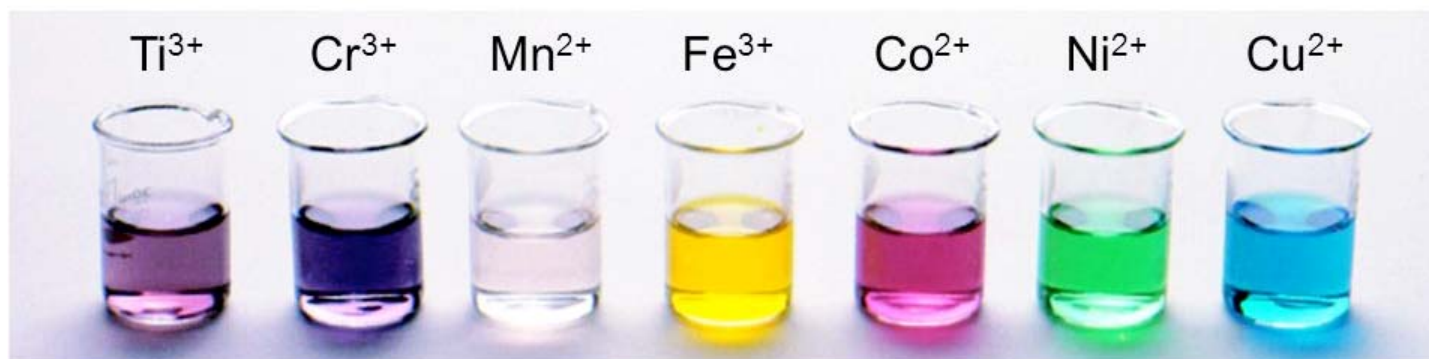


Transition Metal Coordination Chemistry

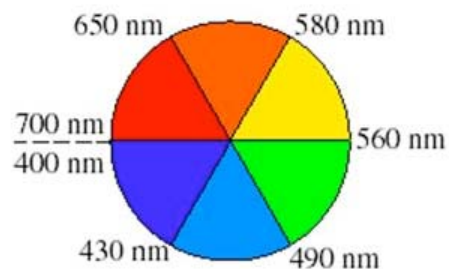
Chemistry 362 : Spring 2019



Aquo complexes of first row transition metal ions.



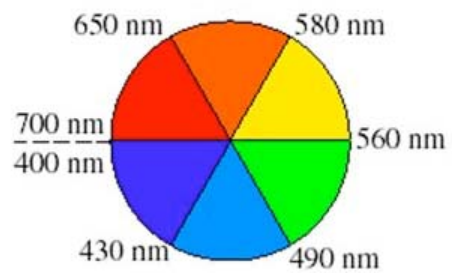
Complexes will be colorless if no light is absorbed or if the absorbed wavelength is not in the visible region.



Electronic configurations of metal ions:



Complexes will be colorless if no light is absorbed or if the absorbed wavelength is not in the visible region.



What we already know:

- The dative or coordinate covalent bond
- The valence bond approach to keeping track of electrons in Lewis acid/Lewis base adducts;
- The Hard/Soft, LA/LB, approach to binding preferences
- How to assemble molecular orbitals from linear combination of atomic orbitals
- We remember!!!.

What we want to know:

- Explanations/predictions of properties:
 - Colors/spectroscopy
 - Magnetism
 - Compositions and Structures
 - Isomers
 - Symmetry point group designations
- Dependence of the above on ligands and on Metals
- We Can Do It!!!.

Alfred Werner: Father of Coordination Chemistry.



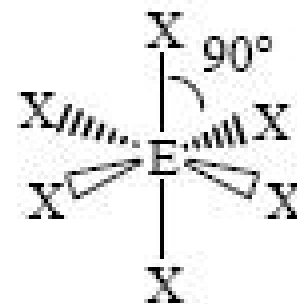
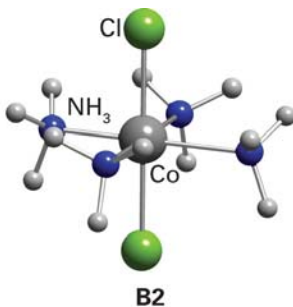
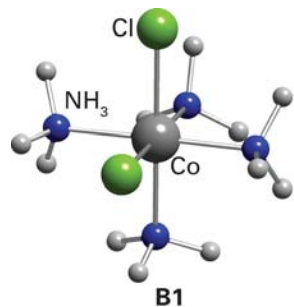
1866-1919

Nobel Prize in Chemistry, 1913

Structure of $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ is NOT $\text{Co}(\text{NH}_3\text{-NH}_3\text{-NH}_3\text{-Cl})_3$ but rather is an octahedron with 6 NH_3 directly attached to $\text{Co}(\text{III})$ and 3 Cl^- are dissociable counterions, consistent with electrical conductivity of solutions- a 1:3 electrolyte.

If this analysis is correct then the 1:1 electrolyte $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ should exist in two isomeric forms. It does; one is green and one is purple.

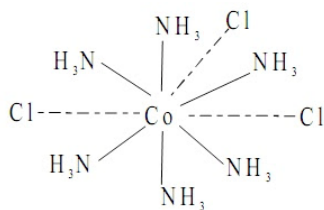
Transition metals have 2 valencies: their coordination number and their charge balance requirement. The octahedron is a common geometry in coordination chemistry.



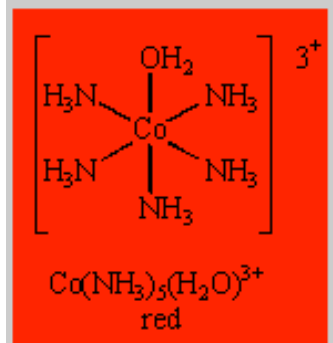
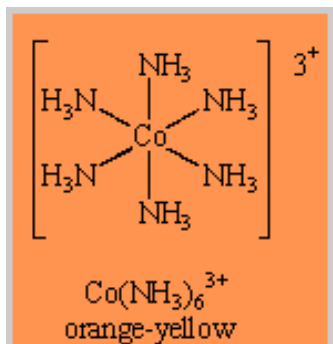
ALFRED WERNER

On the constitution and configuration of higher-order compounds

Nobel Lecture, December 11, 1913



?

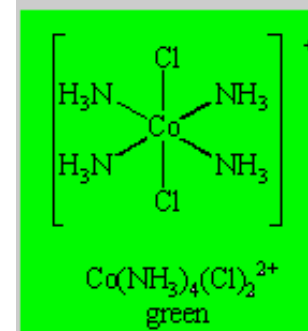
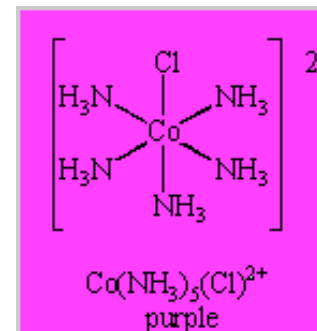


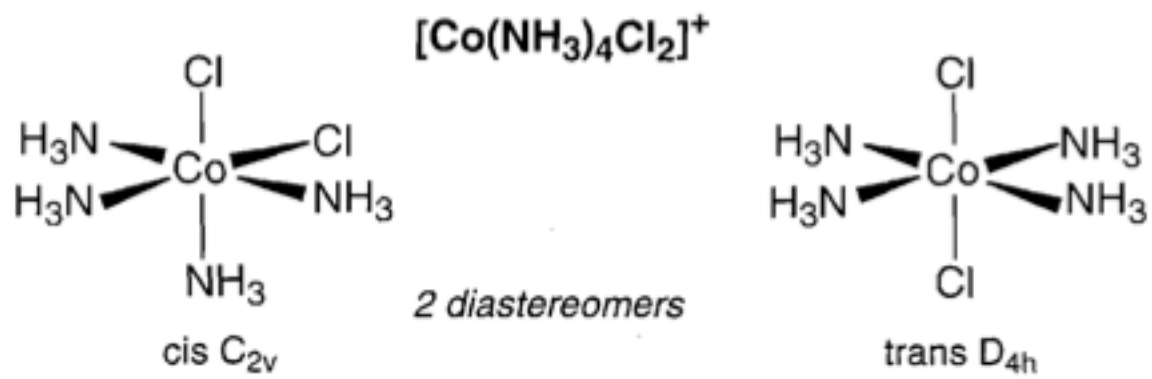
Allow me first of all to express my deeply felt gratitude to the Swedish Academy of Sciences for the distinction granted to me and for the honour of being invited to present to you an account of the progress of our knowledge concerning the structure of the molecules.

I started my scientific work by putting forward a hypothesis on the arrangement of atoms in nitrogen-containing molecules. In the years that followed, the hypothesis has borne much fruit; but I must refrain from discussing it in detail here, because the experimental confirmation of the conclusions to be drawn from it is the merit of my teacher, A. Hantzsch. In the same way I wish to make passing reference only to the ideas put forward in my treatise "Beiträge zur Theorie der Affinität und Valenz" (Contributions to the theory of affinity and valence) because the conclusions to be drawn from them are only now beginning to exert their expected influence. I shall limit myself to a discussion in detail of those of my researches which are concerned with the constitution and configuration of compounds to which little attention was given twenty years ago, by contrast with earlier times, i.e. the constitution and configuration of the so-called molecular compounds. During the great era of development of organic chemistry, during which the theory of structure was perfected, the molecular compounds had become stepchildren, and attention only continued to be given to a few of them because they were of practical interest. **This neglect can be ascribed to the fact that it was impossible to develop the constitution of these compounds on the same valence principle as the constitution of organic compounds.** It must therefore be stressed all the more that one of the most important groups of molecular compounds, i.e. metal ammonias, were carefully tended at that time in Sweden, by C. W. Blomstrand and P. T. Cleve. These two scientists had recognized the theoretical importance of these compounds whose characteristics had prompted Berzelius to number them with the "paired compounds". The former contributed to the knowledge of these compounds in the theoretical, the latter in the experimental respect.



1866-1919
Nobel Prize in
Chemistry, 1913





These are real and stable entities. They have thermodynamic stability

Table 7.4 Formation constants of Ni(II) ammines, $[\text{Ni}(\text{NH}_3)_n(\text{OH}_2)_{6-n}]^{2+}$

n	K_f	$\log K_f$	K_n/K_{n-1}	Experimental	Statistical*
1	525	2.72			
2	148	2.17	0.28		0.42
3	45.7	1.66	0.31		0.53
4	13.2	1.12	0.29		0.56
5	4.7	0.63	0.35		0.53
6	1.1	0.04	0.23		0.42

* Based on ratios of numbers of ligands available for replacement, with the reaction enthalpy assumed constant.

