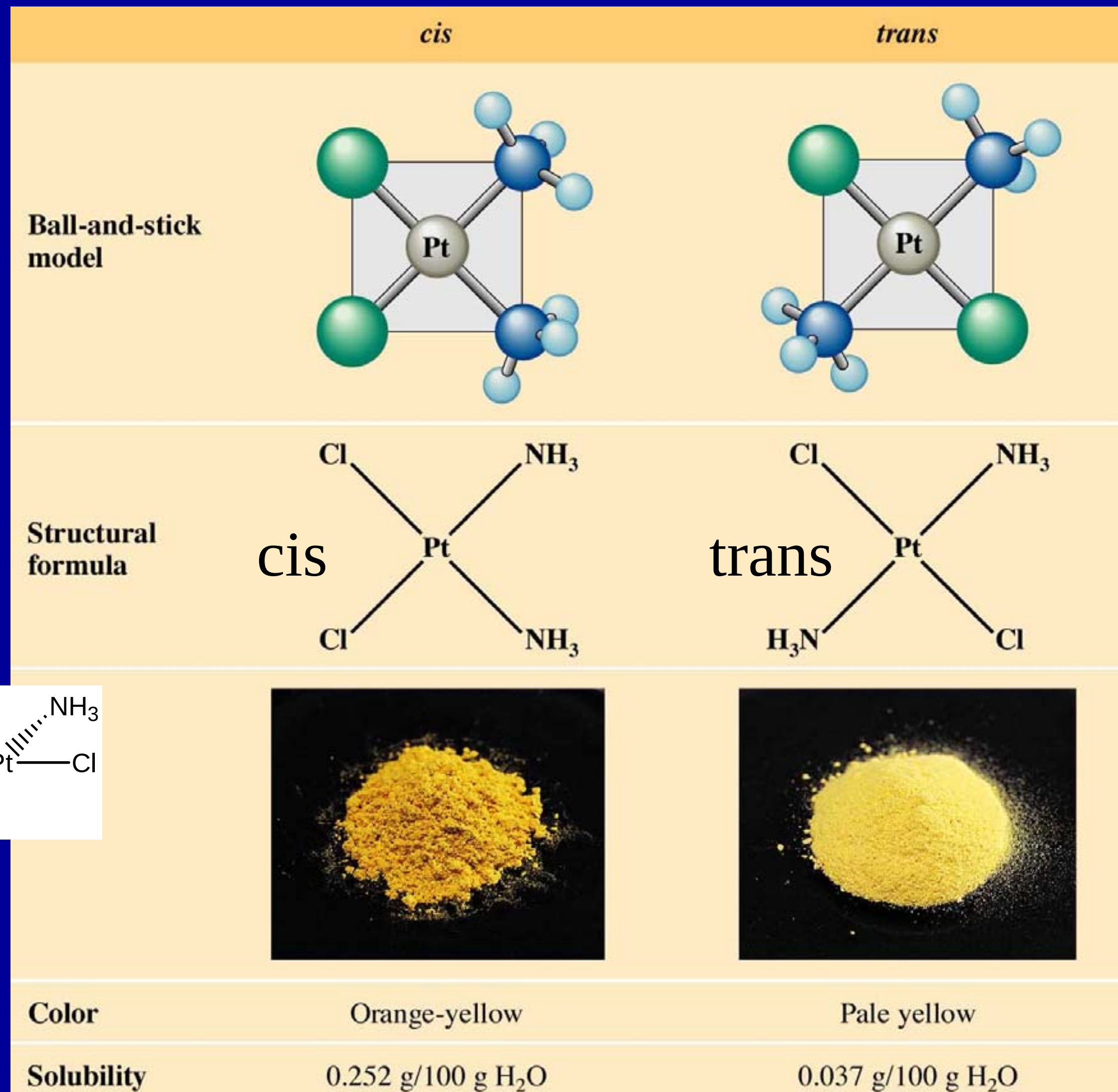


Stereo Isomers

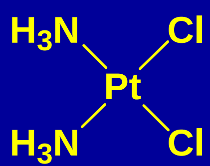
Geometric:

cis-trans

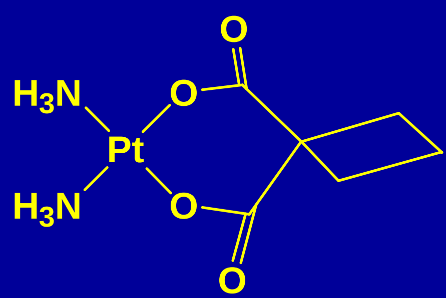
diastereomers



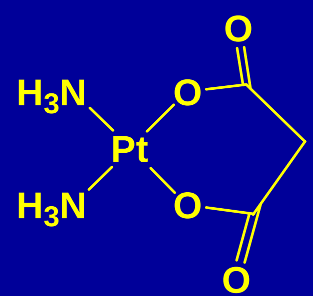
Antitumor Medicine



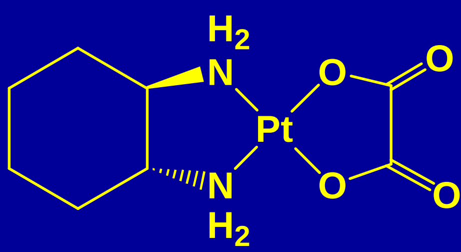
Cisplatin



Carboplatin

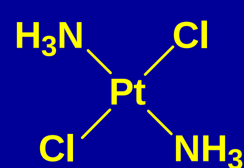


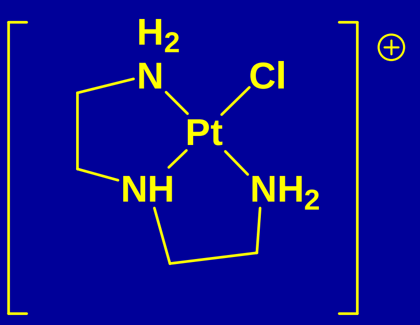
Nedaplatin



Oxaliplatin

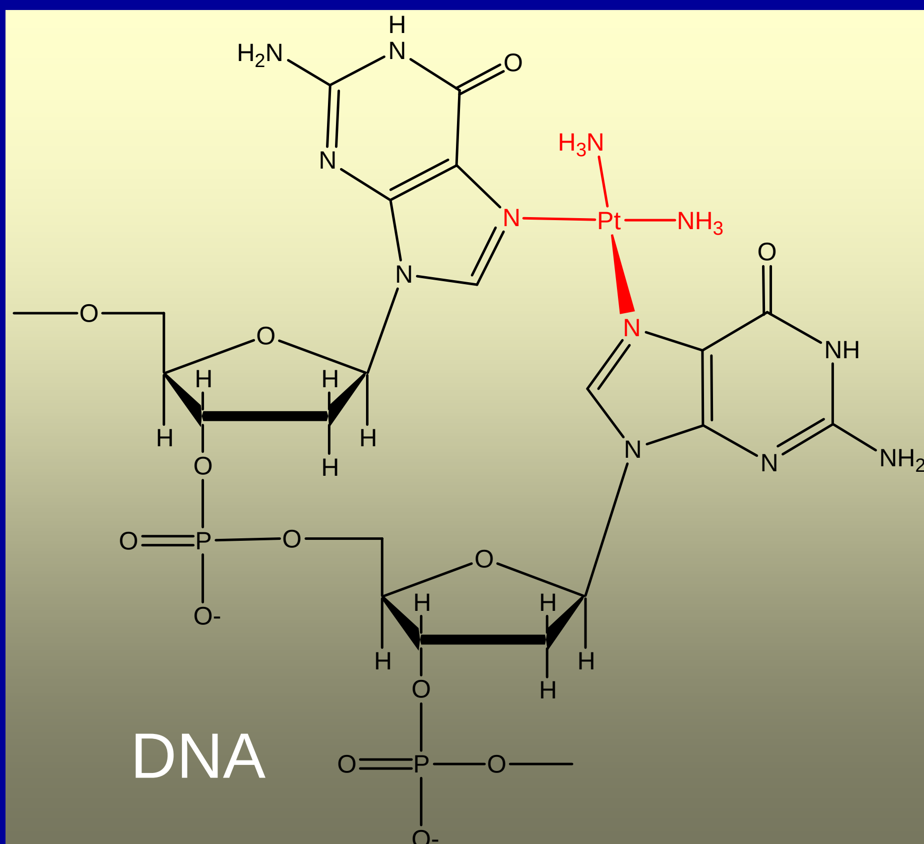
Inactive





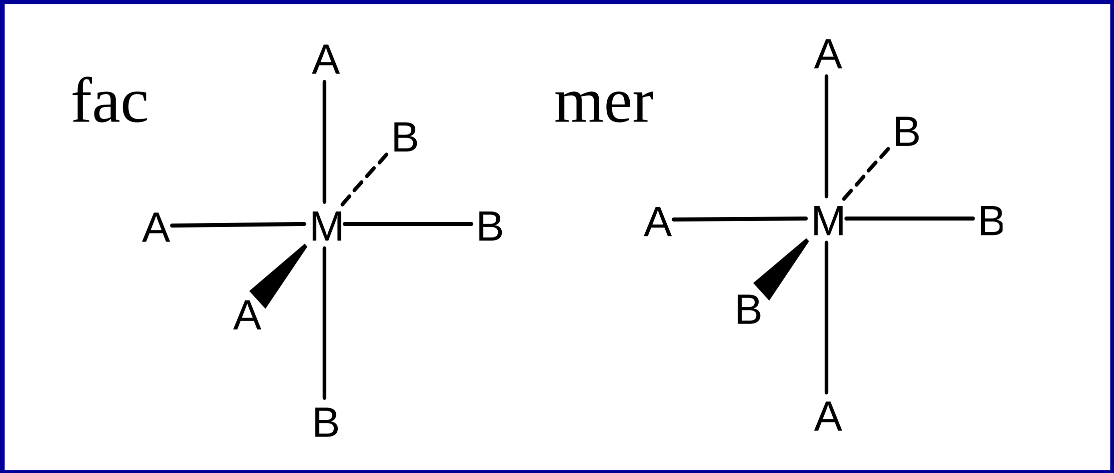
Stereo Isomers

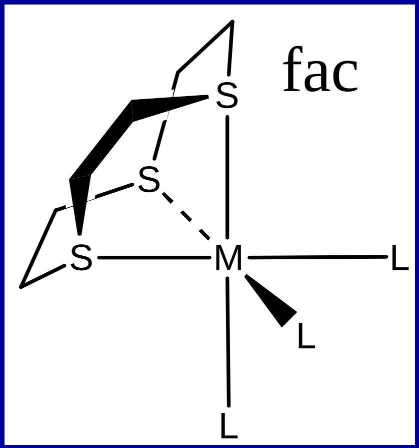
Cisplatin = cancerostatics

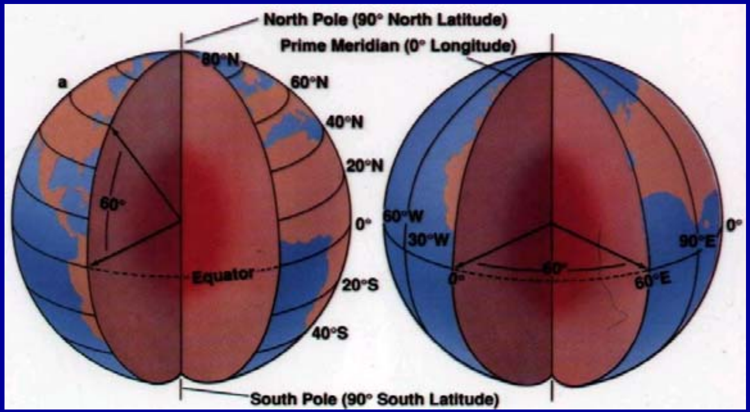


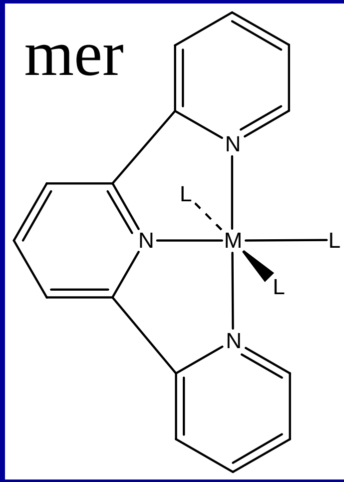
Stereo Isomers

Geometric: mer-fac, diastereomers



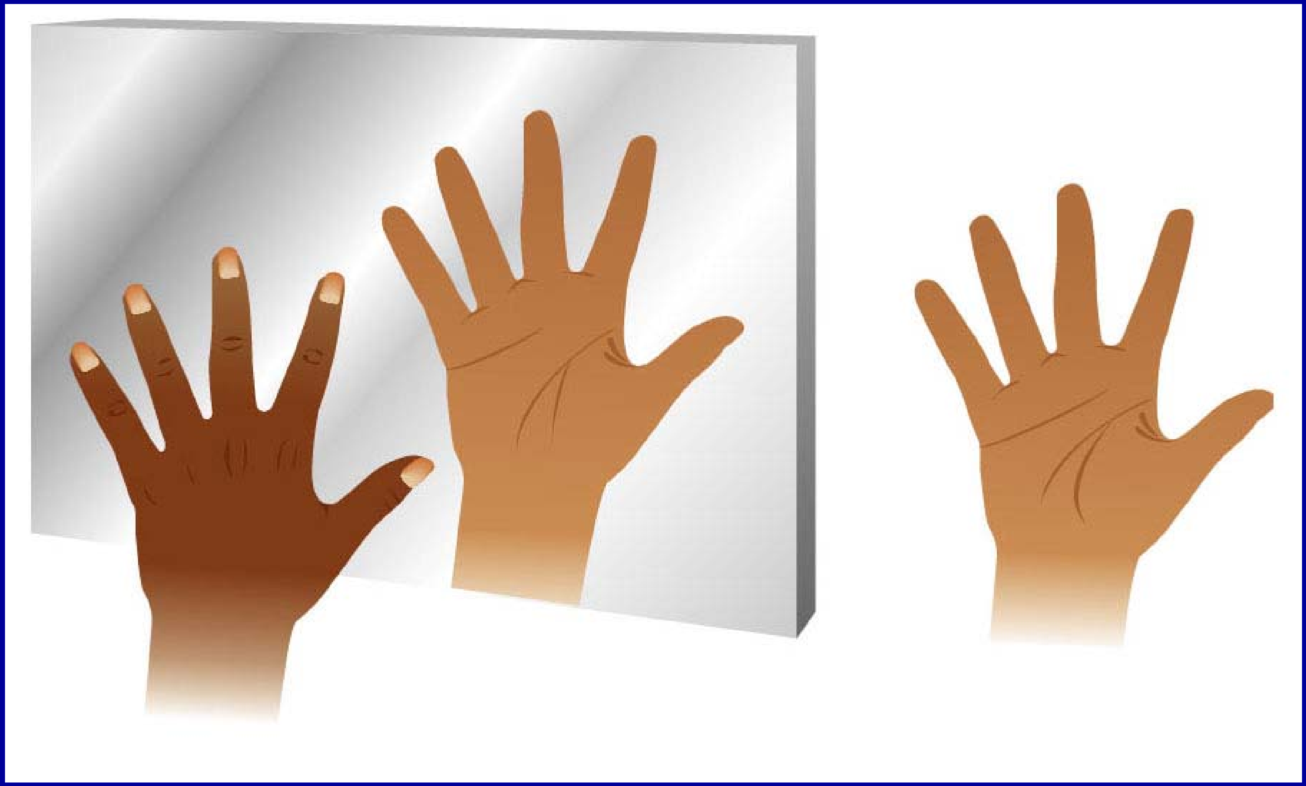






Stereo Isomers

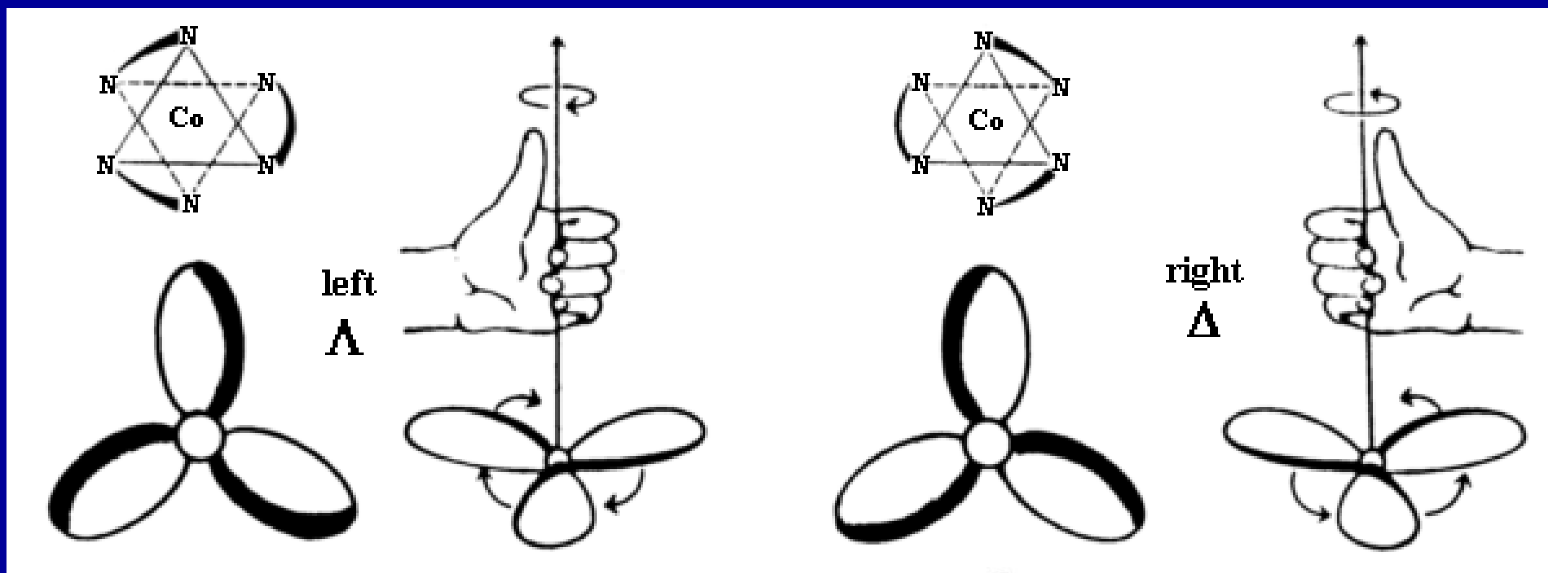
Optical: enantiomers

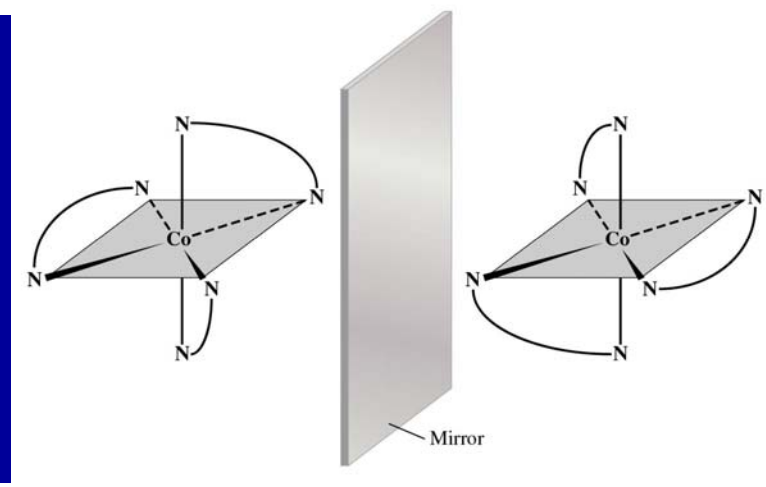


Stereo Isomers

Optical: enantiomers

$[Co(en)_3]^{3+}$



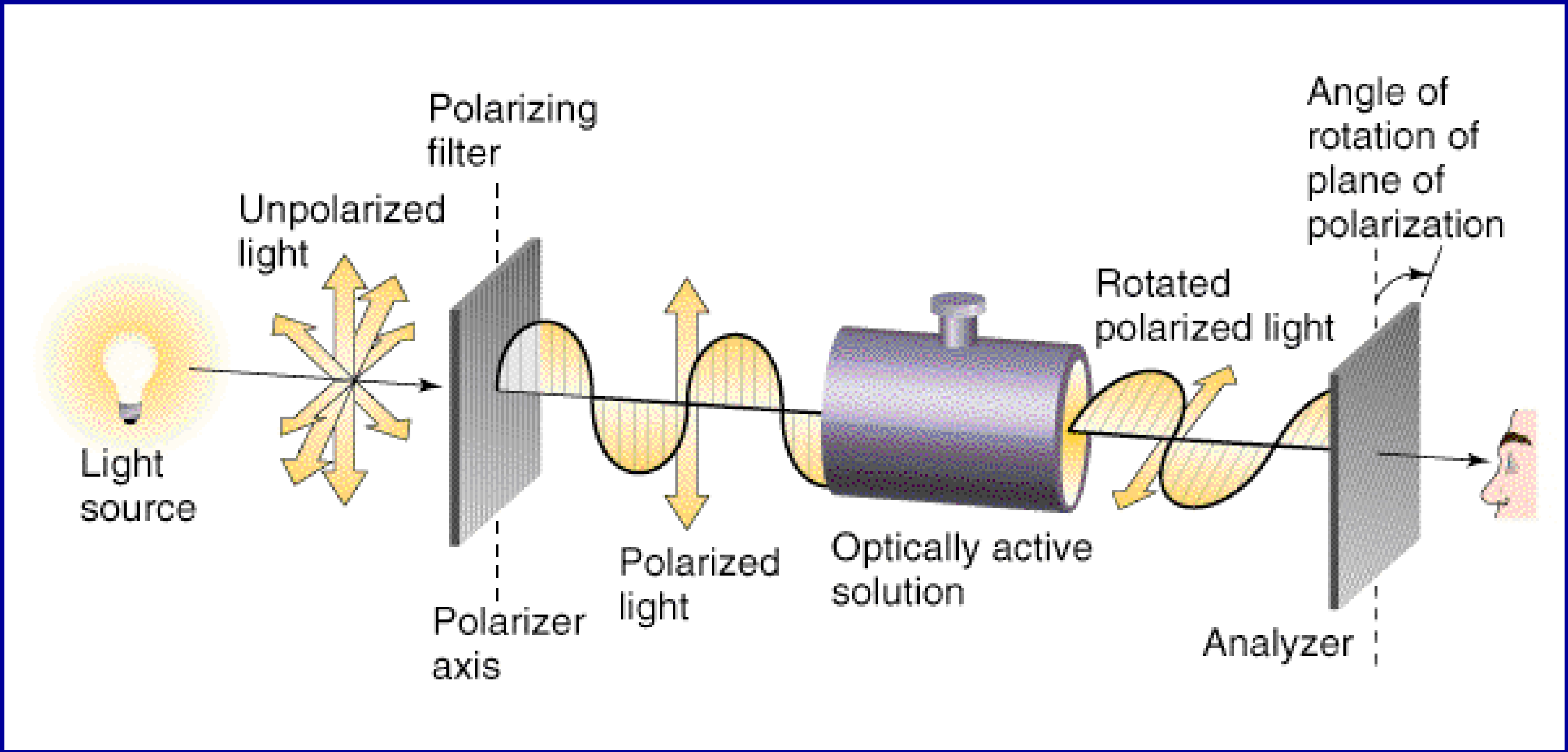


No S_n

S_1 = symmetry plane

S_2 = inversion center

Optical Rotation



Bonding in Complexes

1) VB

2) CFT = Crystal Field Theory 1929 Hans Bethe

Electrostatic interactions between ligands and metal

3) LFT = Ligand Field Theory

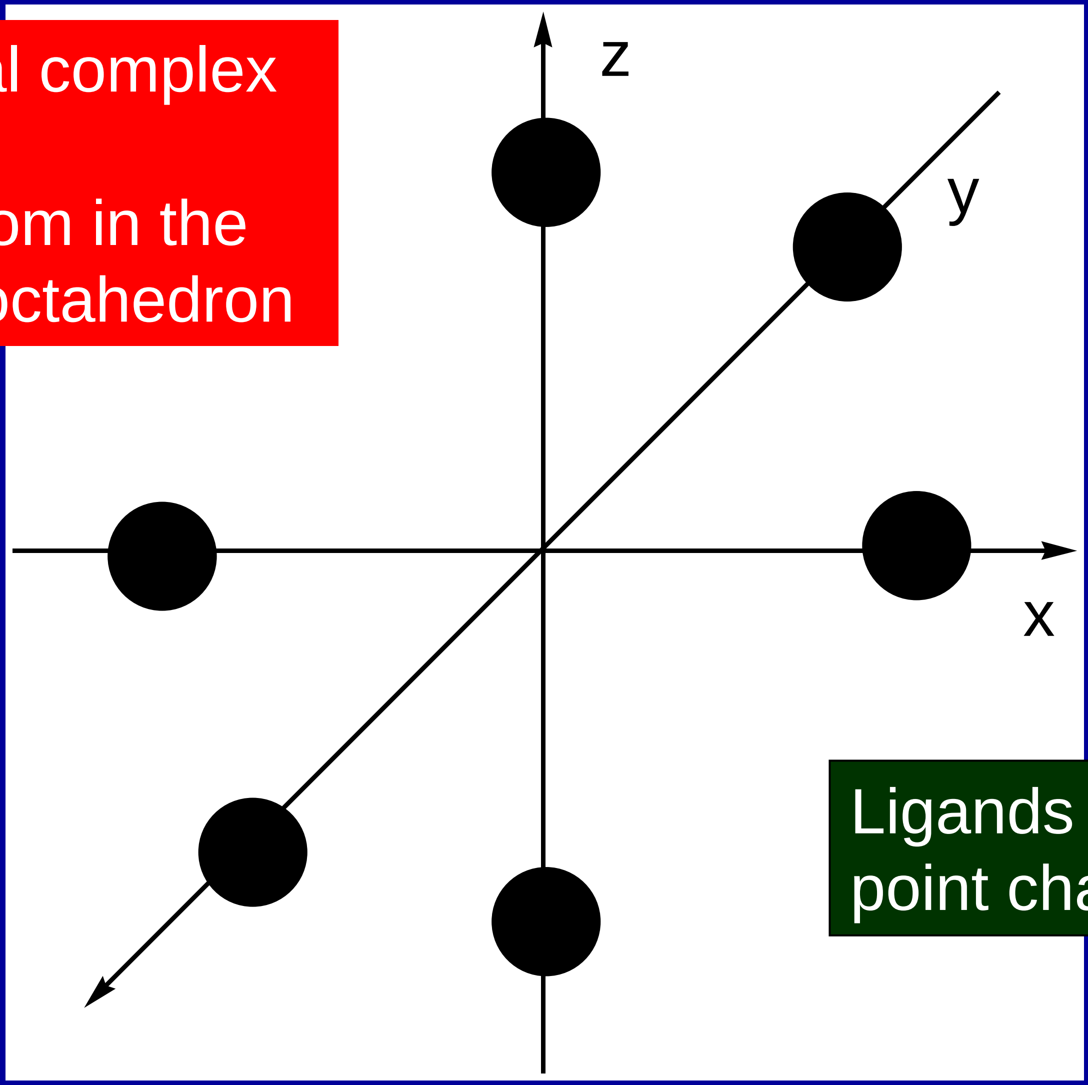
1935 modification J. H. Van Vleck   covalence

4) MO

Ligand Field Theory

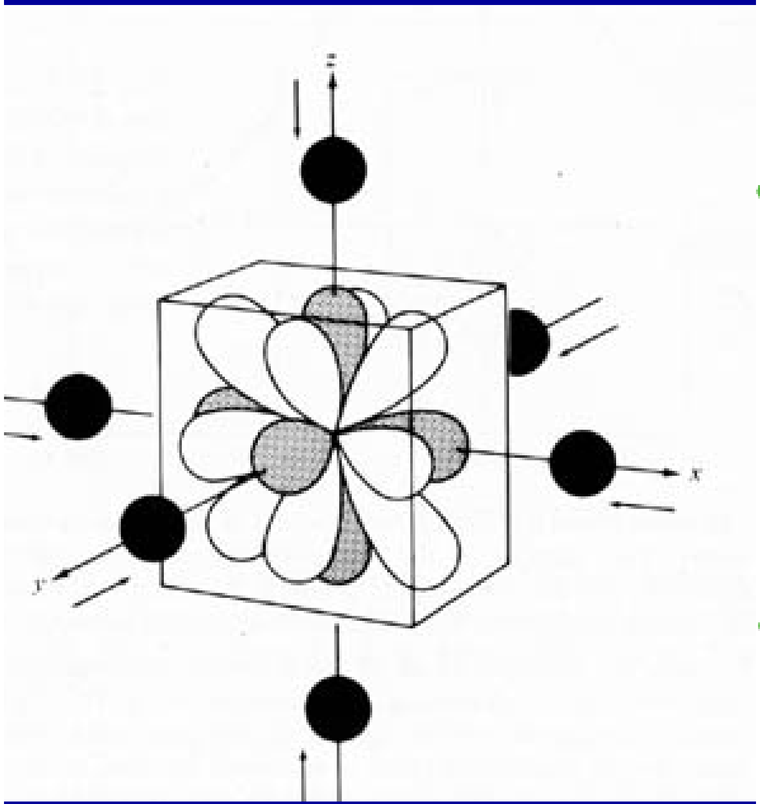
Octahedral complex

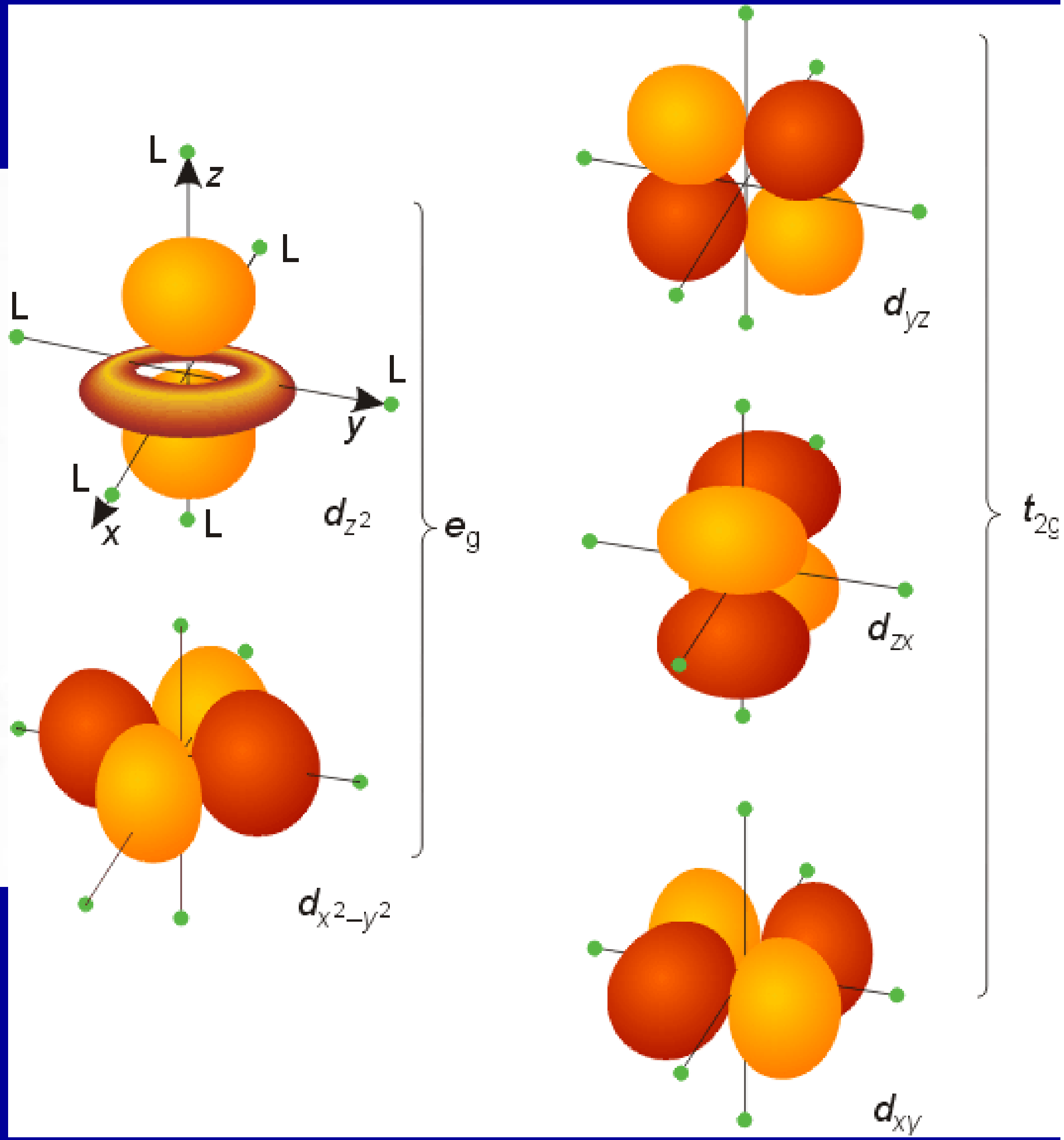
Central atom in the center of octahedron



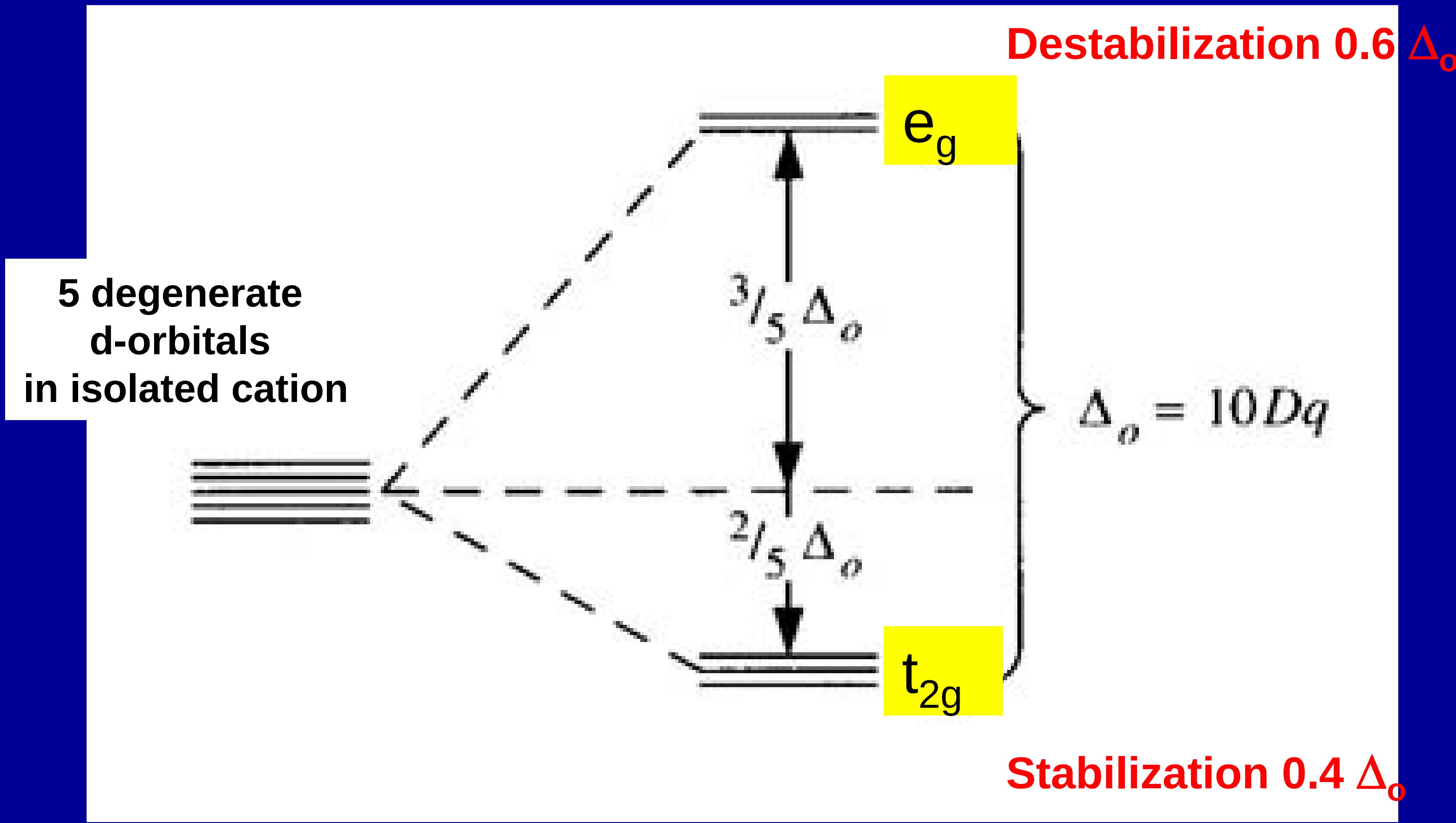
Ligands as negative point charges

d-Orbitals in Octahedral Ligand Field

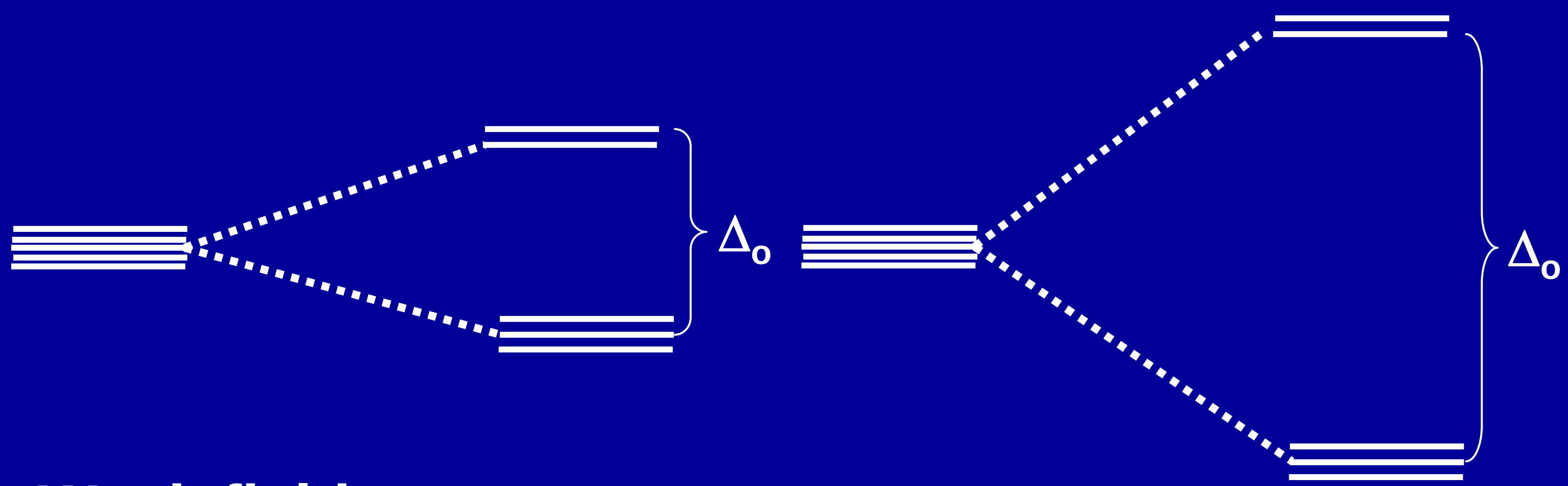




Splitting of d-Levels in O_h Field



CFSE = Crystal Field Stabilization Energy



Weak field

Δ_o < P (pairing energy)

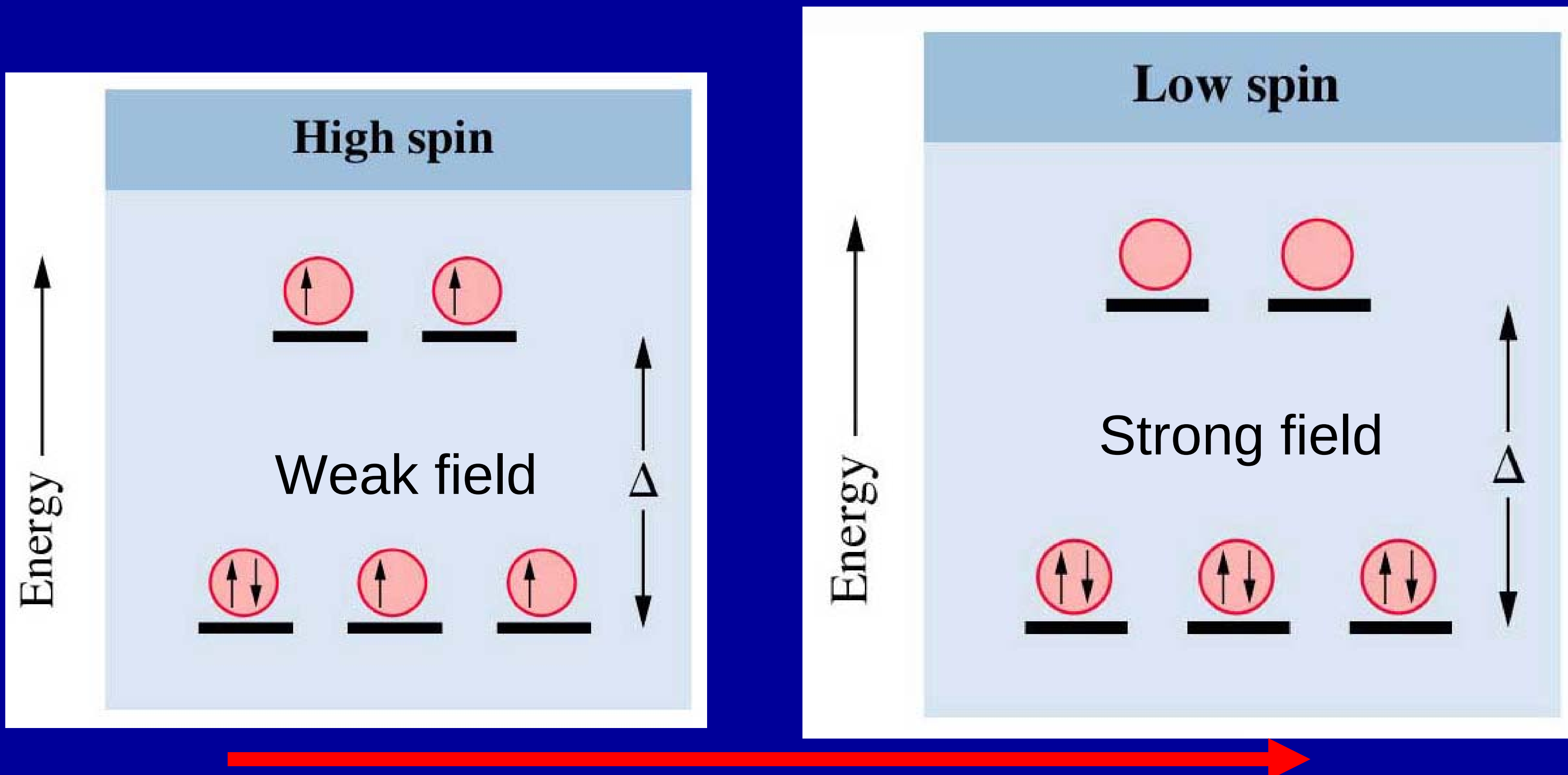
High spin complexes

Strong field

Δ_o > P (pairing energy)

Low spin complexes

Crystal Field Stabilization Energy



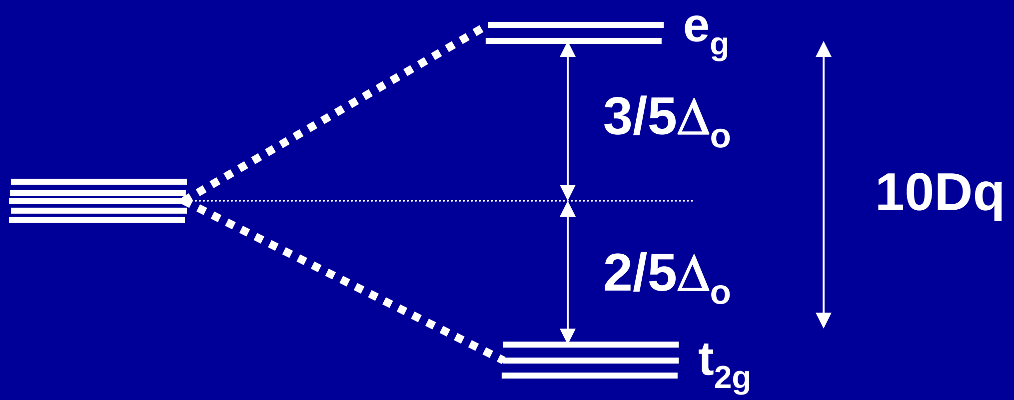
Δ_o increases

	Weak field			Strong field		
		e	CFSE		e	CFSE
d^1	$t_{2g}^{\ 1}$	1	0.4 Δ_o	$t_{2g}^{\ 1}$	1	0.4 Δ_o
d^2	$t_{2g}^{\ 2}$	2	0.8 Δ_o	$t_{2g}^{\ 2}$	2	0.8 Δ_o
d^3	$t_{2g}^{\ 3}$	3	1.2 Δ_o	$t_{2g}^{\ 3}$	3	1.2 Δ_o
d^4	$t_{2g}^{\ 3}\,e_g^{\ 1}$	4	0.6 Δ_o	$t_{2g}^{\ 4}$	2	1.6 Δ_o
d^5	$t_{2g}^{\ 3}\,e_g^{\ 2}$	5	0.0 Δ_o	$t_{2g}^{\ 5}$	1	2.0 Δ_o
d^6	$t_{2g}^{\ 4}\,e_g^{\ 2}$	4	0.4 Δ_o	$t_{2g}^{\ 6}$	0	2.4 Δ_o
d^7	$t_{2g}^{\ 5}\,e_g^{\ 2}$	3	0.8 Δ_o	$t_{2g}^{\ 6}\,e_g^{\ 1}$	1	1.8 Δ_o
d^8	$t_{2g}^{\ 6}\,e_g^{\ 2}$	2	1.2 Δ_o	$t_{2g}^{\ 6}\,e_g^{\ 2}$	2	1.2 Δ_o

$$\text{CFSE} = (n\ t_{2g})\ 0.4\ \Delta_o - (n\ e_g)\ 0.6\ \Delta_o$$

e = number of unpaired electrons

Splitting of d-Levels in O_h Field

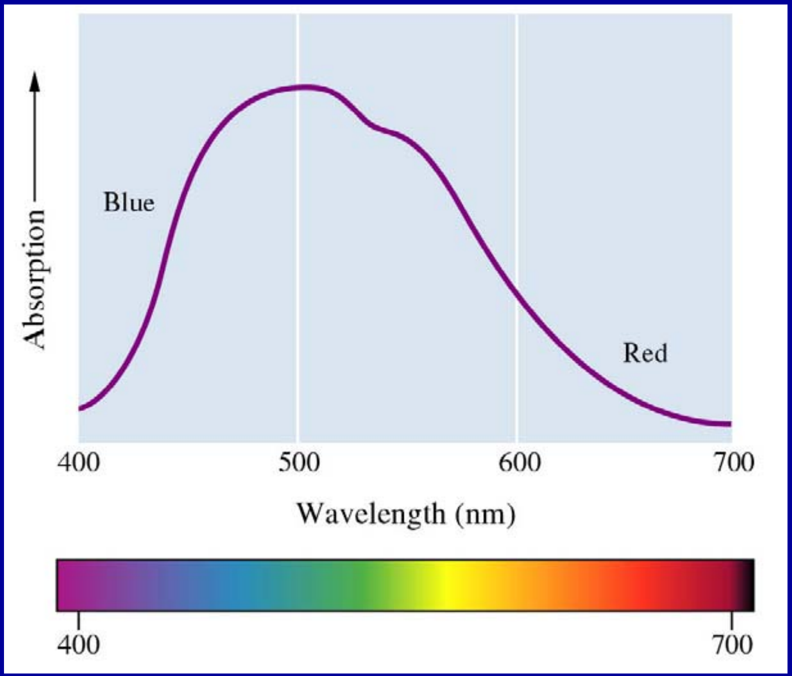


$[Ti(H_2O)_6]^{3+}$ d^1

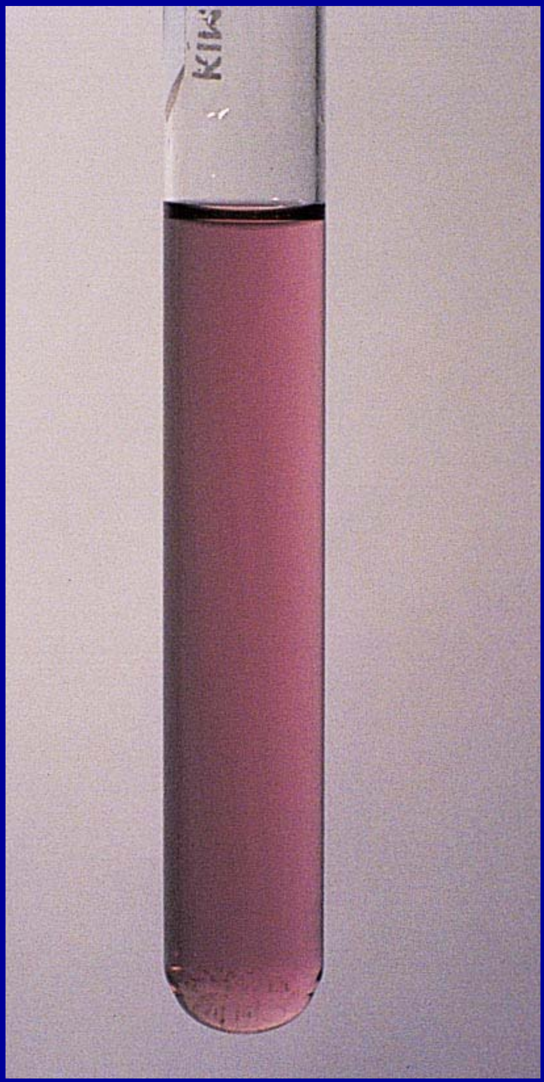
$t_{2g}^1 e_g^0 \longrightarrow t_{2g} e_g^1$