Gibbs Free Energy

- Two ways to calculate

$$-\Delta G_R^\circ = \Delta H_R^\circ - T \Delta S_R^\circ$$

$$-\Delta G_R^\circ = \sum n_i G_{f,i}^\circ(\text{products}) - \sum n_j G_{f,j}^\circ(\text{reactants})$$

- ΔG_R° and K_{eq} are related:

$$-\Delta G_R^\circ = -RT \ln K_{eq}$$

$$-\Delta G_R^\circ = -5.708 \log K_{eq} \text{ at } 25^\circ\text{C}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C][D]}{[A][B]}$$

ΔG° = standard free energy change

R = gas constant = $1.98 \times 10^{-3} \text{ kcal mol}^{-1} \text{ deg}^{-1}$

T = usually room temperature = 298 K

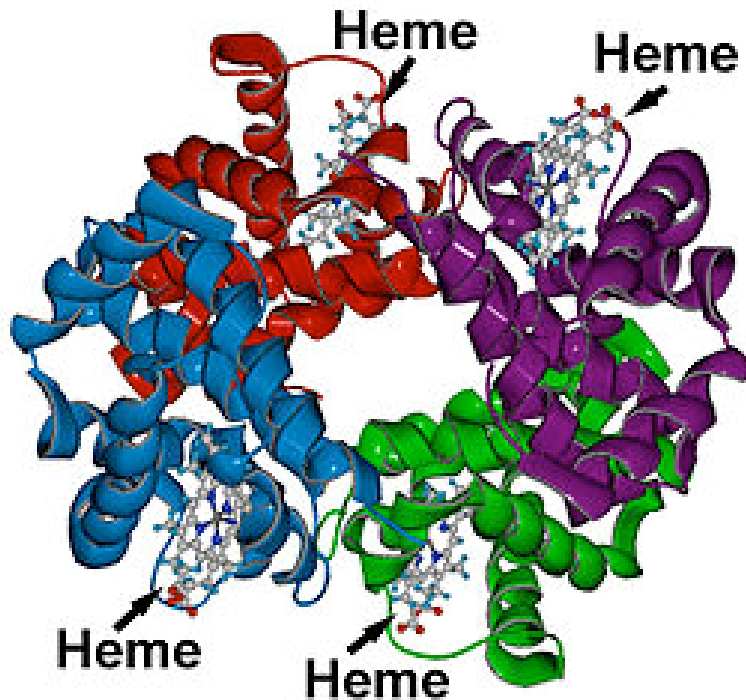
$$K = \frac{[C][D]}{[A][B]}$$

Properties of Transition Metal Complexes

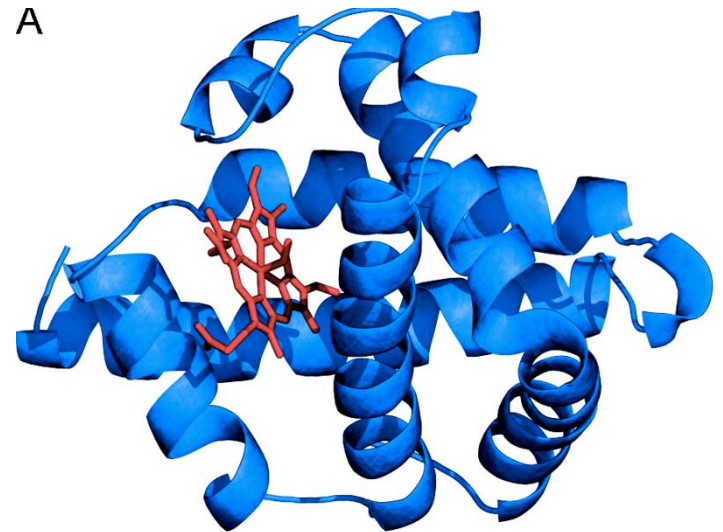
1. Highly colored (absorb light in visible, transmit light which eye detects)
2. Metals may exhibit multiple oxidation states
3. May exhibit paramagnetism that is dependent on metal oxidation state and on ligand field.
4. Reactivity includes:
 - A) Ligand exchange processes:**
 - i) Associative (S_N2 ; expanded coordination no.)
 - ii) Dissociative (S_N1 ; slow step is ligand loss)
 - B) Redox Processes**
 - i) inner sphere atom transfer;
 - ii) outer sphere electron processes)
 - iii) Oxidative Addition and Reductive Elimination

*Prime examples: The magical porphyrin ligand:
Hemoglobin, myoglobin and
Other proteins that have "Heme iron"
When oxygenated, hemoglobin is red and diamagnetic.
When deoxygenated, blue and paramagnetic!
What's going on here????*

Hemoglobin (blood)



Myoglobin (muscles)



**Discovery of the magnetic behavior of hemoglobin:
A beginning of bioinorganic chemistry**

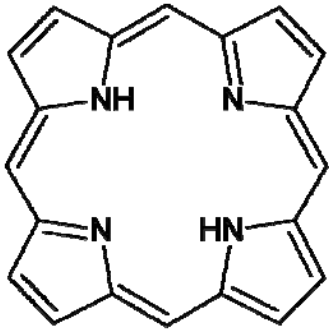
Kara L. Bren, Richard Eisenberg, and Harry B. Gray

PNAS 2015 Oct 27; 112(43): 13123–13127.

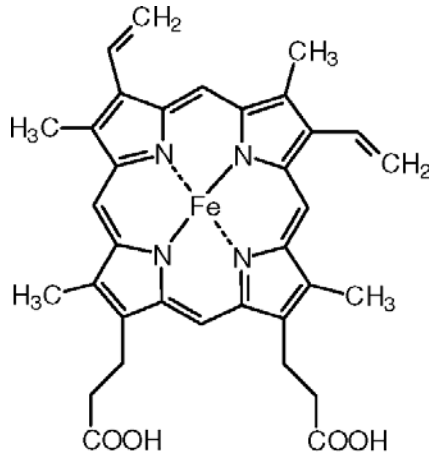
Professor Kara Bren, U. Rochester:

Chemistry Department lecture: Wednesday, April 11, 2019
Room 2104

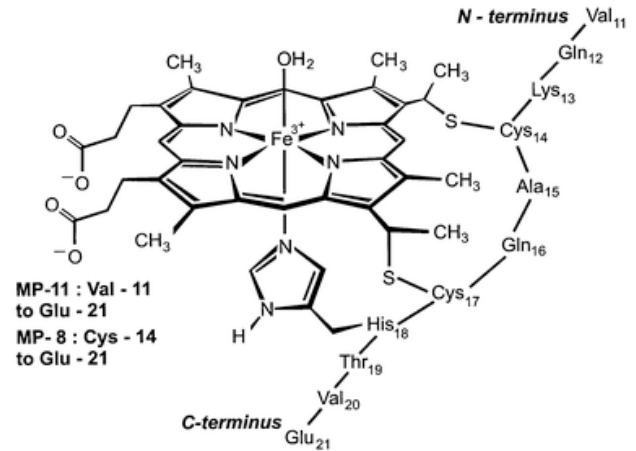
The magical porphyrin ligand



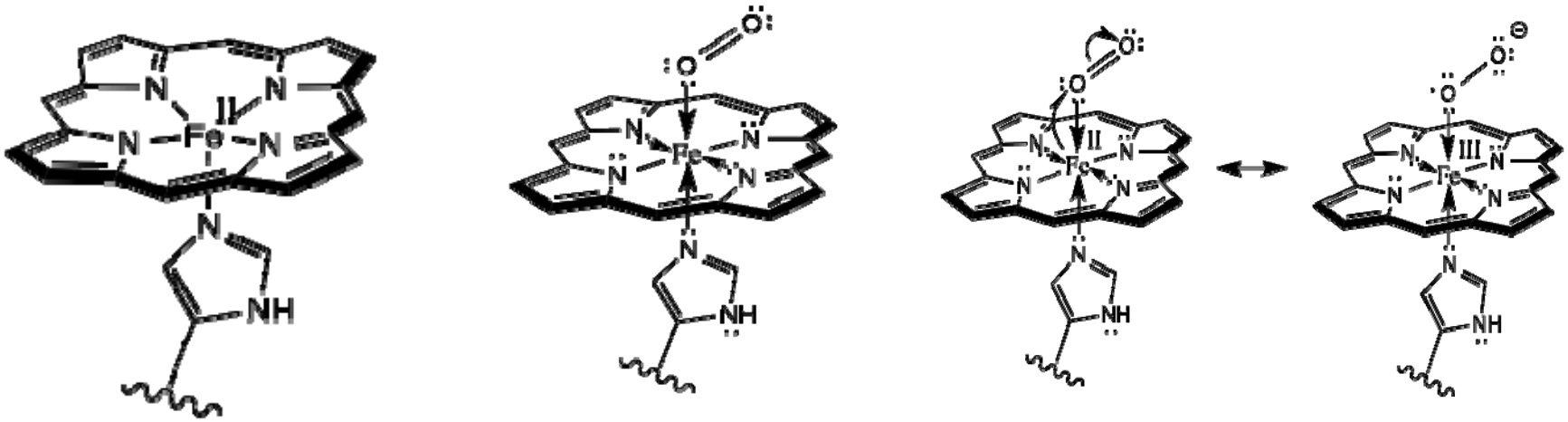
Protonated porphyrin ligand



Heme Fe^{II}



Met-hemoglobin Fe^{III}



Overview of Transition Metal Complexes

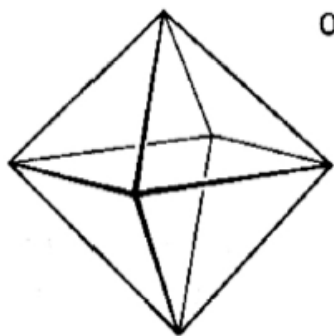


1. The coordinate covalent or dative bond applies in $L:\rightarrow M$
2. Lewis bases are called LIGANDS—all serve as σ -donors
some are π -donors as well, and some are π -acceptors
3. Specific coordination number and geometries
depend on metal and number of d-electrons
4. HSAB theory useful
 - a) Hard bases stabilize high oxidation states
 - b) Soft bases stabilize low oxidation states

A TEP (Thermal Ellipsoid Plot) of

a single molecule of tungsten hexacarbonyl, $W(CO)_6$

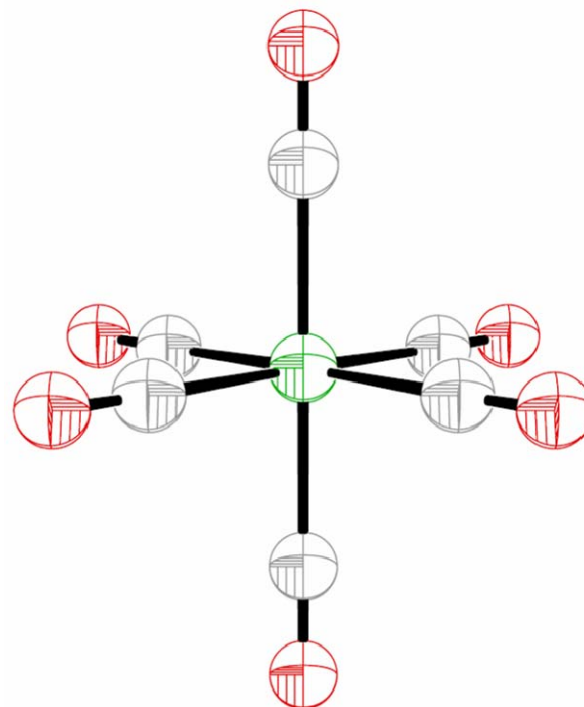
Thermal ellipsoids indicate extent of thermal motion. The tighter, rounder the atom, the better the structure. This one looks great.



Octahedron
Faces: 8 equilateral triangles
Vertices: 6
Edges: 12

An octahedron has 48 symmetry operations:
 $E, 8 C_3, 6 C_4, 6 C_2, I, 6 S_4, 8 S_6, 3 \sigma_h, 6 \sigma_d$

Low valent metal complexes
As well. But use different
Ligands.