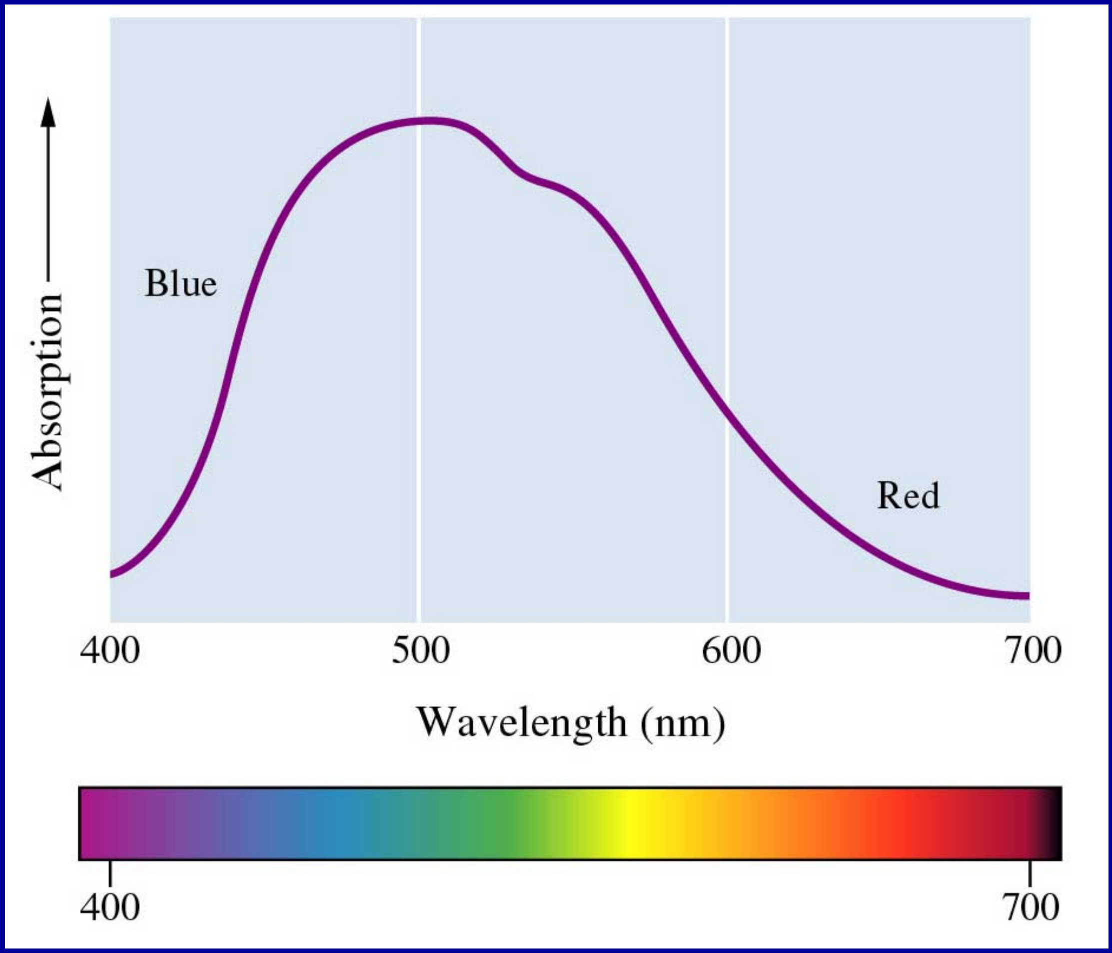
pink

243 kJ mol^{-1} (Δ_o)

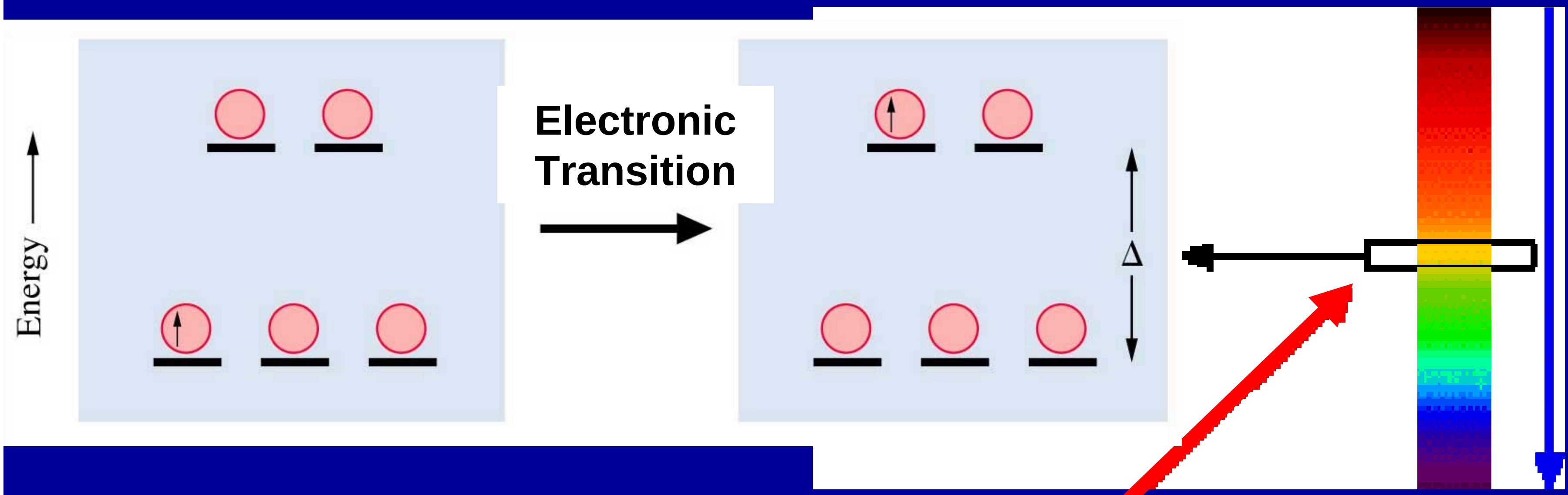


UV-vis Absorption Spectrum of $[Ti(H_2O)_6]^{3+}$



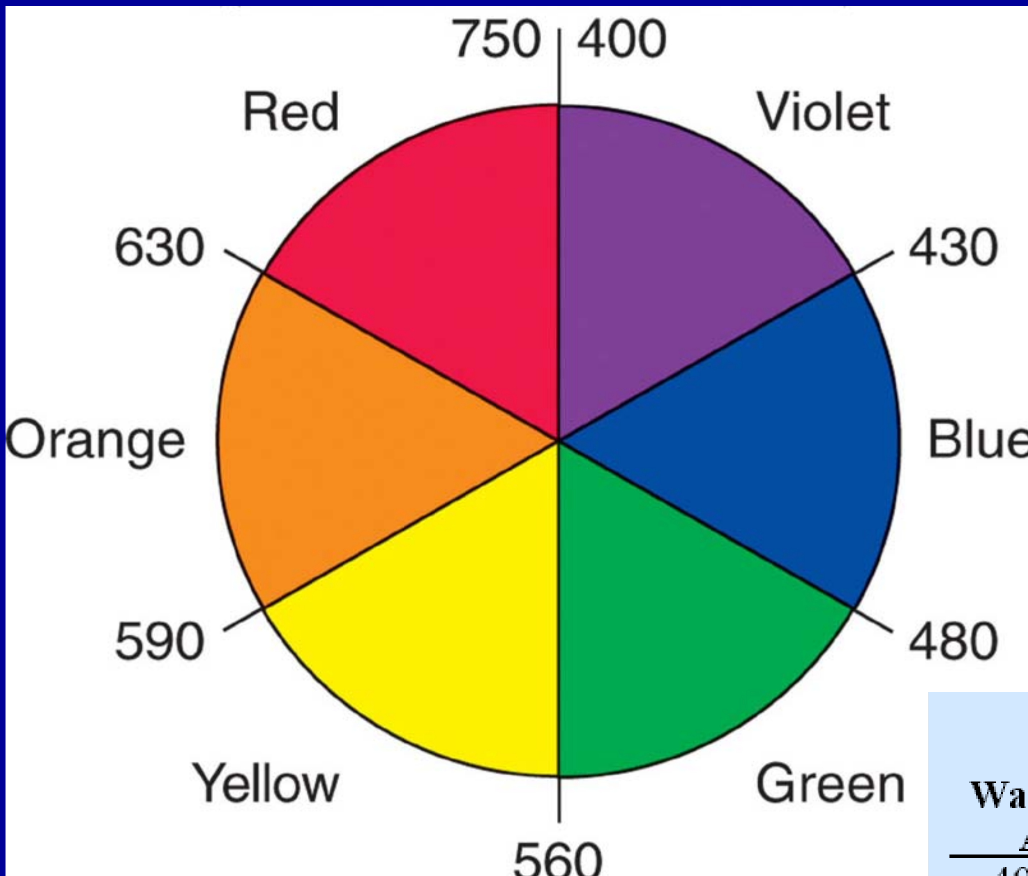


Electronic Transitions



Energy increases

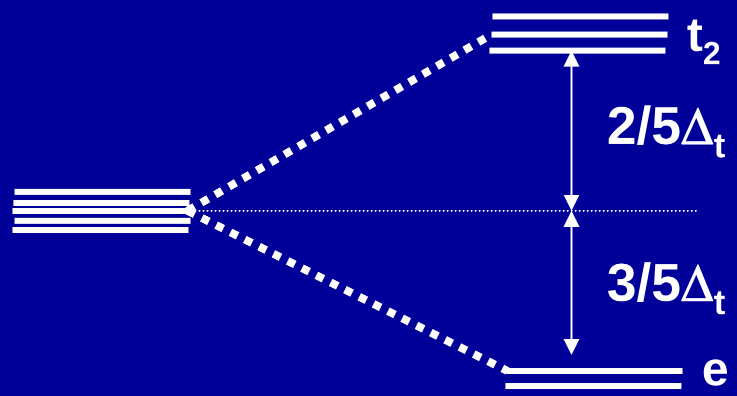
This energy is just sufficient to excite electron



Wavelength (Color) Absorbed	Color Observed
400 nm (**violet**)	**yellow-green**
450 nm (**blue**)	**orange**
490 nm (**blue-green**)	**red**
530 nm (**green**)	**purple**
570 nm (**yellow-green**)	**violet**
580 nm (**yellow**)	**dark blue**
600 nm (**orange**)	**blue**
650 nm (**red**)	**blue-green**
720 nm (**purple**)	**green**

E

Splitting of d-Levels in T_d Field

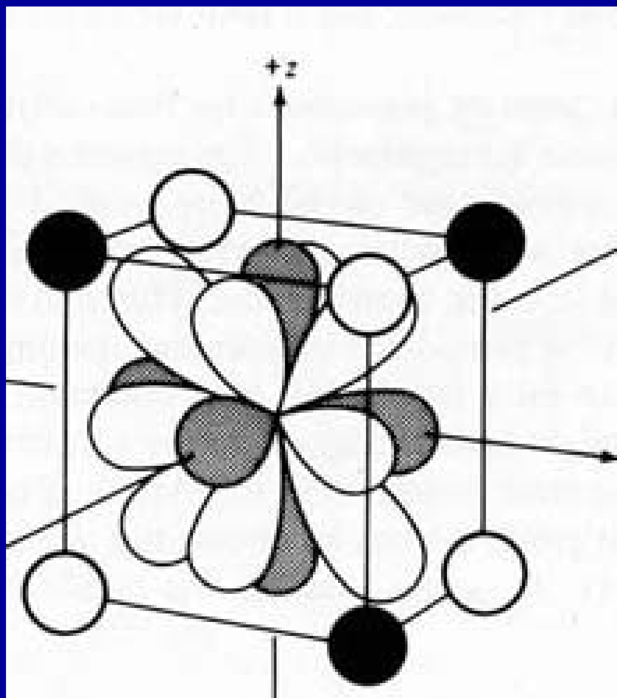


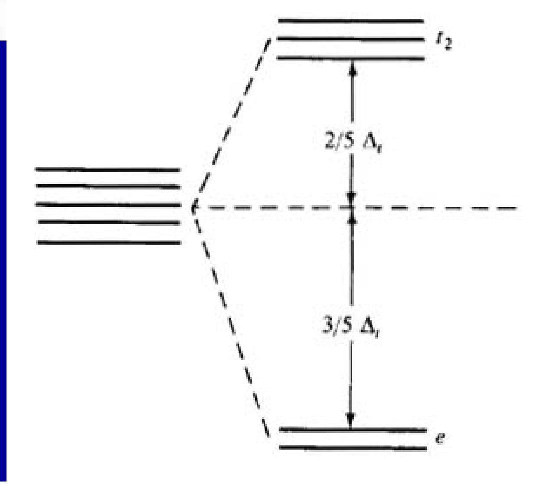
$\Delta_t = 4/9\ \Delta_o$

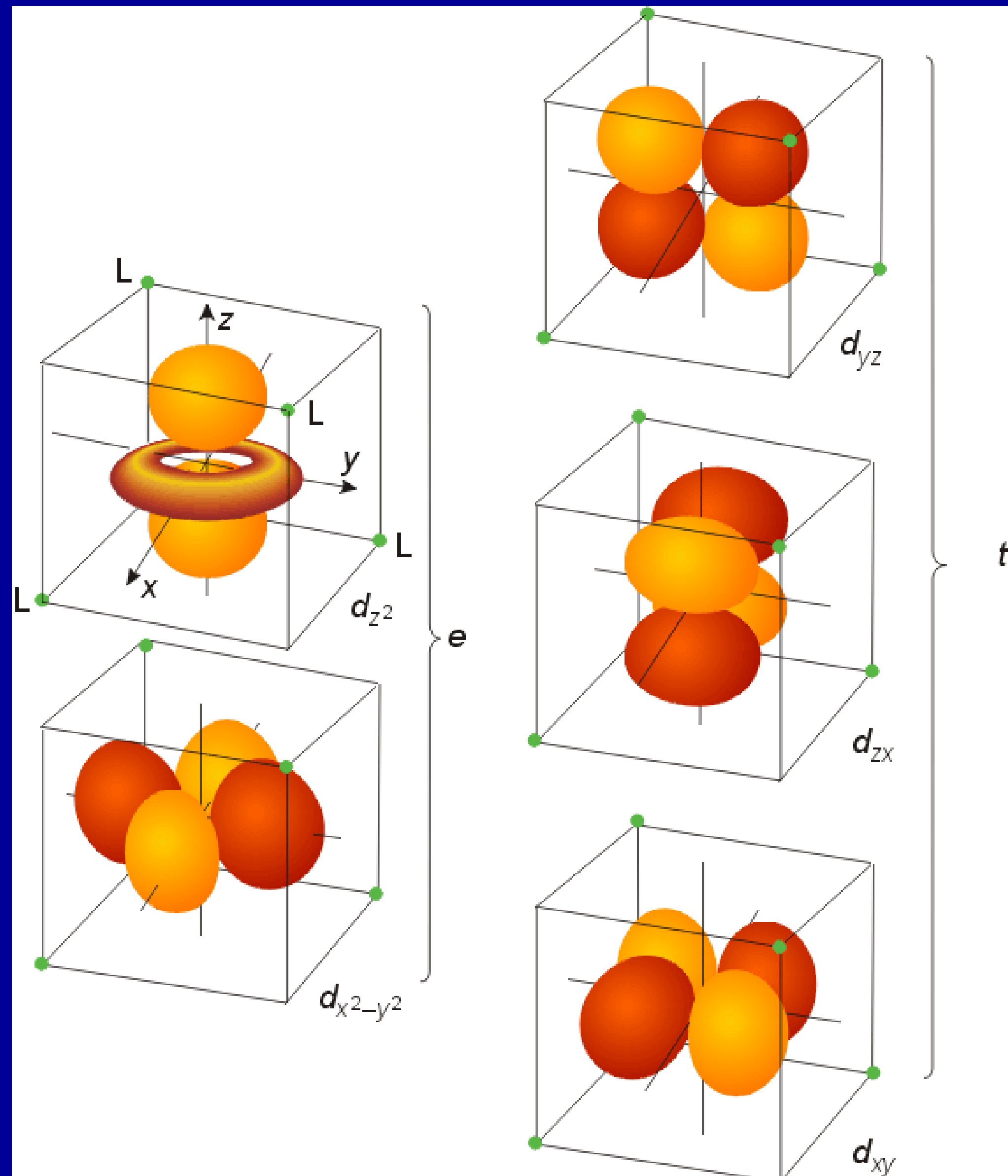
T_d complexes are always high spin

No d-orbital points directly to ligands = weaker interaction

d-Orbitals in Tetrahedral Ligand Field

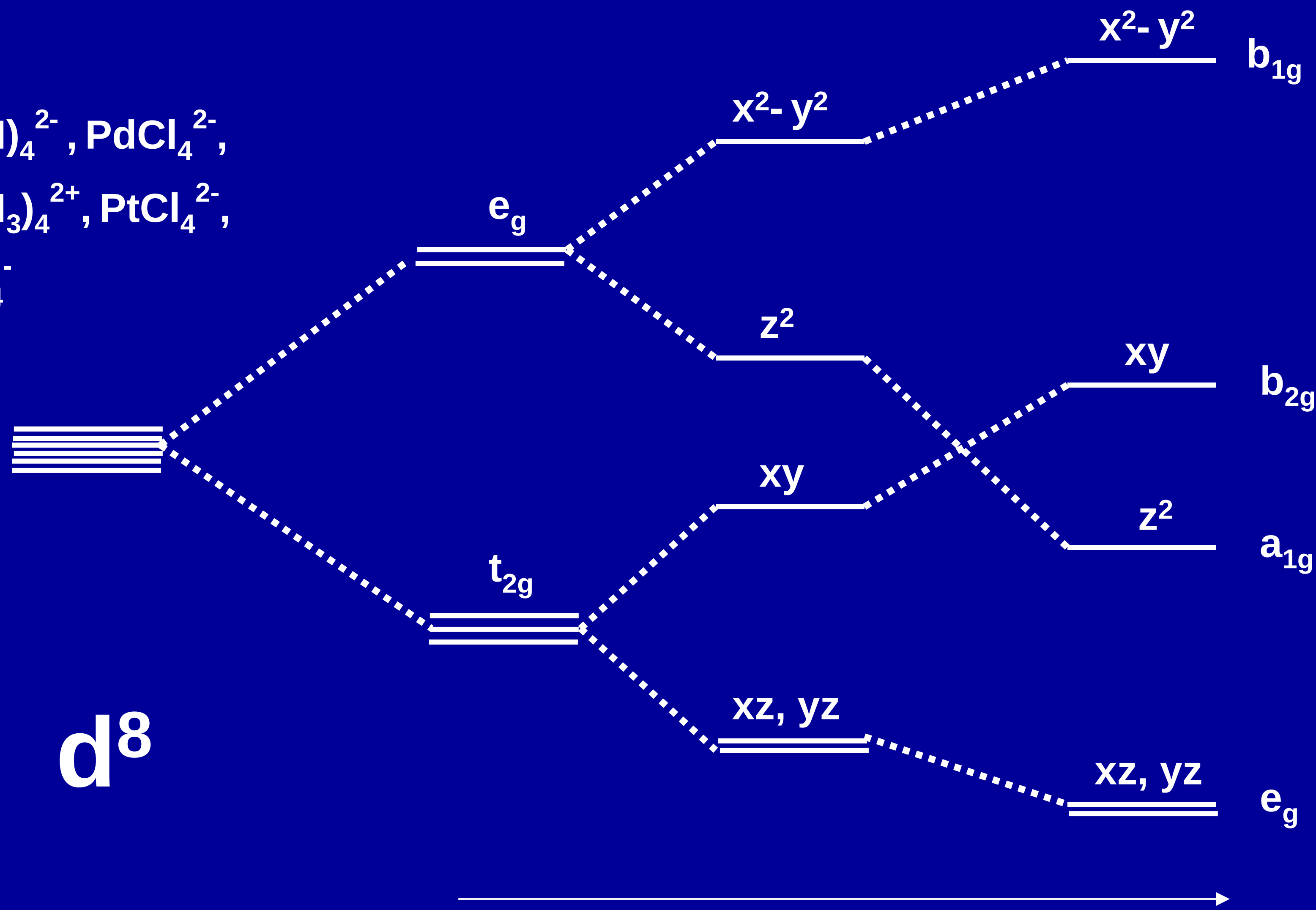






Splitting of d-Levels in Square Planar Field (d^8)

$Ni(CN)_4^{2-}$, $PdCl_4^{2-}$,
$Pt(NH_3)_4^{2+}$, $PtCl_4^{2-}$,
$AuCl_4^-$



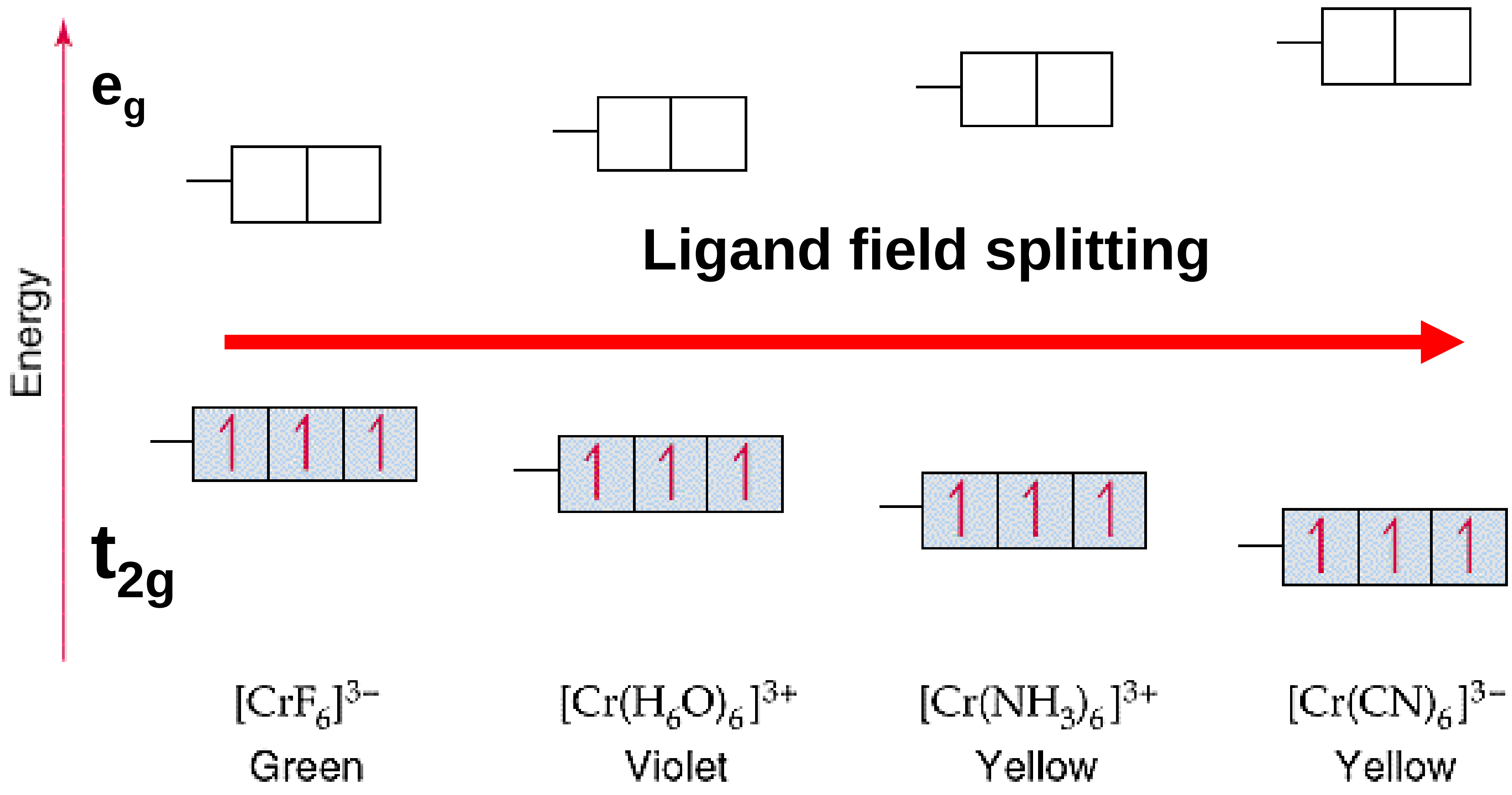
Removing ligands in z direction

18-electron Rule

Number of d-electrons of neutral metal
+ 2 e neutral ligands
+ 1 e anionic ligands Sum 18 for stabile complexes

$Cr(CO)_6$	Cr	d^6
	6 × CO	6 × 2 = 12
	Sum	18
$[Co(NH_3)_3Cl_3]$	Co	d^9
	3 × NH_3	3 × 2 = 6
	3 × Cl	3 × 1 = 3
	Sum	18

Properties of Complexes



Ligand Field Splitting Factors

Spectrochemical Series:

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, F^- < OH^- < ox, O^{2-} < H_2O < NCS^- < py, NH_3 < en < bpy, phen < NO_2^- < CH_3^-, C_6H_5^- < CN^- < CO$

Central atom:

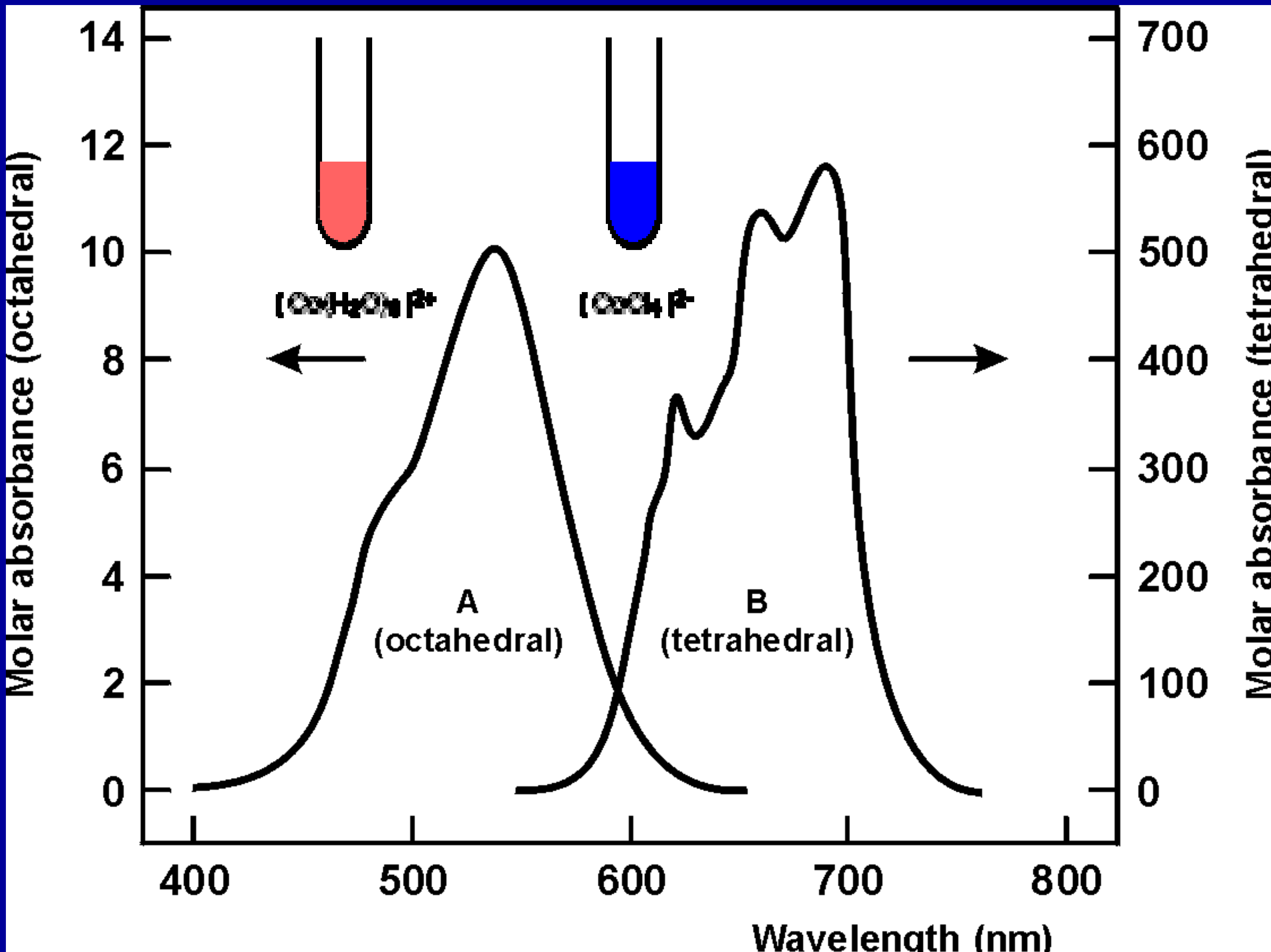
3d < 4d < 5d

2+ < 3+ < 4+

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{3+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

Type of coordination **$4/9\ \Delta_o = \Delta_t$**

Bond length and strength M-L



Molar absorbance (octahedral)
14
12
10
8
6
4
2
0
A
(octahedral)
B
(tetrahedral)
700
600
500
400
300
200
100
0
Molar absorbance (tetrahedral)
400
500
600
700
800
Wavelength (nm)