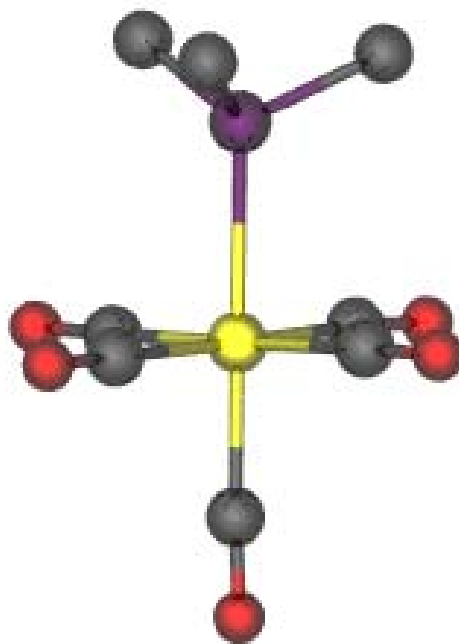
18-electron "Rule"
Achieving closed shell of
closest inert gas



Ball and Stick structure of $\text{W(CO)}_5(\text{PMe}_3)$

NOTE:

- ❖ PMe_3 is placed along the unique (z) axis
- ❖ Symmetry operations/elements are lost as compared to W(CO)_6 . What are they?



Oxidation States in 3d Transition Metals

element	ox. state range* (molecular compounds)	common (stable) ox. states**
Ti	0 → 4+	3+, 4+
V	1- → 5+	3+, 4+, 5+
Cr	2- → 6+	2+, 3+, 6+
Mn	1- → 7+	2+, 3+, 4+, 7+
Fe	2- → 6+	0, 2+, 3+
Co	1- → 3+	2+, 3+
Ni	0 → 4+	1+, 2+, 3+
Cu	1+ → 3+	1+, 2+
Zn	2+	2+

*Relative oxidation state stabilities are highly ligand-dependent; very rare oxidation states are omitted. **Most frequently encountered oxidation states in boldface.

Oxidation states and electronic configuration give a clue as to which ligands will form the more stable complexes and also to the coordination number (the number of ligands around the metal) of the metal within the complex.

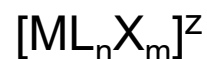
4. Electron Configurations of Atoms and Common Oxidation States of the First Transition Series

Free Atom	Oxidation States			Atom in Molecule	
Sc(4s ² 3d ¹)	- -	Sc ³⁺ (d ⁰)	- -	- -	- -
Ti(4s ² 3d ²)	- -	Ti ⁴⁺ (d ⁰)	Ti ³⁺ (d ¹)	Ti ²⁺ (d ²)	Ti ⁰ (d ⁴)
V(4s ² 3d ³)	V ⁵⁺ (d ⁰)	V ⁴⁺ (d ¹)	V ³⁺ (d ²)	V ²⁺ (d ³)	V ⁰ (d ⁵)
Cr(4s ¹ 3d ⁵)	Cr ⁶⁺ (d ⁰)	Cr ³⁺ (d ³)	Cr ²⁺ (d ⁴)	- -	Cr ⁰ (d ⁶)
Mn(4s ² 3d ⁵)	Mn ⁷⁺ (d ⁰)	Mn ³⁺ (d ⁴)	Mn ²⁺ (d ⁵)	- -	Mn ⁰ (d ⁷)
Fe(4s ² 3d ⁶)	Fe ⁴⁺ (d ⁴)	Fe ³⁺ (d ⁵)	Fe ²⁺ (d ⁶)	- -	Fe ⁰ (d ⁸)
Co(4s ² 3d ⁷)	- -	Co ³⁺ (d ⁶)	Co ²⁺ (d ⁷)	Co ¹⁺ (d ⁸)	Co ⁰ (d ⁹)
Ni(4s ² 3d ⁸)	- -	Ni ³⁺ (d ⁷)	Ni ²⁺ (d ⁸)	Ni ¹⁺ (d ⁹)	Ni ⁰ (d ¹⁰)
Cu(4s ¹ 3d ¹⁰)	- -	Cu ³⁺ (d ⁸)	Cu ²⁺ (d ⁹)	Cu ¹⁺ (d ¹⁰)	- -
Zn(4s ² 3d ¹⁰)	- -	Zn ²⁺ (d ¹⁰)	- -	- -	- -

5. Oxidation State

Here, z = charge on the complex unit.

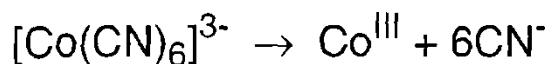
$$\text{ox. state} = z - \sum_N \text{L charge}$$



ligand removed from complex with closed shell configuration

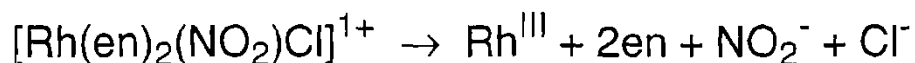
examples:

octahedral

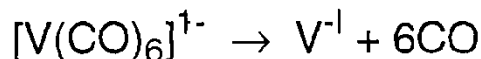
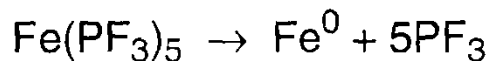


positive oxidation states usually written as Roman numerals

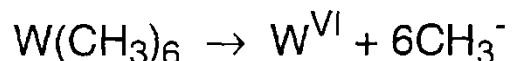
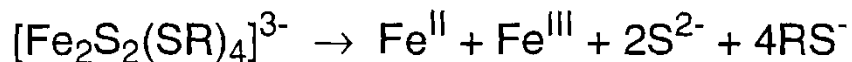
Square pyramidal



Trigonal bipyramidal



Tetrahedral



An oxidation state is a formalism which affords that d^n configuration consistent with molecular properties.

What geometries are prominent?

Octahedral

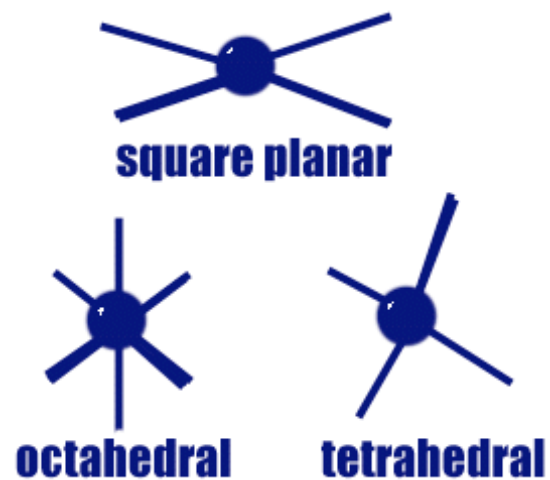
Trigonal Bipyramidal

Square planar

Tetrahedral

Trigonal planar

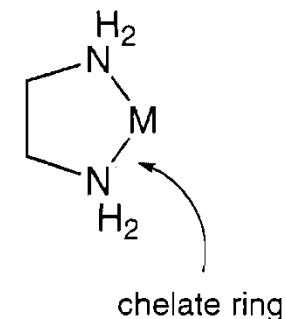
Linear



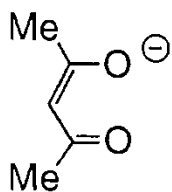
Classification of Ligands, I: type of donor orbitals involved: σ ; $\sigma + \pi$; $\sigma + \pi^*$; $\pi + \pi^*$

3. Ligands

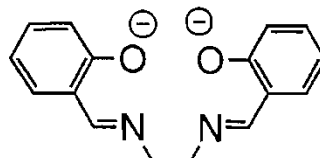
- σ : NH_3 , NR_3 , $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (en), $-\text{CH}_3$, $-\text{C}_2\text{H}_5$, ...
 σ -bonding only



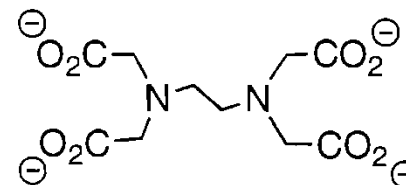
- $\sigma + \pi$ (lp): F^- , Cl^- , Br^- , I^- , NCO^- , NCS^- , N_3^- , ...
 π -donors
- OH^- , OR^- , H_2O , O^{2-}
- R_2S , R_2Se , R_2Te
- SH^- , SR^- , S^{2-} , Se^{2-} , Te^{2-}
- R_2N^- , RN^{2-} , N^{3-} , R_2P^- , RP^{2-} , P^{3-}



acac
bidentate chelate

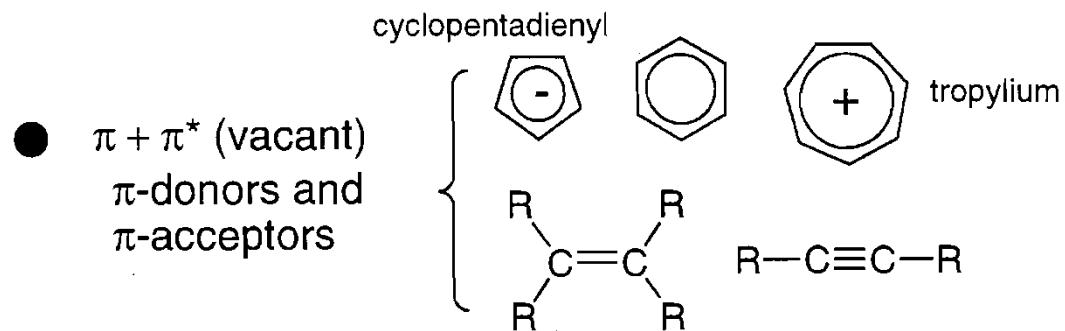
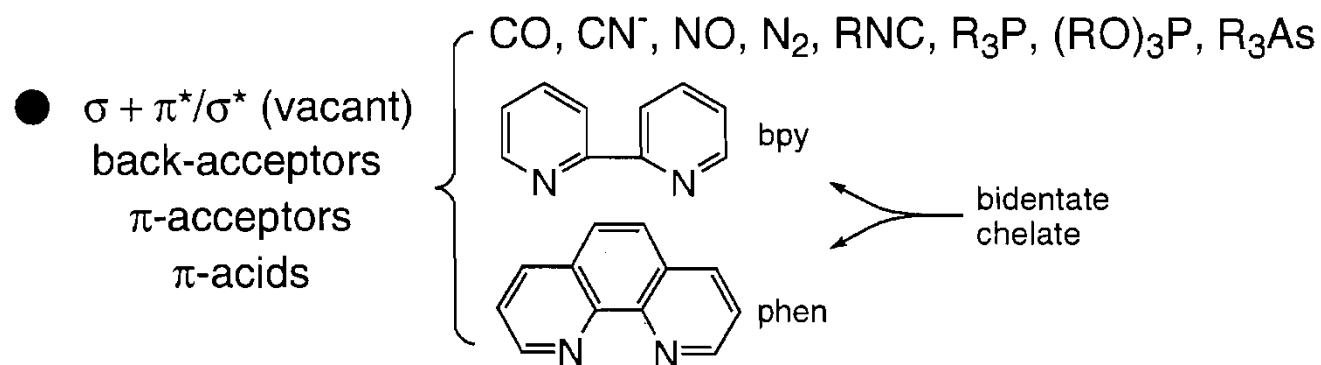


salen
tetradentate chelate



EDTA
hexadentate chelate

Ligands, Classification I, continued



These ligands form *organometallic* molecules.