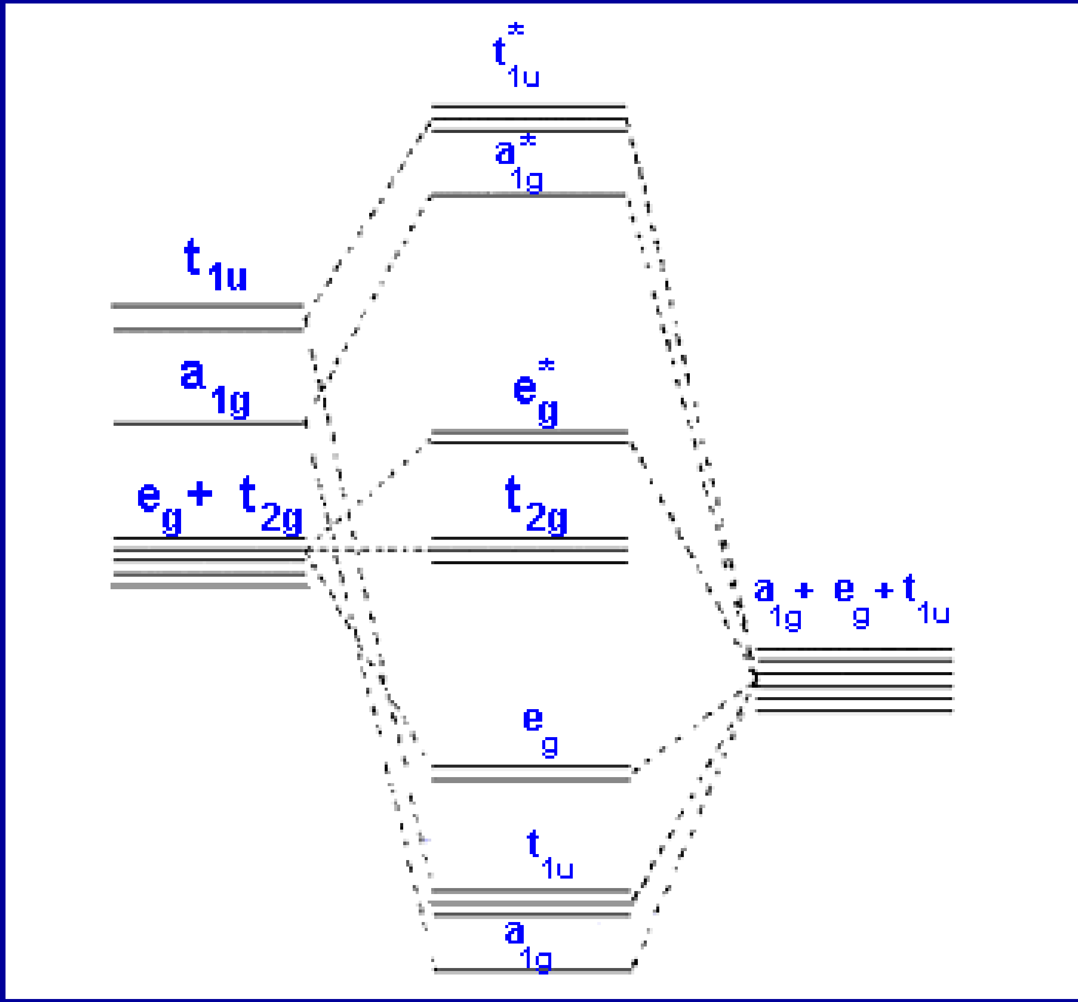
Bonding in Complexes by MO

3 x np

1x ns

5x (n–1) d

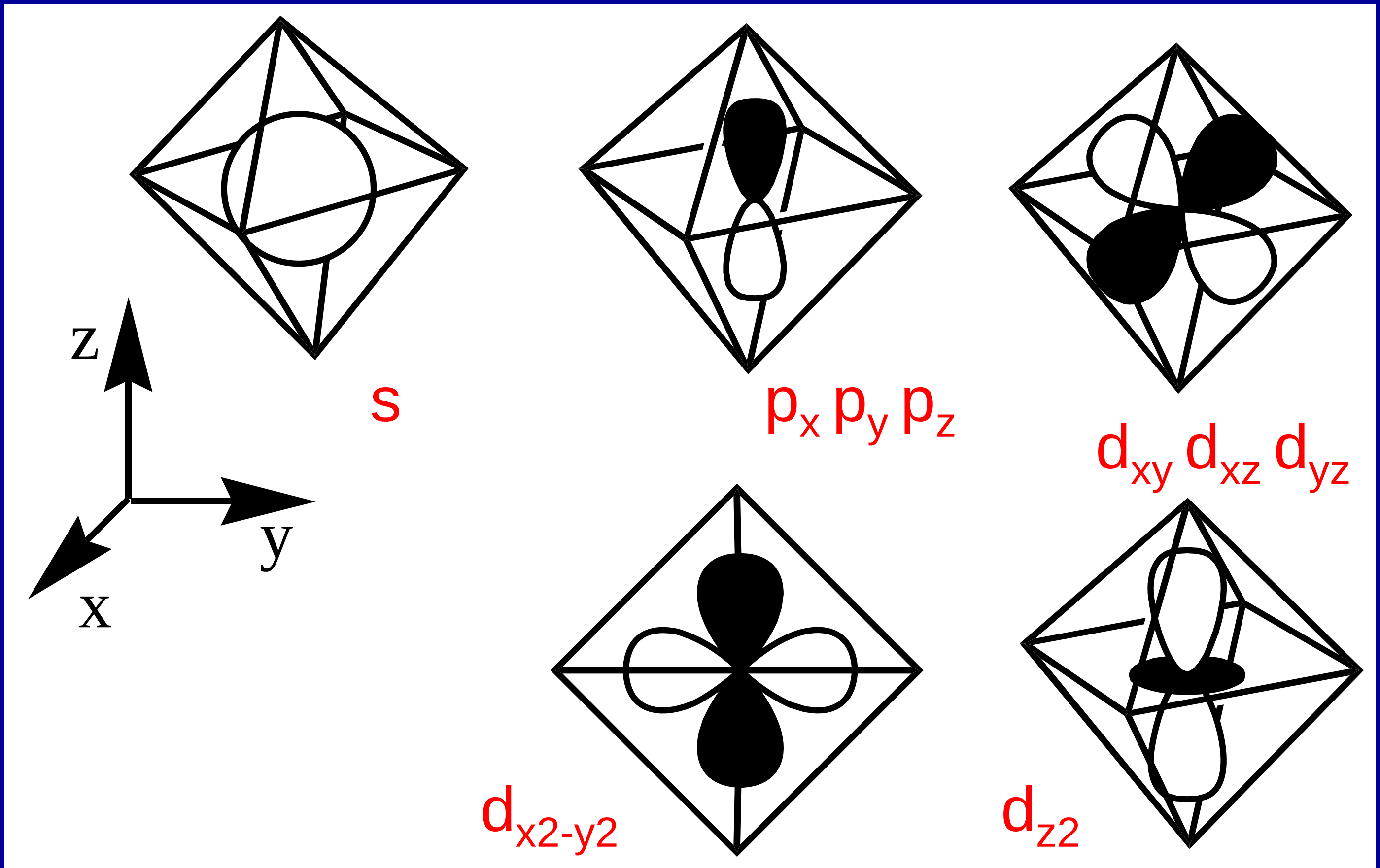
Orbitals of metal



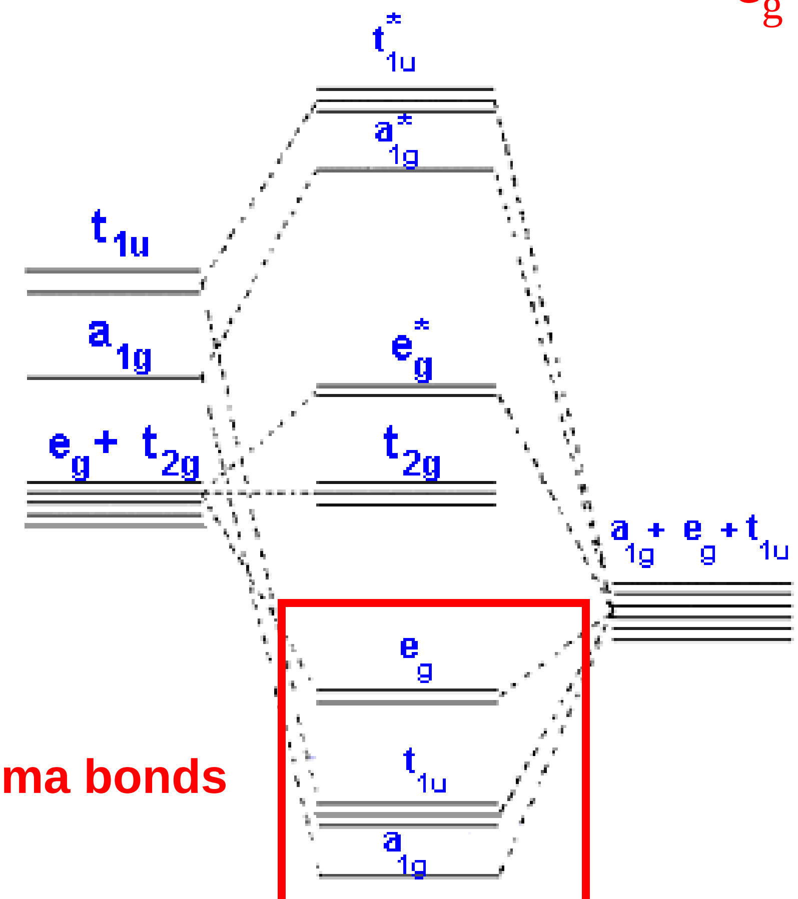
SALCAO

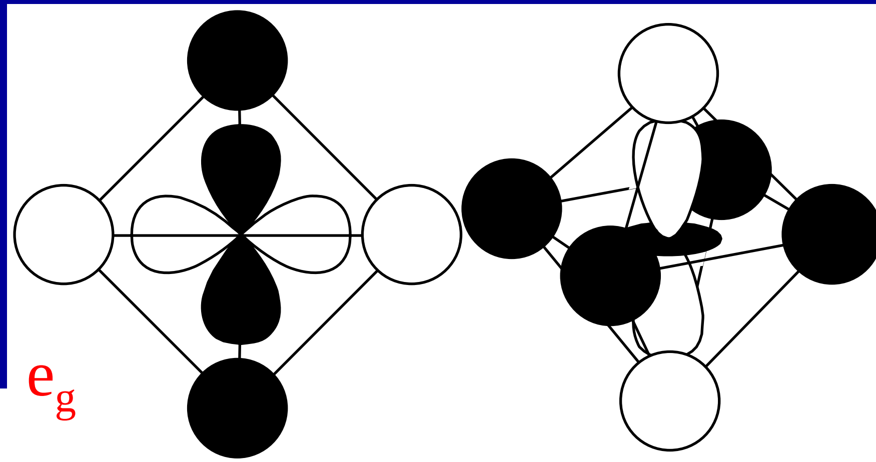
Orbitals of ligands

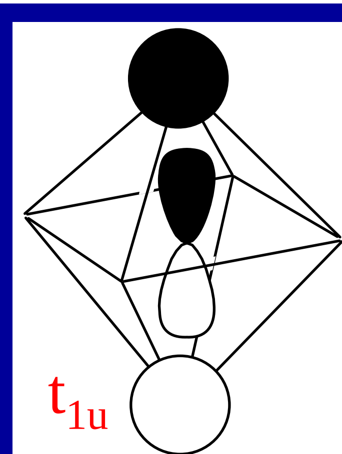
Metal Valence Orbitals



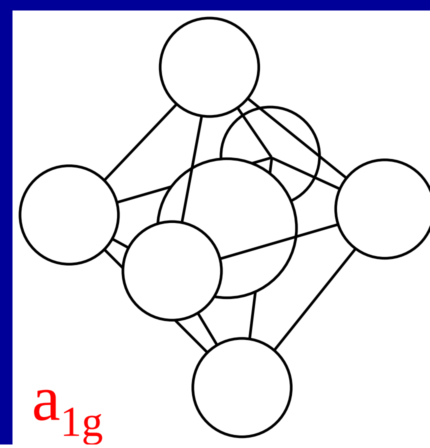
M-L Sigma bonds



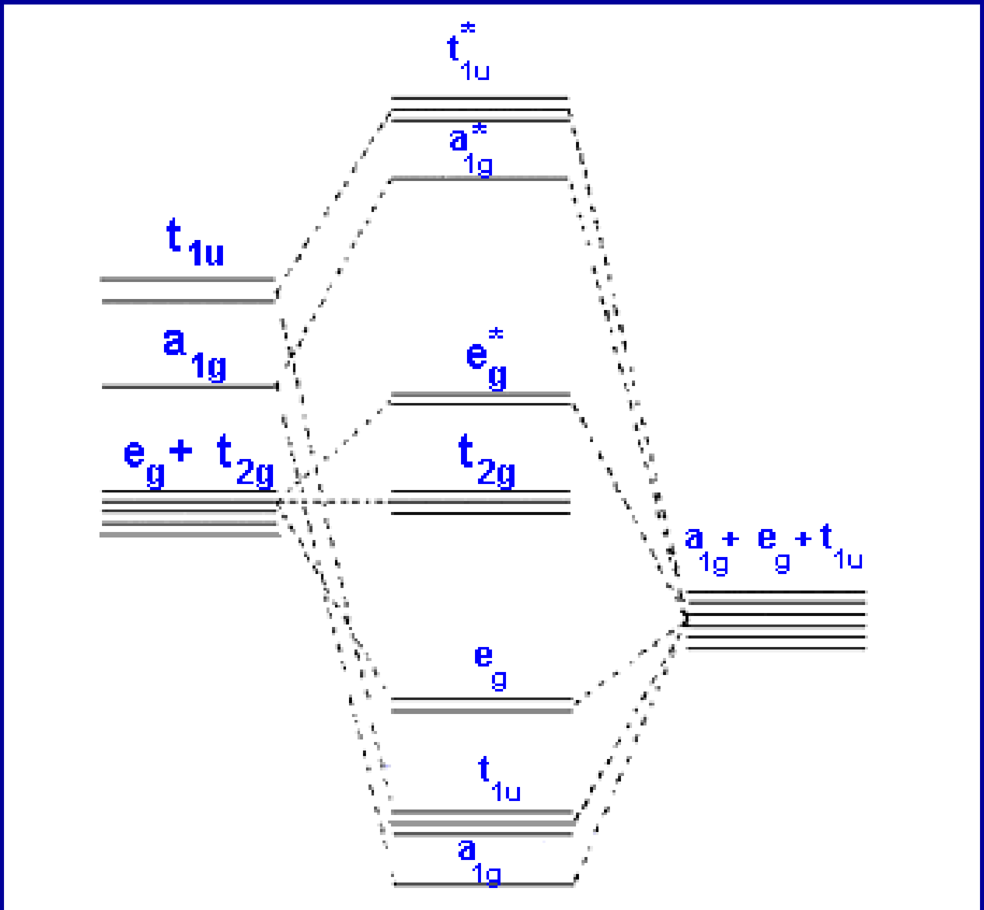


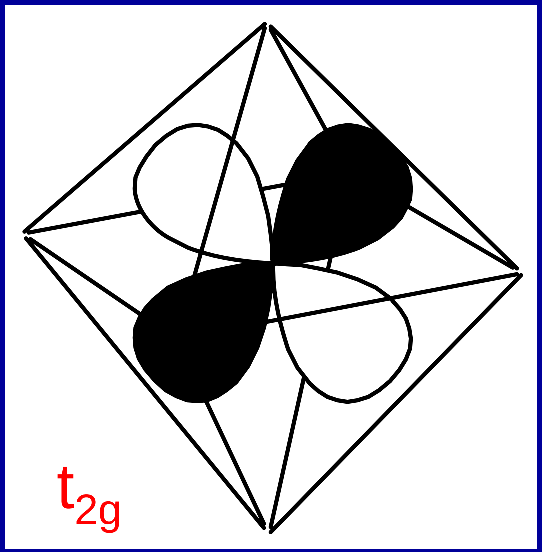


3 x np

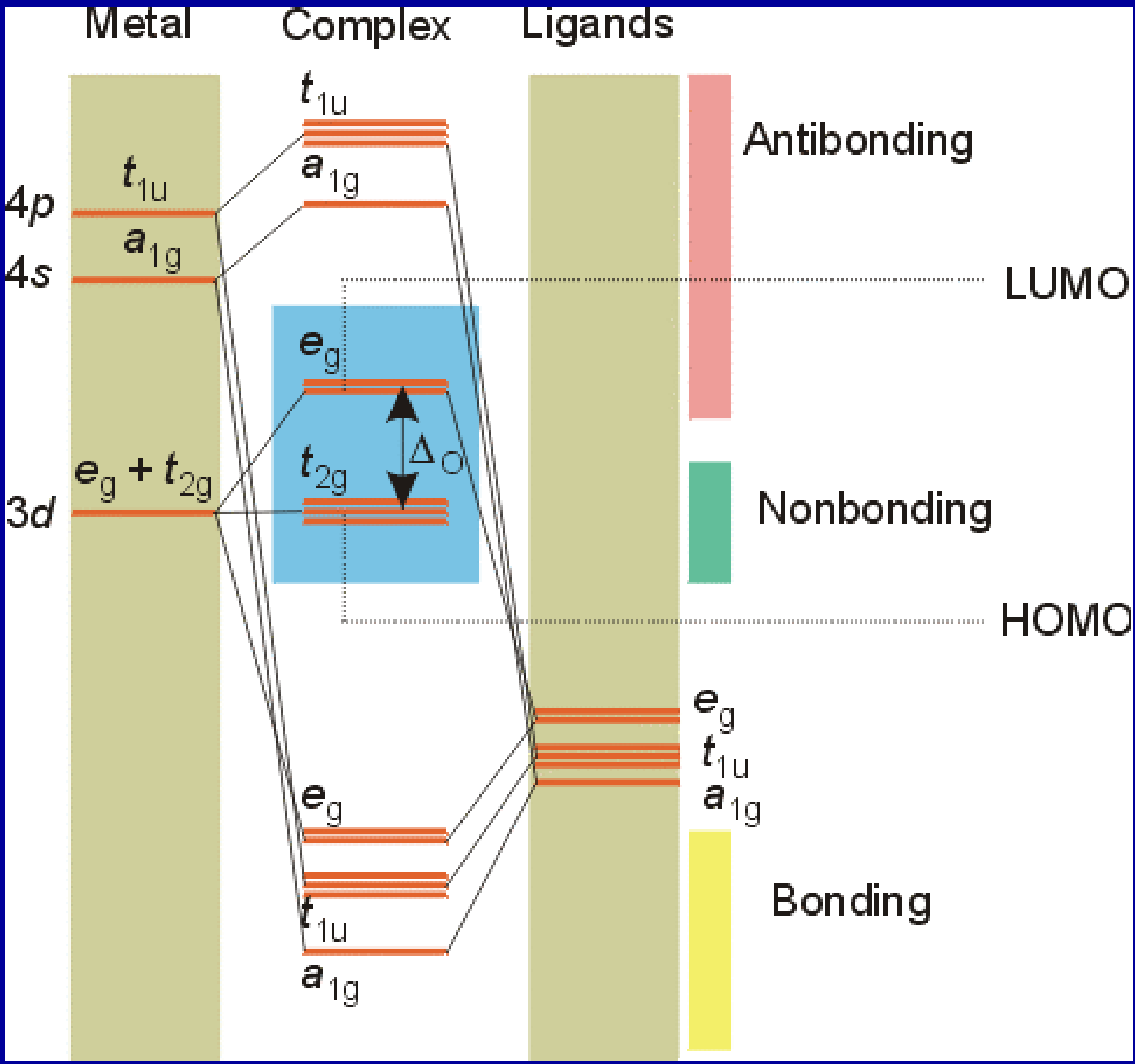


Nonbonding d-Orbitals

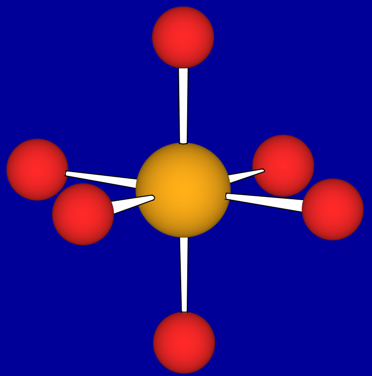


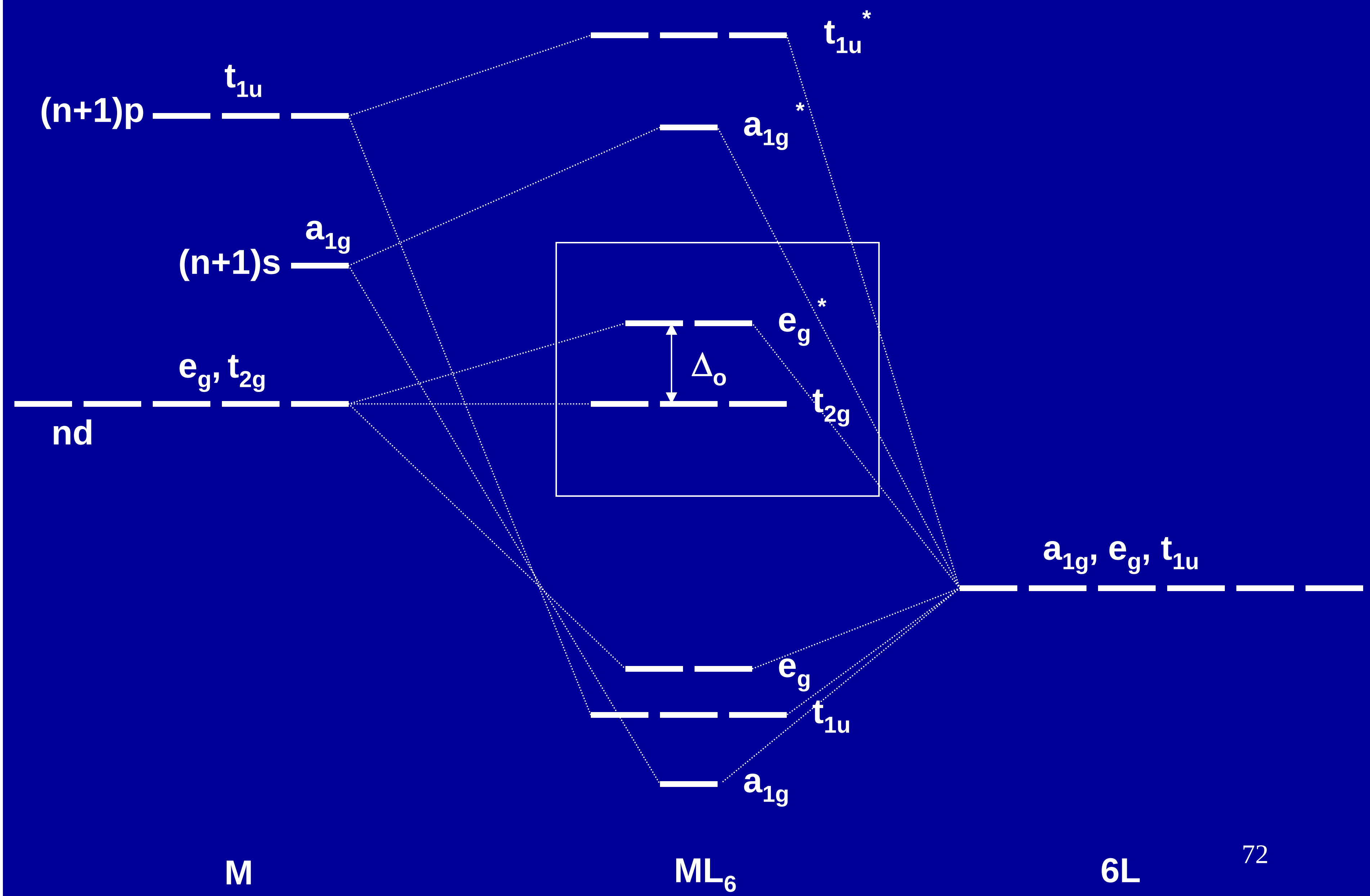


There is no suitable combination of AOs of ligands (for sigma bonding)