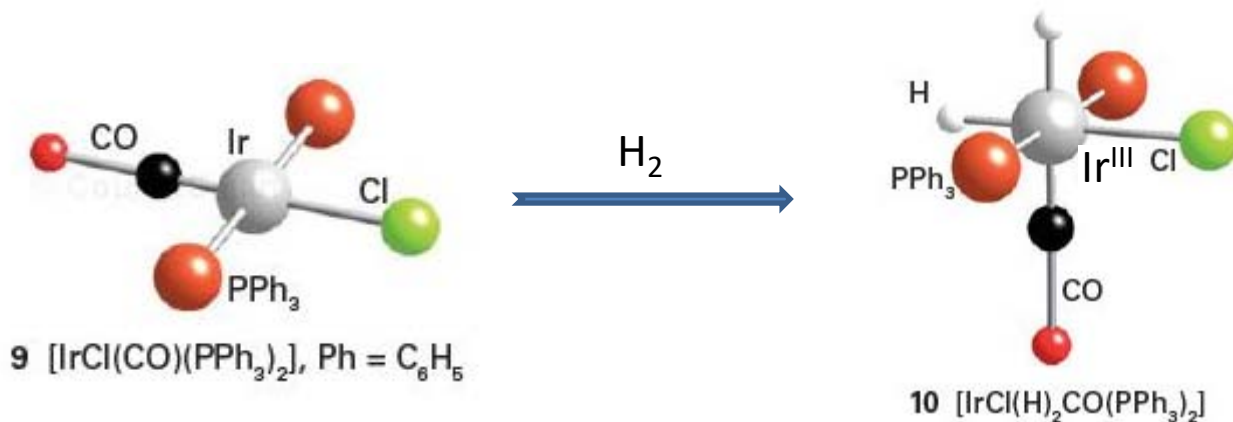
Classification of Ligands: II

The L, X, Z approach

Malcolm Green : The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

- L** ligands are derived from charge-neutral precursors: NH_3 , amines, N-heterocycles such as pyridine, PR_3 , CO, alkenes etc.
- X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. [EDTA](#)⁴⁻ is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.
- Z** ligands are RARE. They accept two electrons **from** the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

Oxidative addition of H_2 to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor, H_2 , becomes two X^- ligands once added to Ir.



An ML_3X complex

An ML_3X_3 complex

An organometallic complex: The compound must contain an M-C bond

Electron count: 16 e

18e

$\text{Ir(I) } d^8 = 8 \text{ e}$

$\text{Ir(III) } d^6 = 6 \text{ e}$

L ligands: $2 \times (2) + 2 = 6$

3 L ligands: $3 \times 2 = 6$

X- ligand: 2

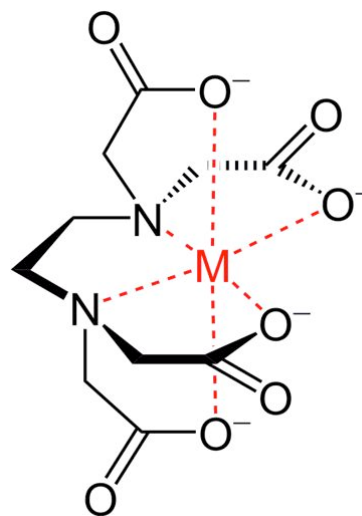
3 X⁻ ligands: $3 \times 2 = 6$

—

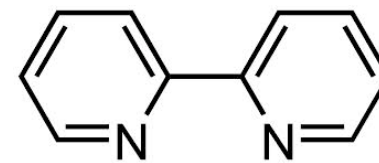
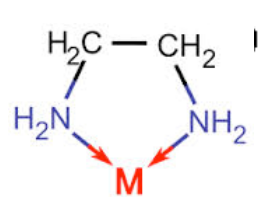
Classification of Ligands: III

A description of properties

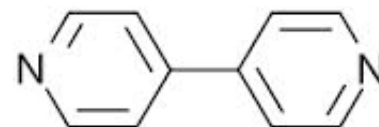
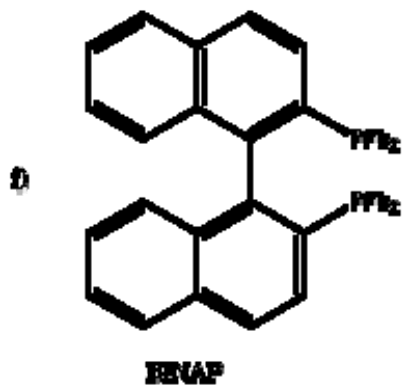
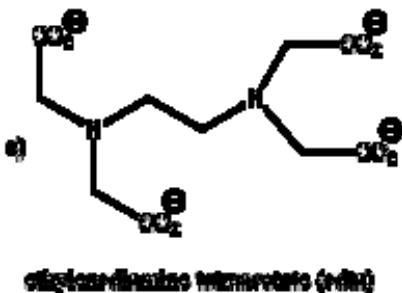
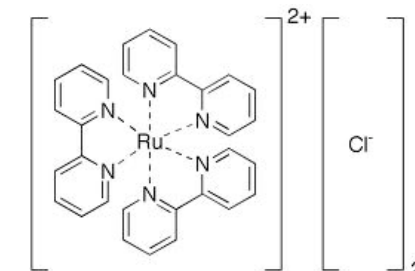
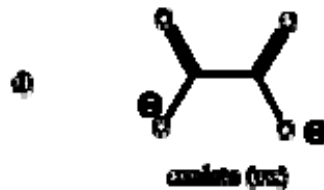
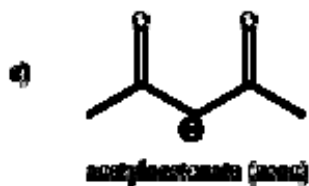
- ❑ Strong Field/Weak Field Ligands
- ❑ Chelating Ligands and Denticity
 - ❖ Polydentate: bi-, tri-, tetra, penta-
 - ❖ Hexadentate, etc.
- ❑ Bridging Ligands
 - ❖ 4-electron bridge; 3 center, 4 electrons
 - ❖ 2-electron bridge; 3-center, 2 electrons
- ❑ Ambidentate Ligands
- ❑ Bulky Ligands
- ❑ Chiral Ligands
- ❑ Hemi-labile Ligands
- ❑ Non-innocent Ligands
- ❑ Spectator Ligands



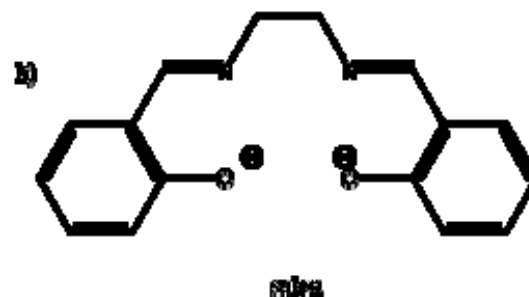
Chelating Ligands/Polydentate Ligands--examples



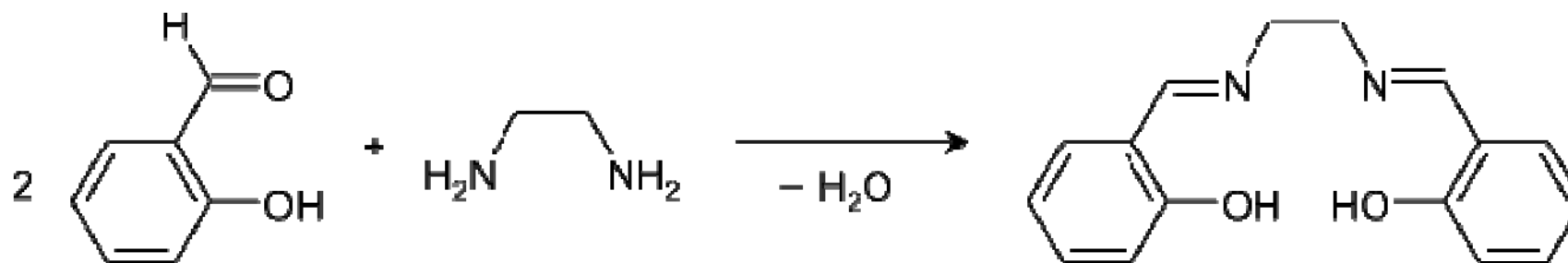
4,4'-bipyridine



4,4'-bipyridine



The Salen ligand and its preparation from salicylaldehyde and ethylene diamine:

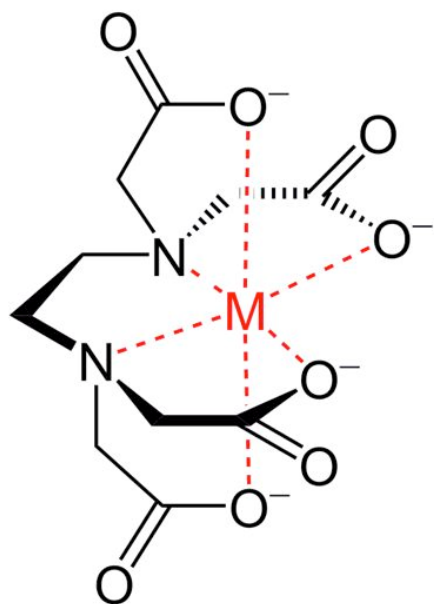
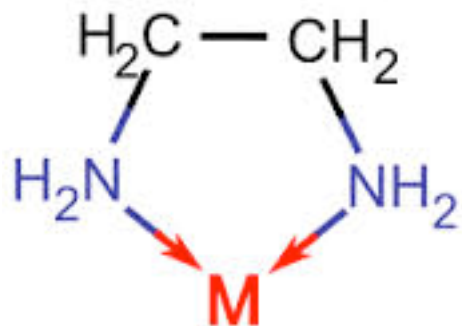
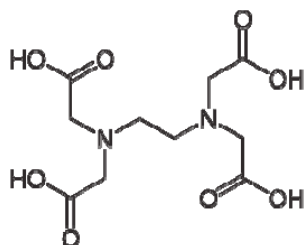


An L₂X₂ tetradentate ligand

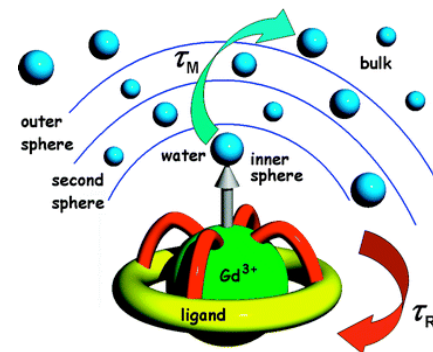
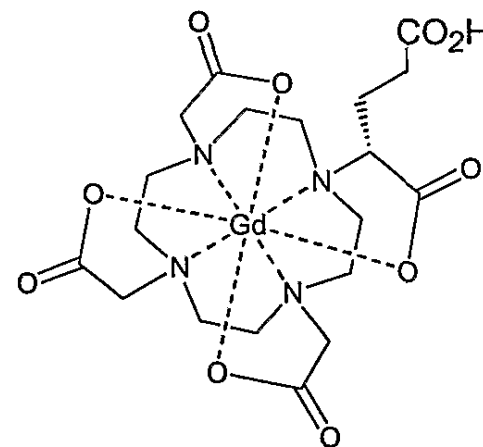


Chelating Ligands/Polydentate Ligands

Ethylenediamine: An L_2 bidentate ligand



Ethylenediaminetetraacetate:
An L_2X_4 hexadentate ligand, an exceptional chelating agent with many uses. In medicine, for lead and mercury poisoning; also for thalassaemia (iron overload).