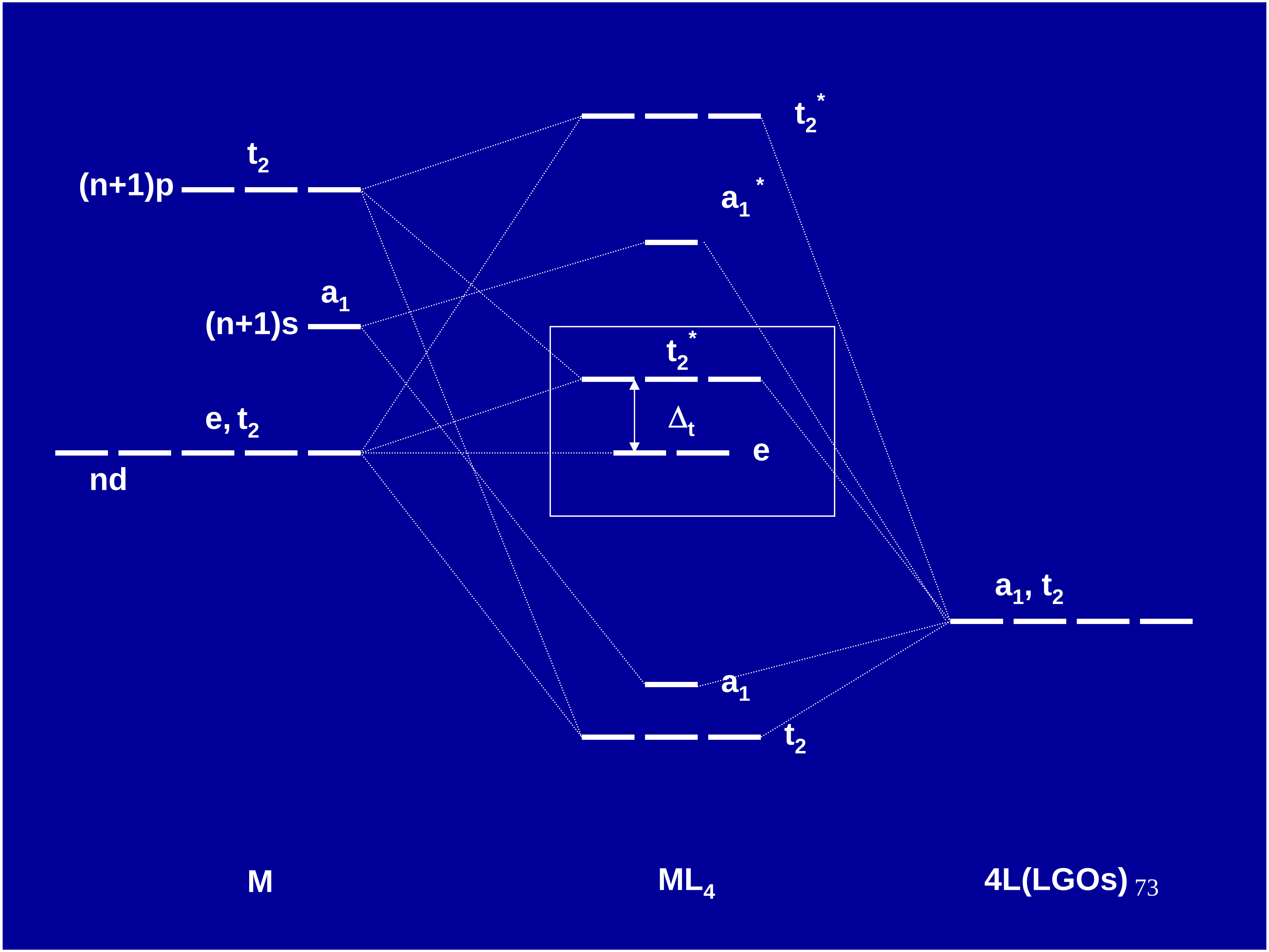


Metal
Complex
Ligands
t_{1u}
a_{1g}
4p
4s
t_{1u}
a_{1g}
Antibonding
LUMO
e_g
Δ_O
t_{2g}
$e_g + t_{2g}$
3d
Nonbonding
HOMO
e_g
t_{1u}
a_{1g}
e_g
t_{1u}
a_{1g}
Bonding

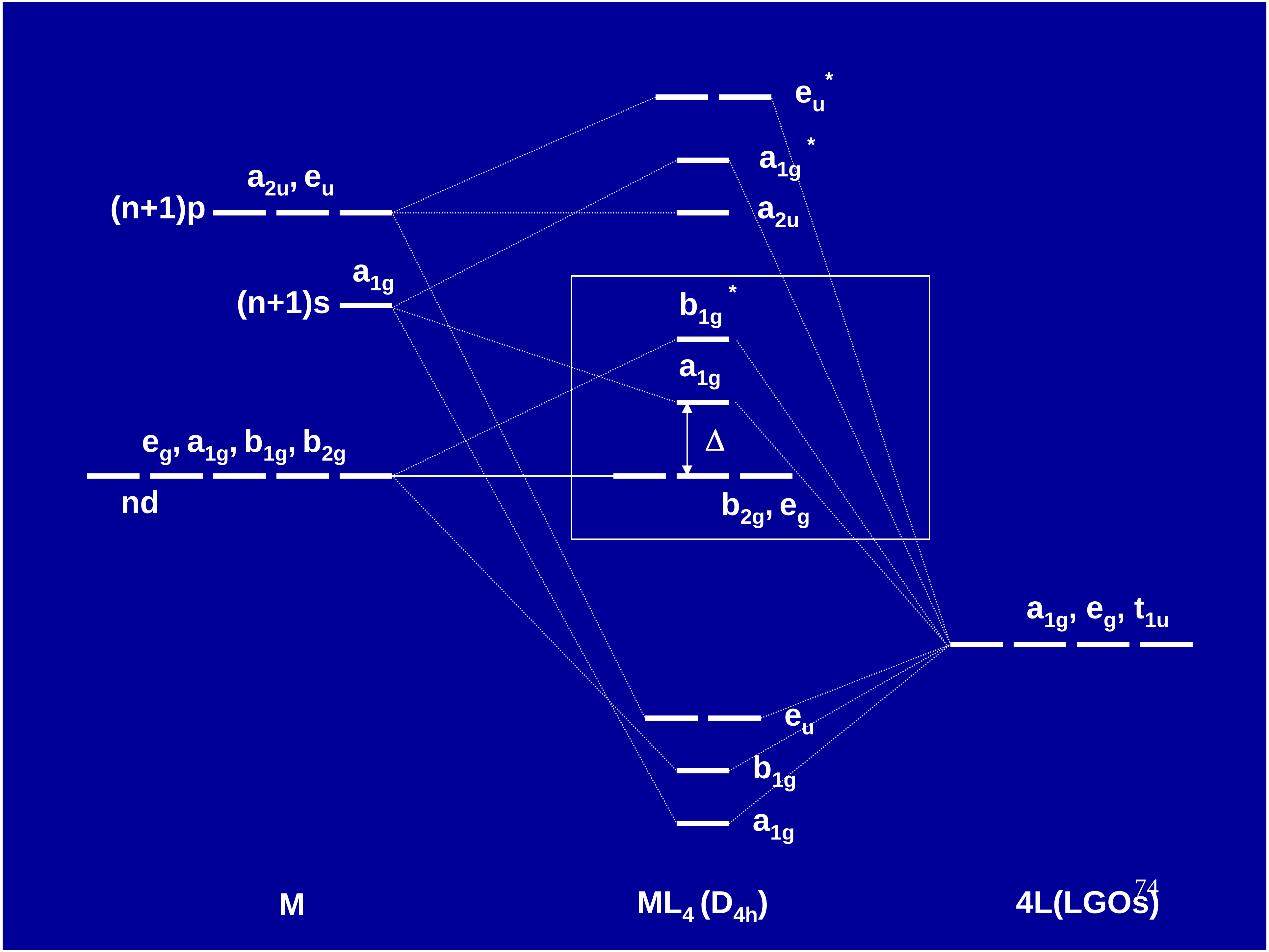




t_{1u}^*
t_{1u}
(n+1)p
a_{1g}^*
a_{1g}
(n+1)s
e_g^*
Δ_o
e_g, t_{2g}
t_{2g}
nd
a_{1g}, e_g, t_{1u}
e_g
t_{1u}
a_{1g}
M
ML_6
6L

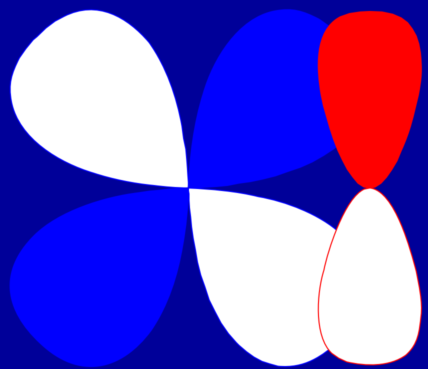


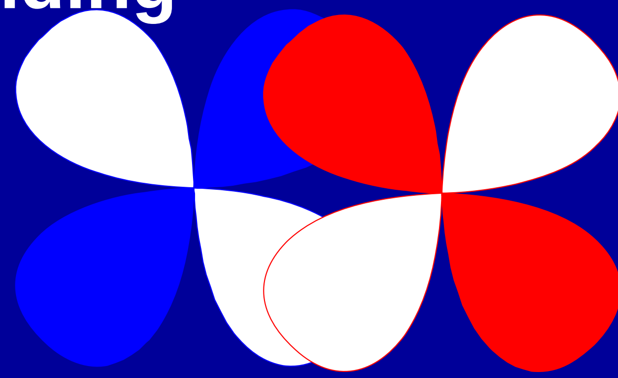
(n+1)p
t2
(n+1)s
a1
e, t2
nd
t2*
a1*
t2*
Δt
e
a1
t2
a1, t2
M
ML4
4L(LGOs)



e_u^*
a_{1g}^*
a_{2u}, e_u
(n+1)p
a_{2u}
a_{1g}
(n+1)s
b_{1g}^*
a_{1g}
Δ
$e_g, a_{1g}, b_{1g}, b_{2g}$
nd
b_{2g}, e_g
a_{1g}, e_g, t_{1u}
e_u
b_{1g}
a_{1g}
M
$ML_4 (D_{4h})$
4L(LGOs)

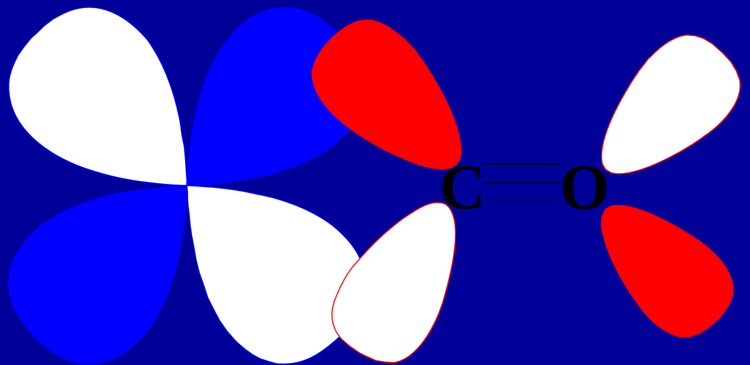
MO in π-Bonding

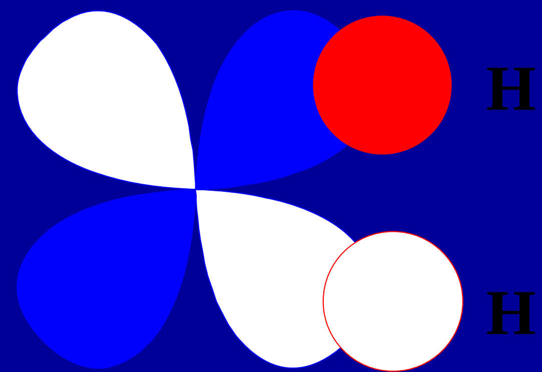




pπ-dπ RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N^-

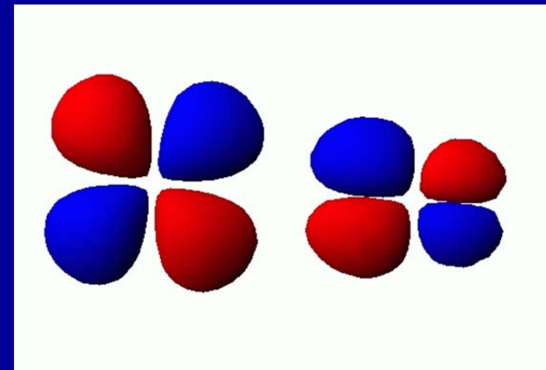
dπ-dπ R_3P, R_3As, R_3S

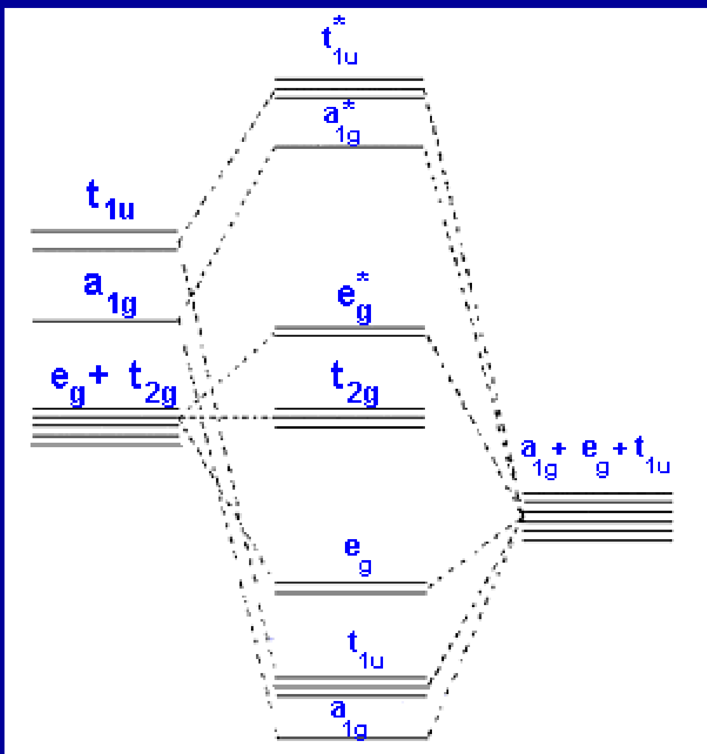




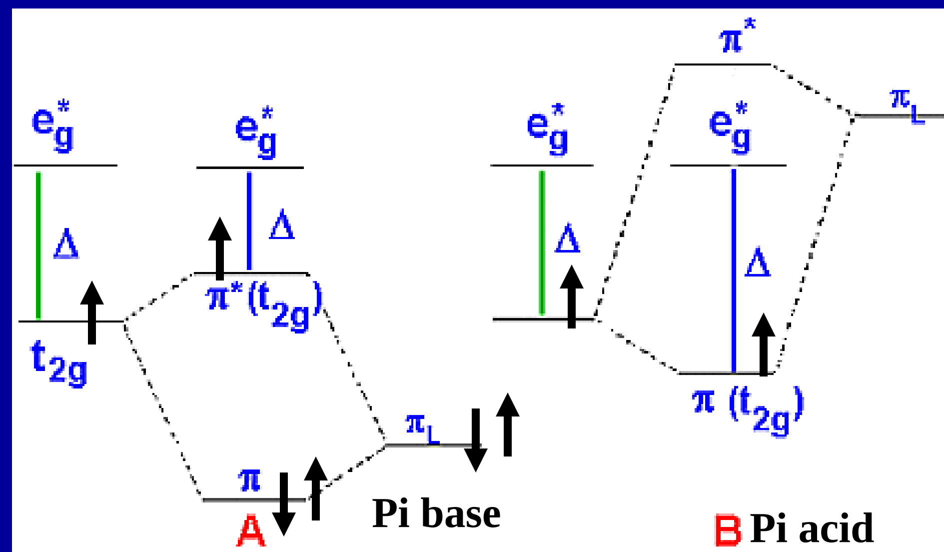
dπ-π* CO, RNC, pyridine, CN^-, N_2, NO_2^-, ethylene

dπ-σ* H_2, R_3P, alkanes

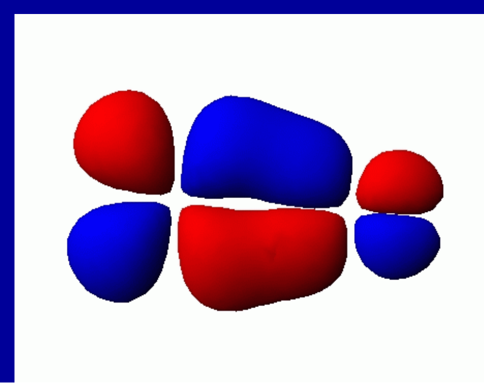




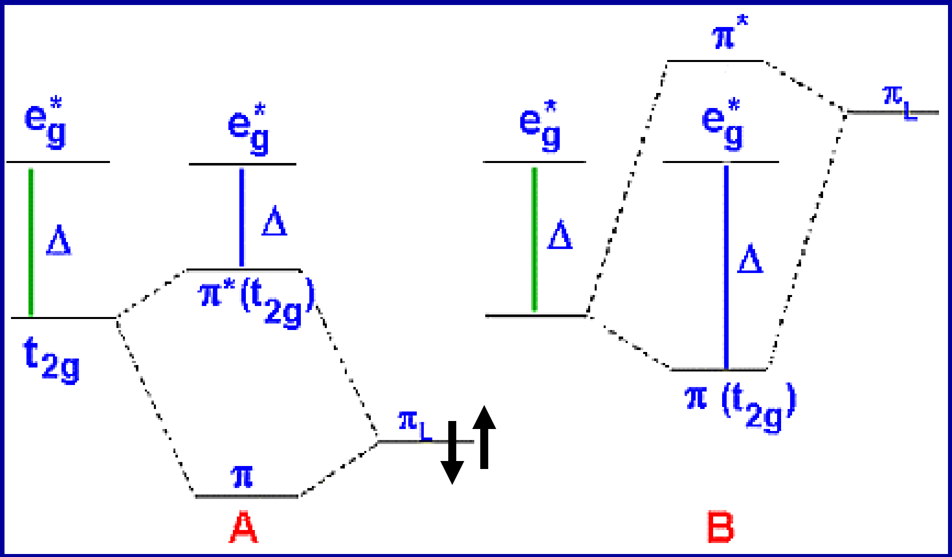
t^*_{1u}
a^*_{1g}
t_{1u}
a_{1g}
e^*_g
$e_g + t_{2g}$
t_{2g}
$a_{1g} + e_g + t_{1u}$
e_g
t_{1u}
a_{1g}



e^*_g
Δ
t_{2g}
e^*_g
Δ
$\pi^*(t_{2g})$
π
A
π_L
Pi base
π^*
e^*_g
Δ
e^*_g
Δ
π_L
$\pi\ (t_{2g})$
B Pi acid



Ligands with pi Orbitals



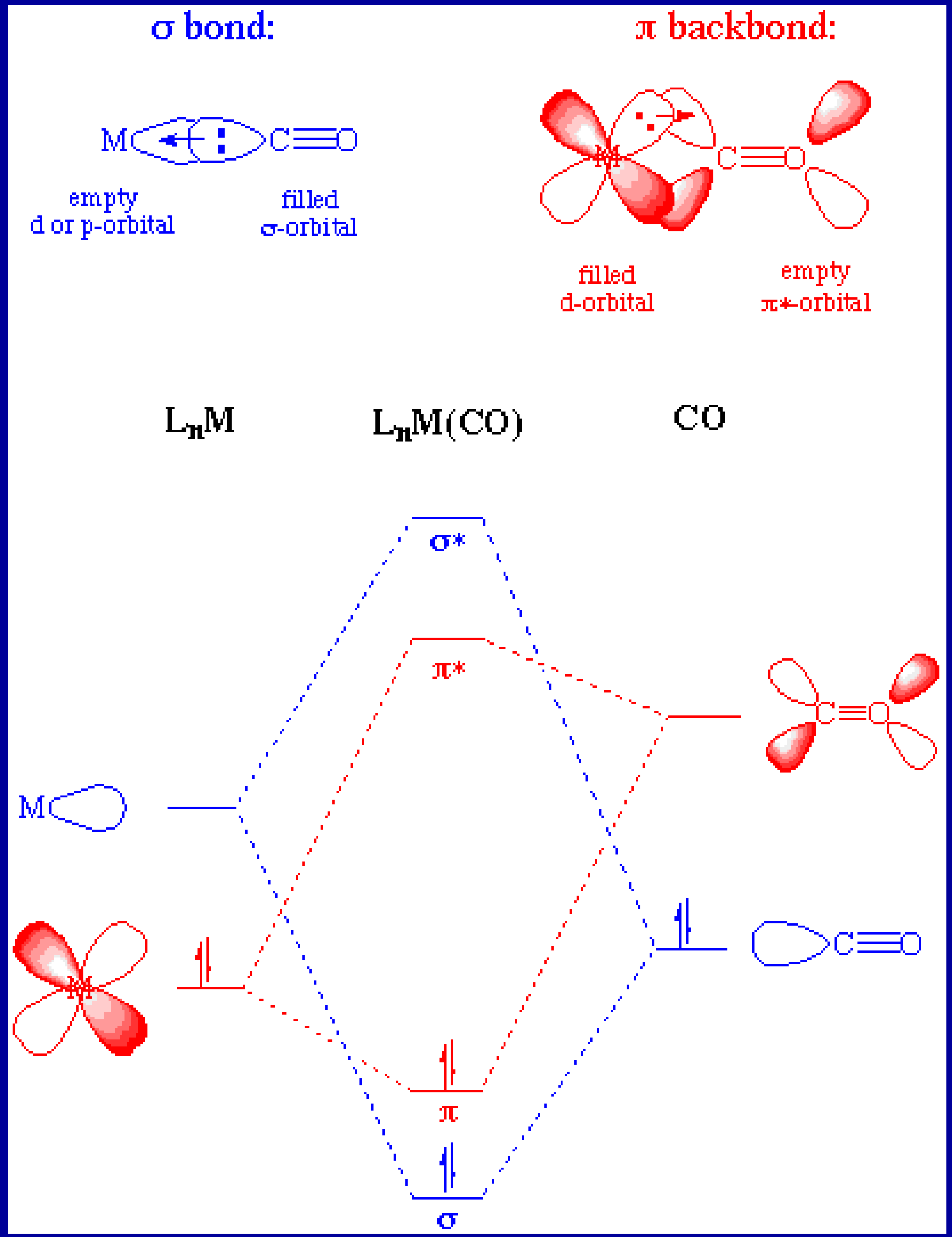
Pi base Pi acid

Back pi donation

M → CO

Sigma donation

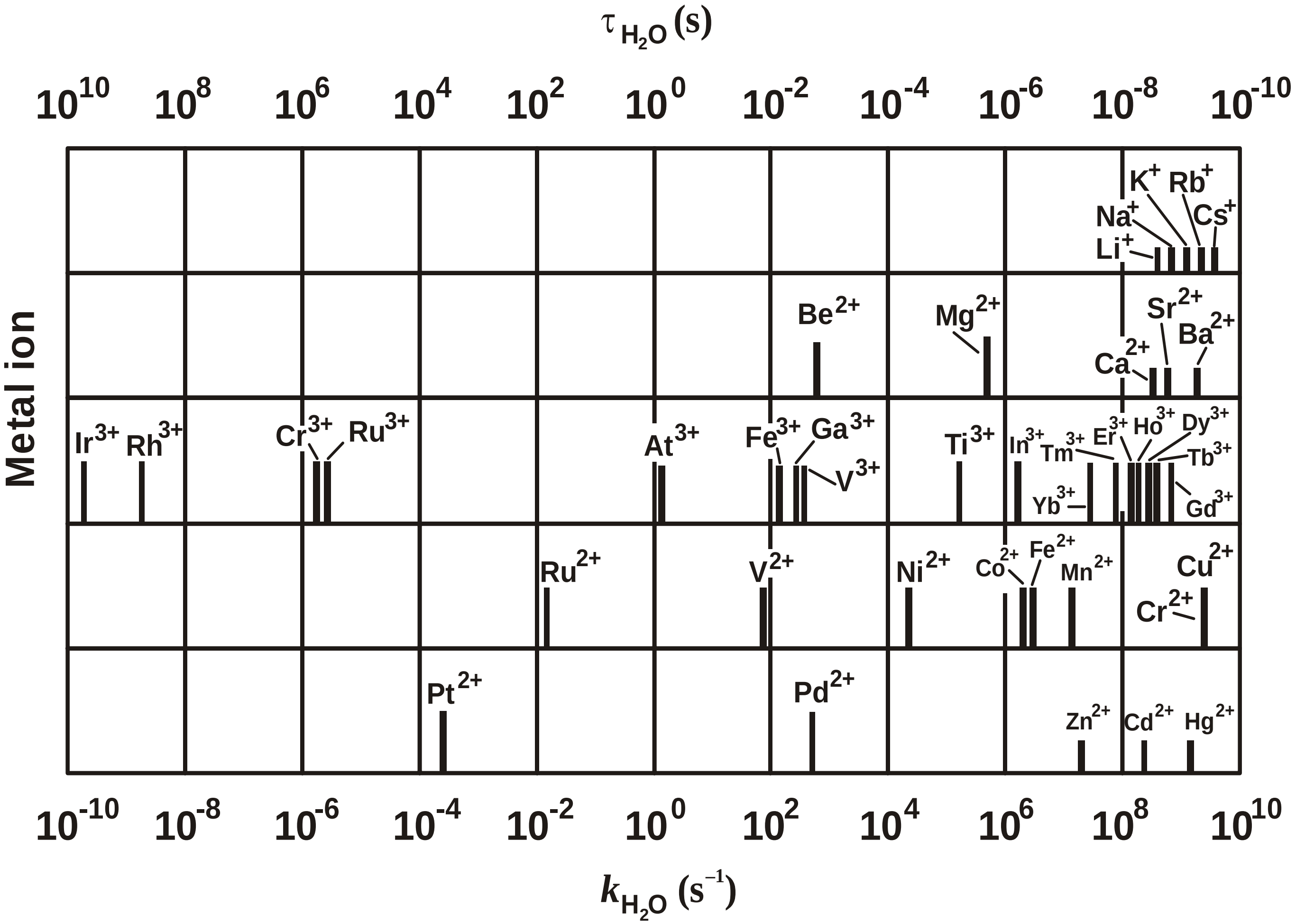
M ← CO



Kinetics

$$[M(H_2O)_n]^{x+} + H_2O^* \longrightarrow [M(H_2O^*)(H_2O)_{n-1}]^{x+} + H_2O$$

INERT



LABILE

Mechanisms of Complex Reactions

Mechanism

Dissociative (D)

$W(CO)_6 \longrightarrow W(CO)_5 + CO$

$W(CO)_5 + PPh_3 \longrightarrow W(CO)_5(PPh_3)$

Associative (A)

$[Ni(CN)_4]^{2-} + {}^{14}CN^- \longrightarrow [Ni(CN)_4({}^{14}CN)]^{3-}$

$[Ni(CN)_4({}^{14}CN)]^{3-} \longrightarrow [Ni(CN)_3({}^{14}CN)]^{2-} + CN^-$

Trans-Influence (thermodynamic effect)

extent to which a ligand weakens the metal-ligand bond of the ligand *trans* to itself

From NMR: SiR_3 > Ph > R > $P(OR)_3$ > CN > AsR_3 > NR_3 > Cl > Br > I

From X-ray: R > H > CR_2 ≈ PR_3 > AsR_3 > CO > C_2H_4 > Cl

Trans-Effect (kinetic effect)

extent to which a ligand effects the rate of exchange of the ligand *trans* to itself

Dissociative mechanism, *trans* effect series = *trans* influence series

Associative mechanism: CO, CN, C_2H_4 > PR_3 > H > Me > Ph > py > I > Br > Cl > NH_3