So, how do we mix these ligands and metals with their various oxidation states to get stable molecules?

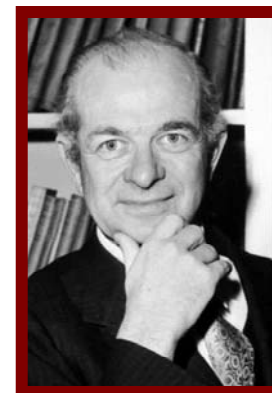
1. Hard/Soft Acid Base Approach to stability
2. Knowledge of preferred coordination numbers and geometries

- high oxidation states stabilized by anionic π -donor ligands of electronegative atoms
- low oxidation states stabilized by neutral π -acceptor ligands

examples:

	"high"	"low"
Ti	$[\text{TiF}_6]^{2-}$, TiO_2	$\text{Ti}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2$
V	$[\text{VF}_6]^{2-}$, $[\text{VOCl}_4]^{1-}$, $[\text{VO}_2\text{Cl}_2]^{1-}$	$[\text{V}(\text{CO})_6]^{0,1-}$
Cr	$[\text{CrO}_4]^{2-}$, $[\text{CrOCl}_4]^{1-}$, $[\text{CrF}_6]^{2-}$	$[\text{Cr}(\text{CNR})_6]^{1+}$, $\text{Cr}(\text{CO})_6$, $[\text{Cr}(\text{CO})_5]^{2-}$
Mn	$[\text{MnO}_4]^{1-,2-}$, $[\text{MnCl}_6]^{2-}$	$\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Mn}_2(\text{CO})_{10}$, $[\text{Mn}(\text{CO})_5]^{1-}$
Fe	$[\text{FeO}_4]^{2-}$, $[\text{FeCl}_4]^{1-}$	$\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{PF}_3)_5$, $[\text{Fe}(\text{CO})_4]^{2-}$
Co	$[\text{CoF}_6]^{3-}$, $[\text{Cr}(\text{en})_3]^{3+}$	$[\text{Co}(\text{CO})_4]^{1-}$, $\text{Co}(\text{CO})_3\text{NO}$, $\text{Co}_2(\text{CO})_8$, $\text{Co}(\text{PR}_3)_3\text{Br}$
Ni	$[\text{NiF}_6]^{2-}$, $[\text{Ni}(\text{diars})_2\text{Cl}_2]^{1+}$	$\text{Ni}(\text{CO})_4$, $\text{Ni}(\text{PF}_3)_4$, $\text{Ni}(\text{PR}_3)_3\text{Br}$, $[\text{Ni}_2(\text{CN})_6]^{4-}$
Cu	$[\text{CuF}_6]^{3-}$	$[\text{Cu}(\text{CN})_2]^{1-}$, $[\text{CuCl}_2]^{1-}$

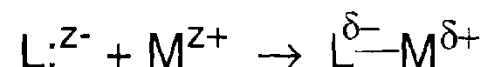
At parity of ligand and coordination number, higher oxidation states become increasingly stable down a vertical group.



Linus Pauling

6. Electroneutrality Principle:

In any molecule, bonding electrons are distributed in such a way that individual atoms are as close to electroneutrality as possible.



Metal-ligand bond formation tends to reduce +ve charge on M (and -ve charge on L^{Z-}), with the result that the *actual* charge on M is much below that corresponding to its oxidation state. The oxidation state conveys the d^n configuration of the coordinated metal.

Naming Coordination Complexes

Table 3.1 Anions and their names when acting as ligands

Free anion	Coordinated anion
Amide (NH_2^-)	amido (or azanido)
Azide (N_3^-)	nitrido (azido will also be met)
Bromide (Br^-)	bromo
Carbonate (CO_3^{2-})	carbonato
Cyanate (CNO^-)	cyanato
Fluoride (F^-)	fluoro (<i>not</i> fluo)
Hydroxide (OH^-)	hydroxo (or hydroxido or hydroxy)
Nitrite (NO_2^-)	nitro or nitrito-N (see text)
Oxide (O^{2-})	oxo (or oxido)
Thiocyanate (SCN^-)	thiocyanato-N (N-bonded), thiocyanato-S (S-bonded)

Table 7.1 Typical ligands and their names

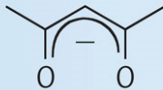
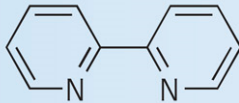
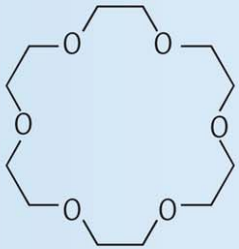
Name	Formula	Abbreviation	Donor atoms	Number of donors
Acetylacetonato		acac ⁻	O	2
Ammine	NH ₃		N	1
Aqua	H ₂ O		O	1
2,2-Bipyridine		bpy	N	2
Bromido	Br ⁻		Br	1
Carbanato	CO ₃ ²⁻		O	1 or 2
Carbonyl	CO		C	1
Chlorido	Cl ⁻		Cl	1
1,4,7,10,13,16-Hexaoxa-cyclooctadecane		18-crown-6	O	6

Table 7.1 (Continued)

Name	Formula	Abbreviation	Donor atoms	Number of donors
4,7,13,16,21-Pentaoxa-1,10-diaza-bicyclo[8.8.5]tricosane		2.2.1 crypt	N, O	2N, 5O
Cyanido	CN ⁻		C	1
Diethylenetriamine	NH(CH ₂ CH ₂ NH ₂) ₂	dien	N	3
Bis(diphenylphosphino)ethane	Ph ₂ P—CH ₂ —CH ₂ —PPh ₂	dppe	P	2
Bis(diphenylphosphino)methane	Ph ₂ P—C—PPh ₂	dppm	P	2
Cyclopentadienyl	C ₅ H ₅ ⁻	Cp ⁻	C	5
Ethylenediamine (1,2-diaminoethane)	NH ₂ CH ₂ CH ₂ NH ₂	en	N	2
Ethylenediaminetetraacetato		edta ⁴⁻	N, O	2N, 4O
Fluorido	F ⁻		F	1
Glycinato	NH ₂ CH ₂ CO ₂ ⁻	gly	N, O	1N, 1O
Hydrido	H ⁻		H	1
Hydroxido	OH ⁻		O	1
Iodido	I ⁻		I	1
Nitrato	NO ₃ ⁻		O	1 or 2
Nitrito—κO	NO ₂ ⁻		O	1
Nitrito—κN	NO ₂ ⁻		N	1
Oxido	O ²⁻		O	1
Oxalato		ox	O	2
Pyridine		py	N	1
Sulfido	S ²⁻		S	1
Tetraazacyclotetradecane		cyclam	N	4
Thiocyanato—κN	NCS ⁻		N	1
Thiocyanato—κS	SCN ⁻		S	1
Thiolato	RS ⁻		S	1
Triaminotriethylamine	N(CH ₂ CH ₂ NH ₂) ₃	tren	N	4
Tricyclohexylphosphine	P(C ₆ H ₁₁) ₃	PCy ₃	P	1
Trimethylphosphine	P(CH ₃) ₃	PMe ₃	P	1
Triphenylphosphine	P(C ₆ H ₅) ₃	PPh ₃	P	1

Table 7.2 Prefixes used for naming complexes

Prefix	Meaning
mono-	1
di-, bis-	2
tri-, tris-	3
tetra-, tetrakis-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

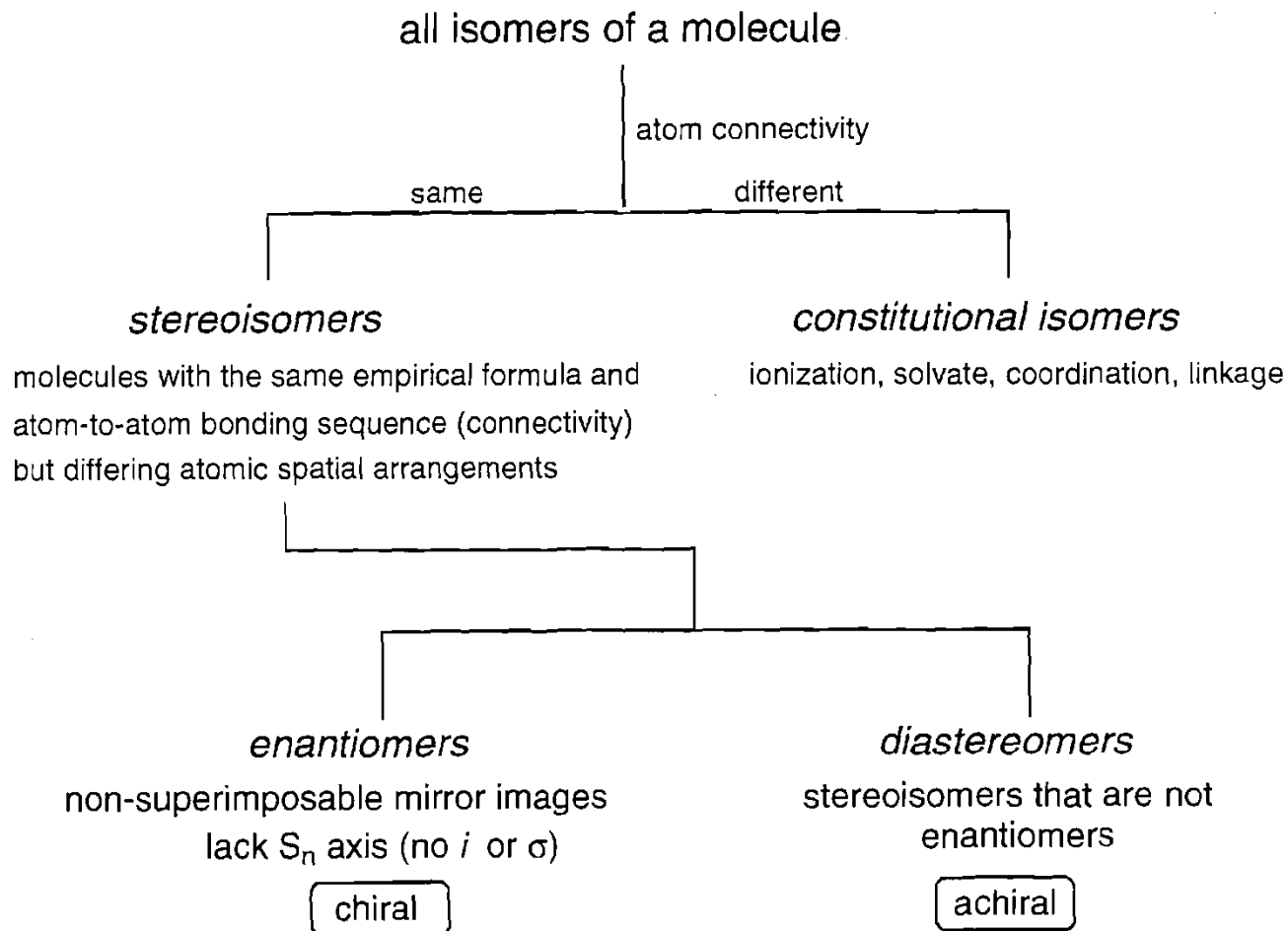
Naming transition metal complexes:

- 1) Cations first, anions second.
- 2) Within the coordination complex:
 - anion ligands first, neutral ligands second, metals last
 - give oxidation state of metal in parentheses
 - if anionic complex, add “ate” to metal name
 - if cationic complex, the metal, followed by ox. state, then the ligands and then counter anions. No need to give number of counter anions

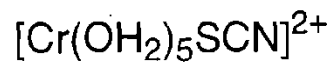
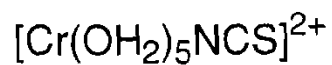
Table 3.2 Examples of the nomenclature of simple coordination compounds. Some of these examples contain, and adequately define, points not explicitly covered in the text

Compound	Nomenclature
$K_2[ReF_8]$	potassium octafluororhenate (note: only ‘potassium’)
$[Cu(NH_3)_4]SO_4$	tetraamminecobalt(II) sulfate (note: ‘aa’ and ‘mm’)
$[CuCl_2(py)_2]$	dichlorobispyridinecopper(II) (note: bipyridine is the present name for the 2,2’-bipyridine ligand—see Table 2.3. More strictly, and as in the text, di(pyridine) should be used to give dichlorodi(pyridine)copper(II). However, in the spoken language an ambiguity can arise)
$[Hg(C_2H_5)_2]$	diethylmercury(II)
$[Ni(PPh_3)_4]$	tetra(triphenylphosphine)nickel(0)
$[Ru(NH_3)_5(N_2)]^{2+}$	pentaamminedinitrogenruthenium(II) (note: similarly, O_2 is dioxygen, but beware confusion with O_2^- , superoxo and O_2^{2-} , peroxy)
$K_2[FeCl_4]$	potassium tetrachloroferrate(II)
$(NH_4)_2[SnCl_6]$	ammonium hexachlorostannate(IV)

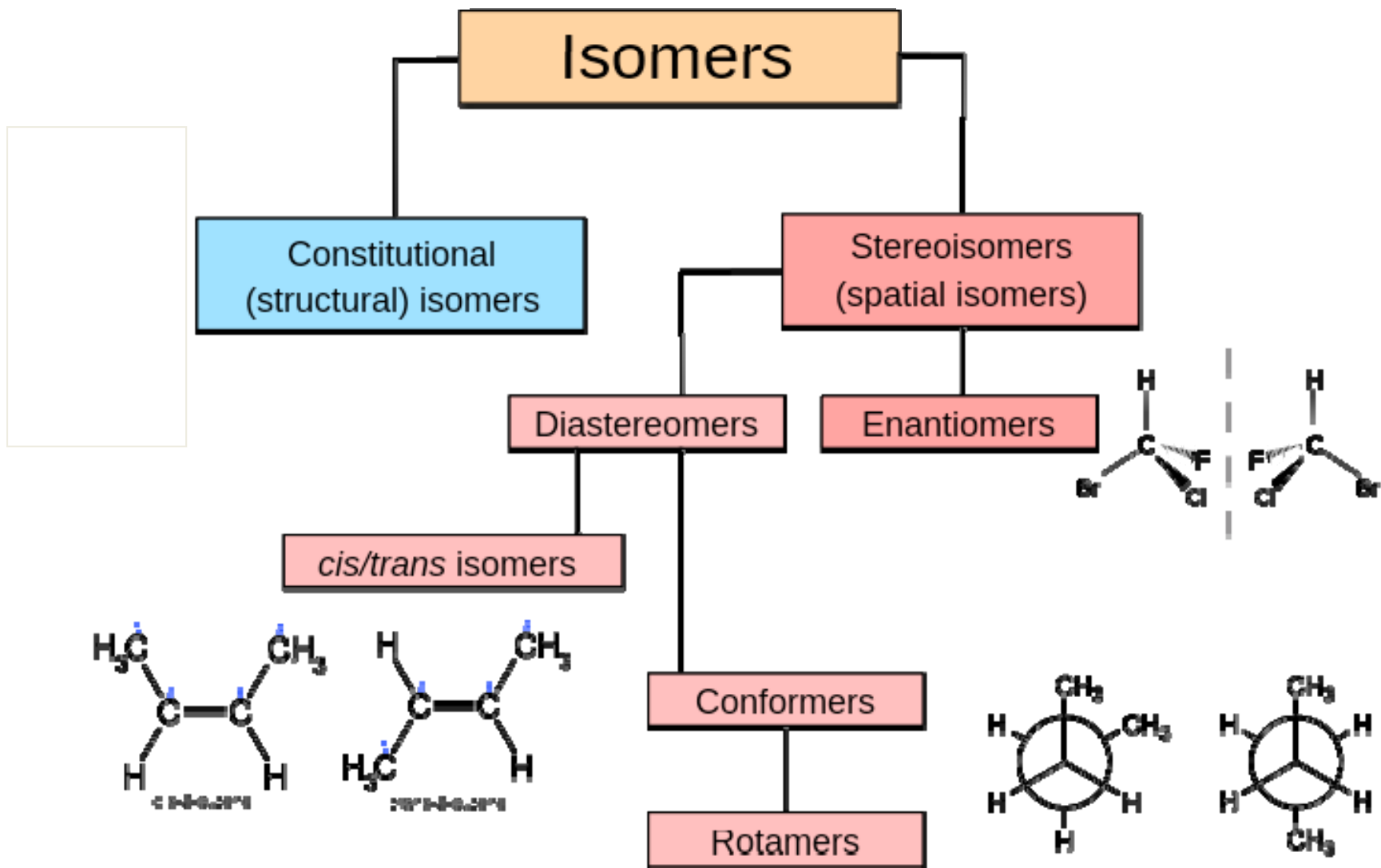
● Isomerism



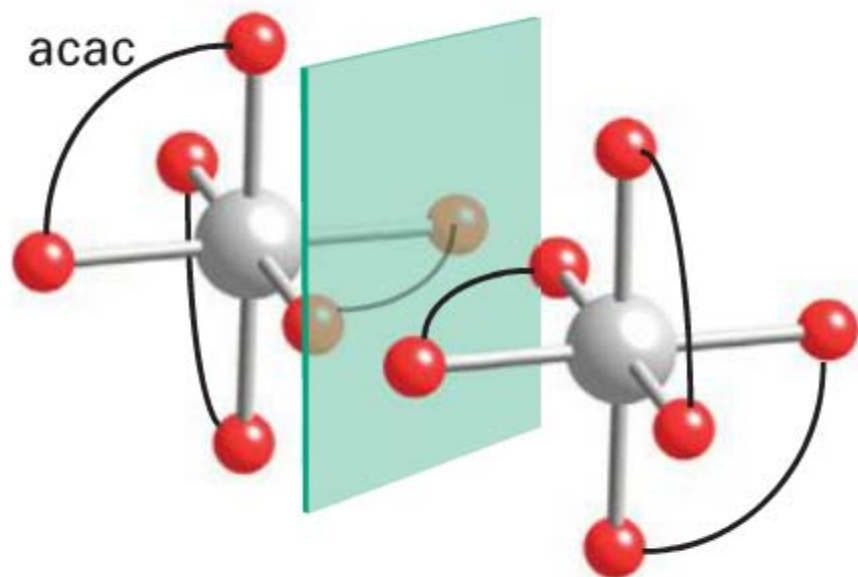
Examples:



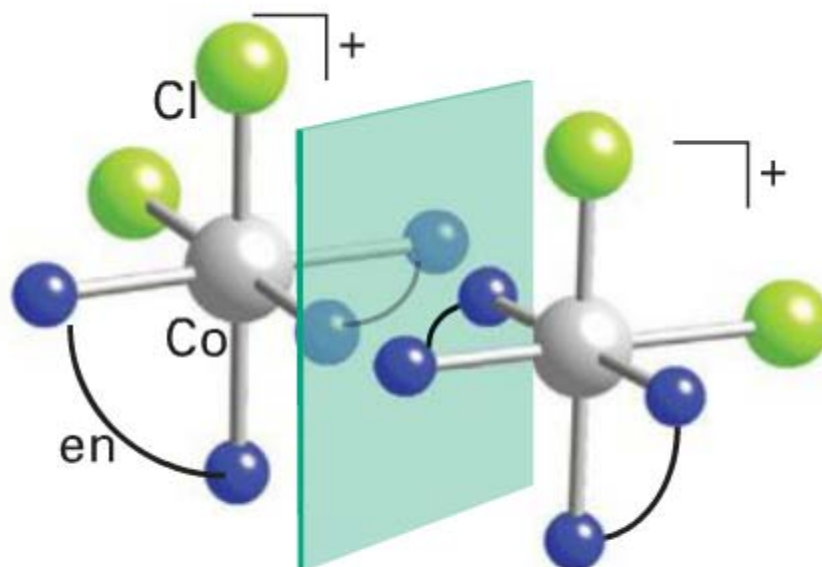
linkage isomers



Structural isomers: diastereomers

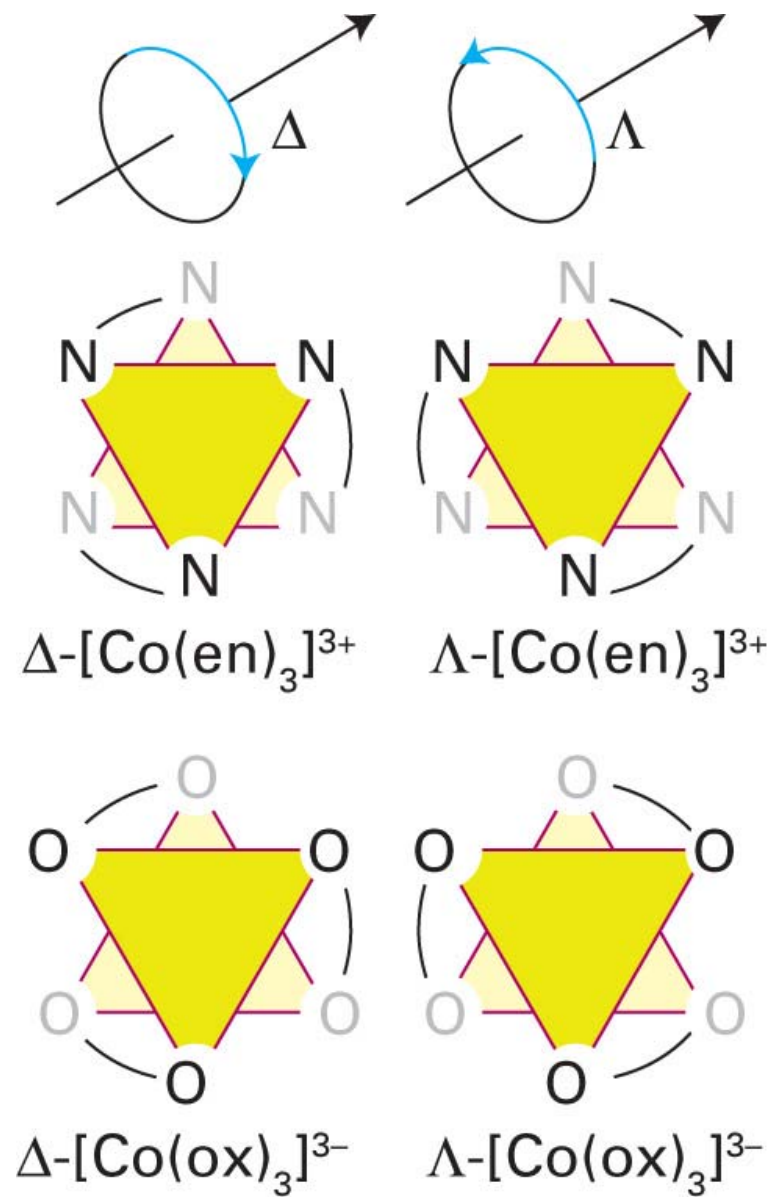


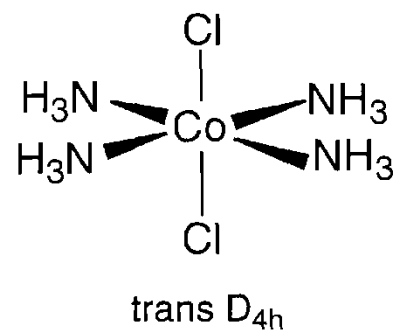
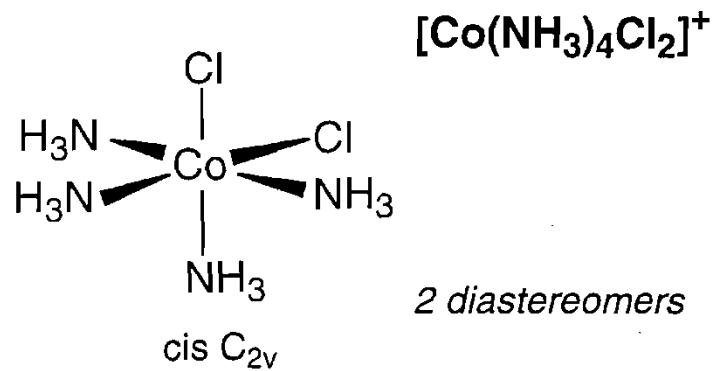
66 $[\text{Mn}(\text{acac})_3]$ enantiomers



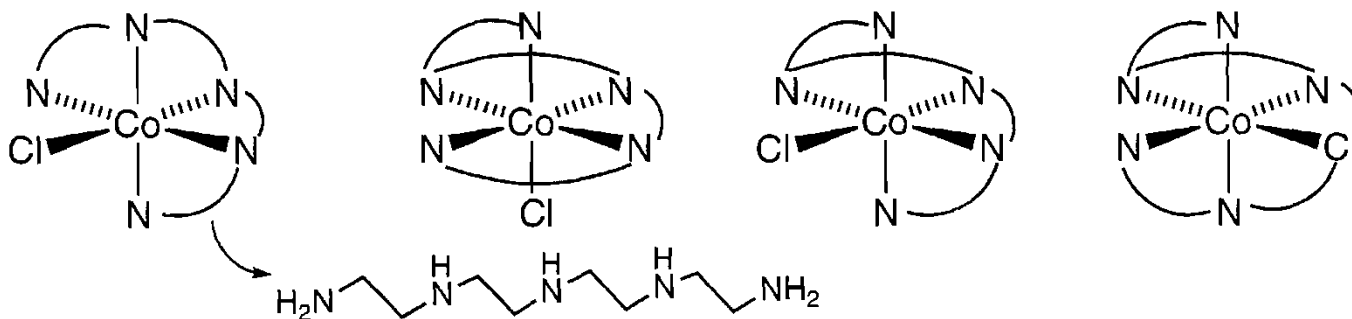
67 *cis*- $[\text{CoCl}_2(\text{en})_2]^+$ enantiomers

2 diastereomers





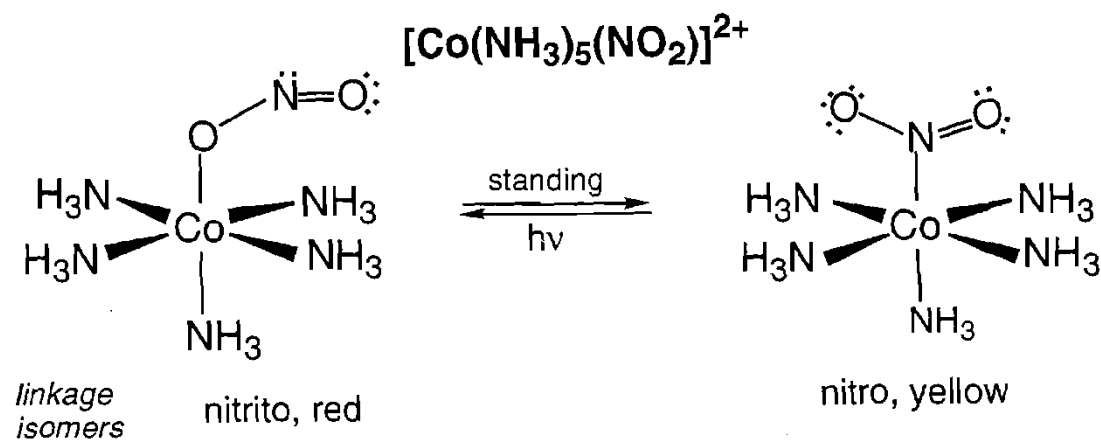
2 diastereomers



each isomer is chiral

Isomers because of the Ligand:

Linkage isomers or Ambi-dentate ligands



Isomers because of the Ligand:

Chirality within the ligand

So, How do we measure stability?

Formation Constant:

$$\Delta G^{\circ} = -RT \ln K_{eq}$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S$$

● Irving-Williams Stability Order

For the reactions $M + nL \rightleftharpoons ML_n$, the following order of stability constants holds under the indicated conditions (very few exceptions).



conditions: M has same charge and is high-spin

does not include Cu(II) binding of axial ligands

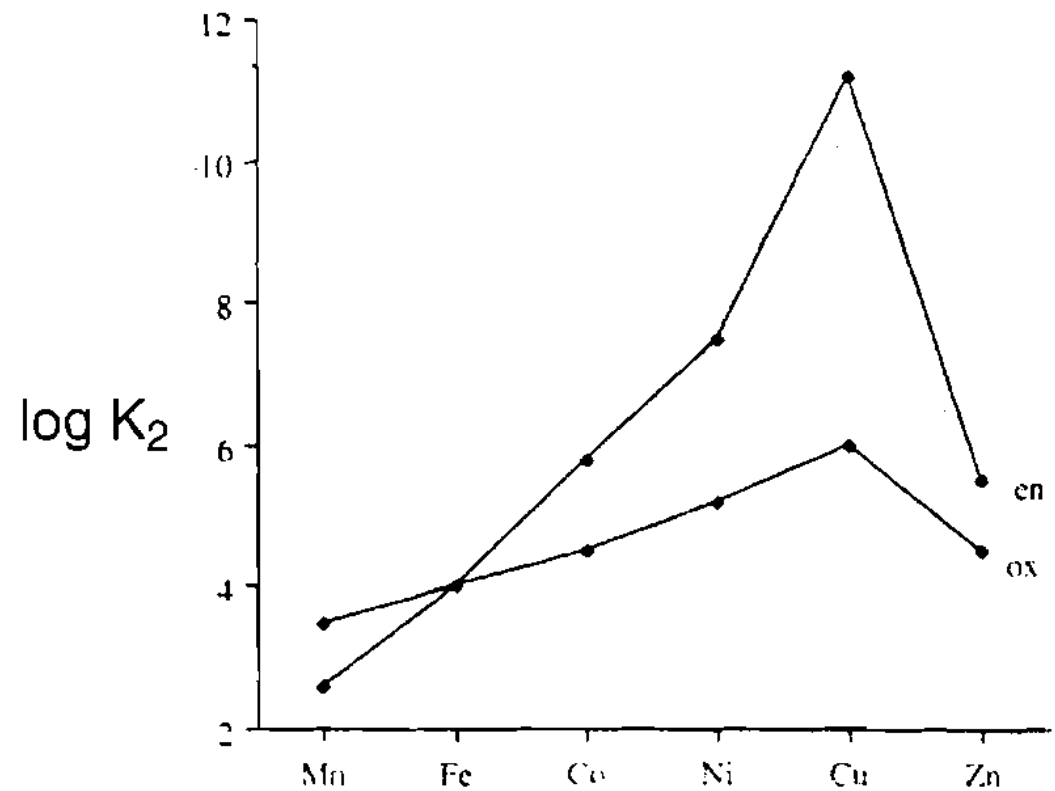


quantity	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
log K ₁ (M ⁻¹)	2.79	4.33	5.94	7.70	10.7	5.78
-ΔG ₂₉₈ (kcal/mol)	3.80	5.90	8.10	10.5	14.6	7.89
-ΔH (kcal/mol)*	2.80	5.09	6.88	8.89	13.0	6.69
TΔS ₂₉₈ (kcal/mol)	1.0	0.81	1.2	1.6	1.6	1.2

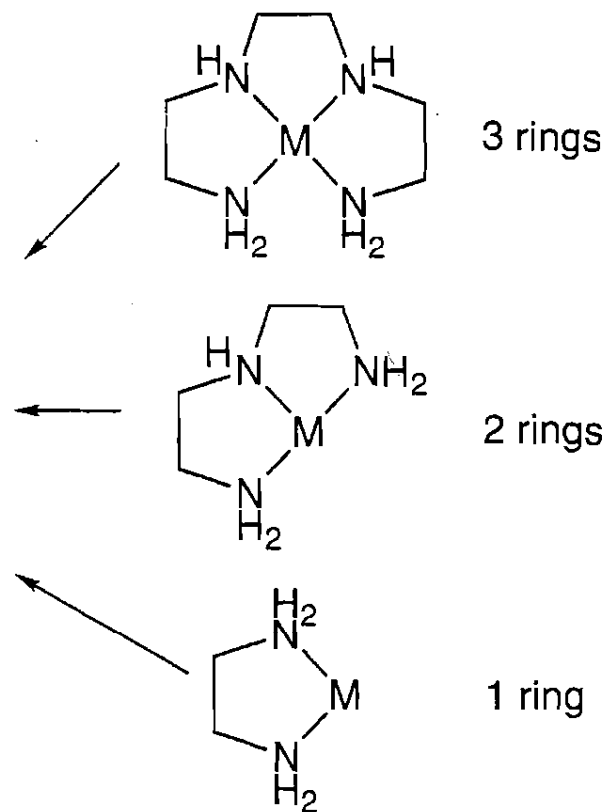
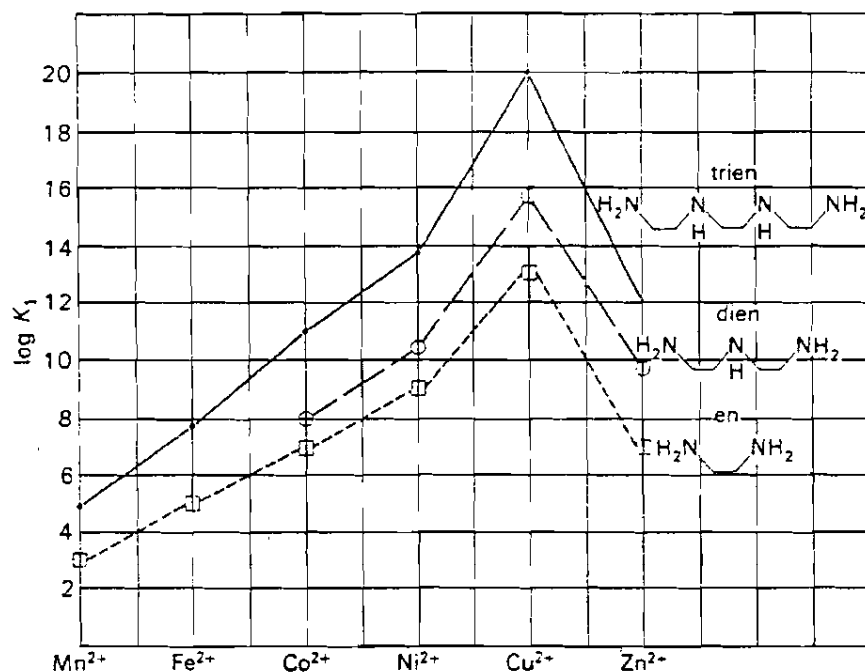
*determined calorimetrically

Reaction is favored
enthalpically and
entropically, but with
 $|\Delta H| \gg T\Delta S$

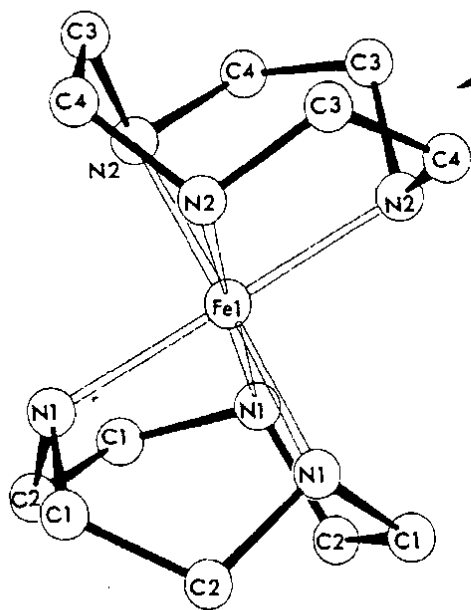
Similar results for
 K_2 reaction.



● number of chelate rings



Stability increases because enthalpy becomes increasingly negative (increased number of M–N bonds) and entropy increases (more water molecules released).



1,4,7-triazacyclononane (tacn)
3 rings/ligand

tacn forms relatively stable complexes
with $\text{M}^{2+,3+}$



log K_1

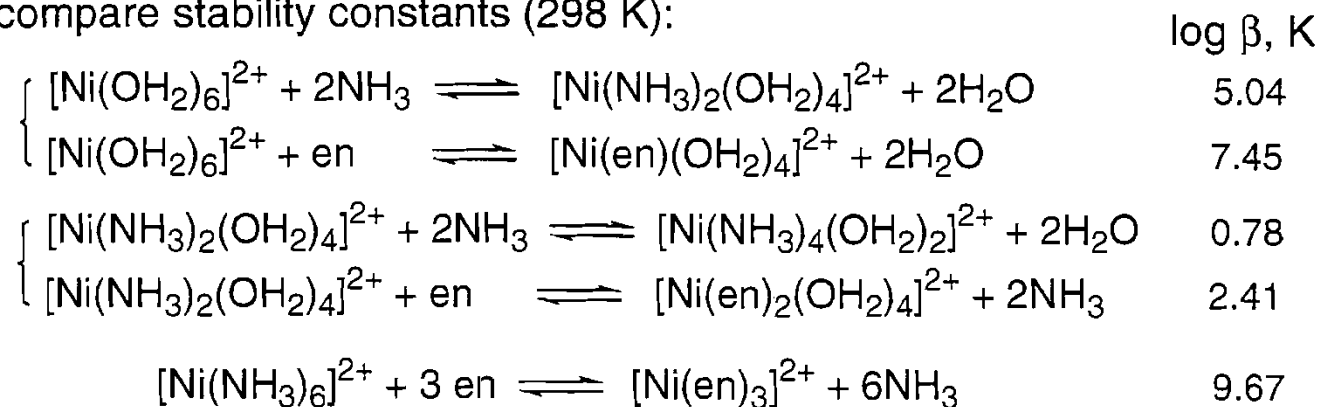
Ni(II)	16.24
Cu(II)	17.5
Zn(II)	11.6

favorable ΔH , ΔS ;
difficult to break M–N bonds because
of semi-rigid ligand structure

The Chelate Effect

● Chelate effect

compare stability constants (298 K):



$$\Delta H = -2.89 \text{ kcal/mol} \quad \text{small favorable contribution}$$

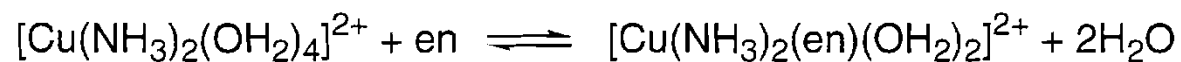
$$\Delta H_{SE} = -2.75 \text{ kcal/mol}$$

$$T\Delta S = 13.2 \text{ kcal/mol}$$

entropy increase (4→7 particles) dominates reaction

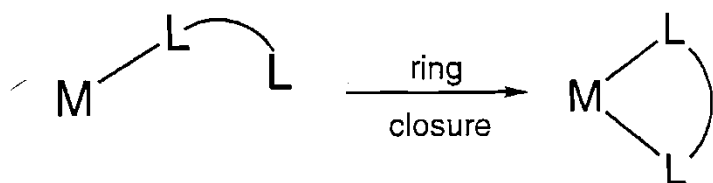
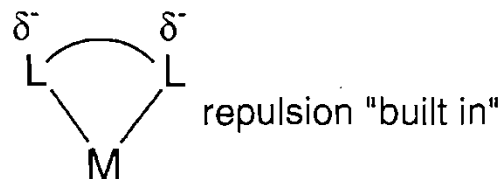
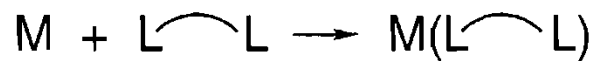
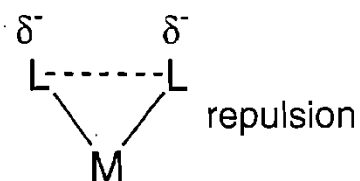
(even though NH_3 more strongly solvated than en)

The Chelate Effect



$$\Delta G = -3.70 \text{ kcal/mol} \quad \Delta H = -1.91 \text{ kcal/mol} \quad T\Delta S = 1.79 \text{ kcal/mol}$$

favorable (2 → 3 particles)



Once the first M-L bond is formed, there is a high probability the second bond will form because of the proximity of the other L atom. Corresponding probability is much lower with two unidentate ligands.

Now, How about those colors and the magnetism?

Where are the electrons? Show me the electrons!!

Color: *Electronic transitions due to energy levels whose gaps are in the visible range of the electromagnetic spectrum.*

Magnetism: *partially filled orbitals, unpaired electrons.*

high spin: maximum no. of d electrons

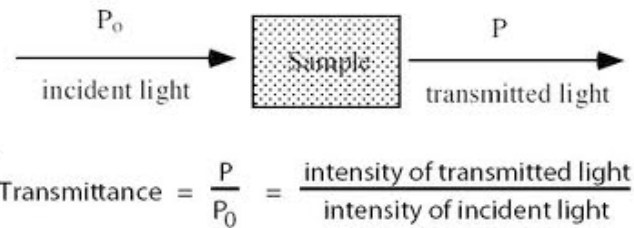
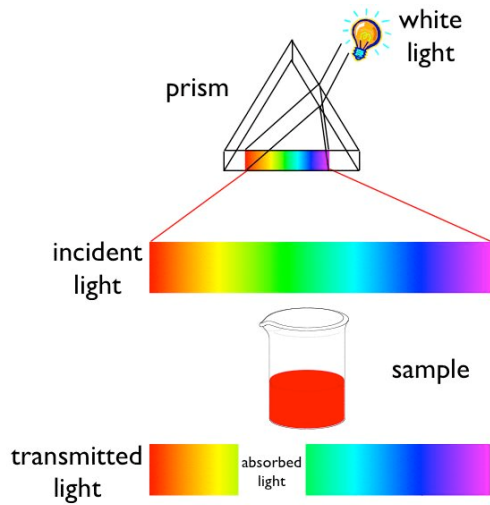
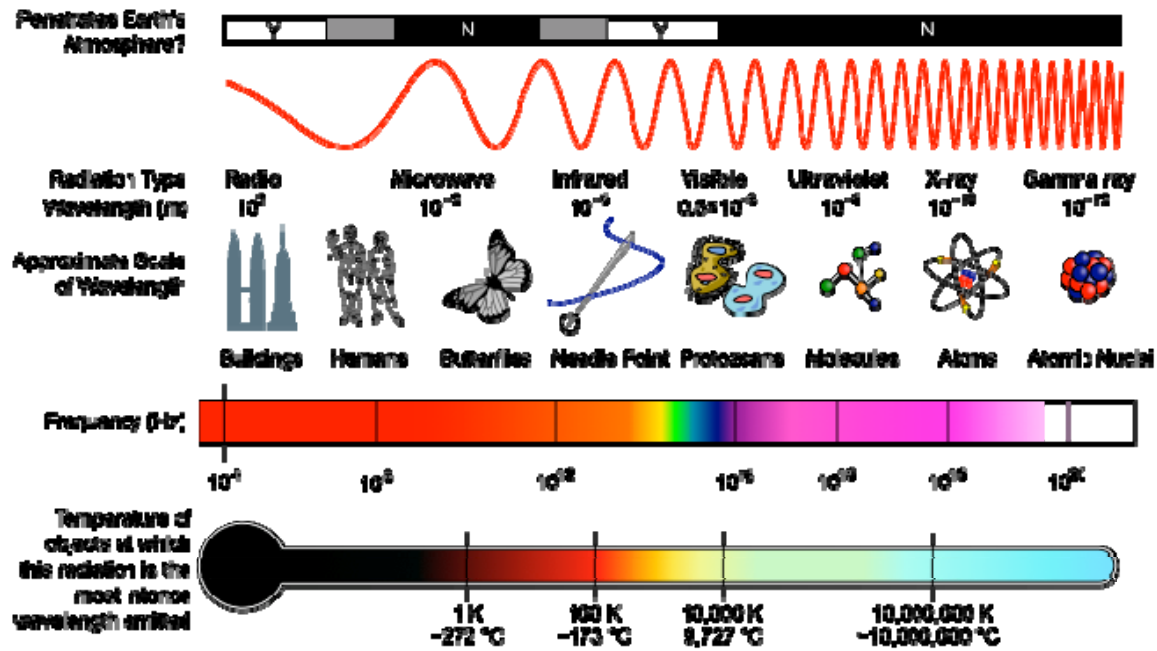
unpaired

low spin: electrons paired up in d orbitals. WHY??

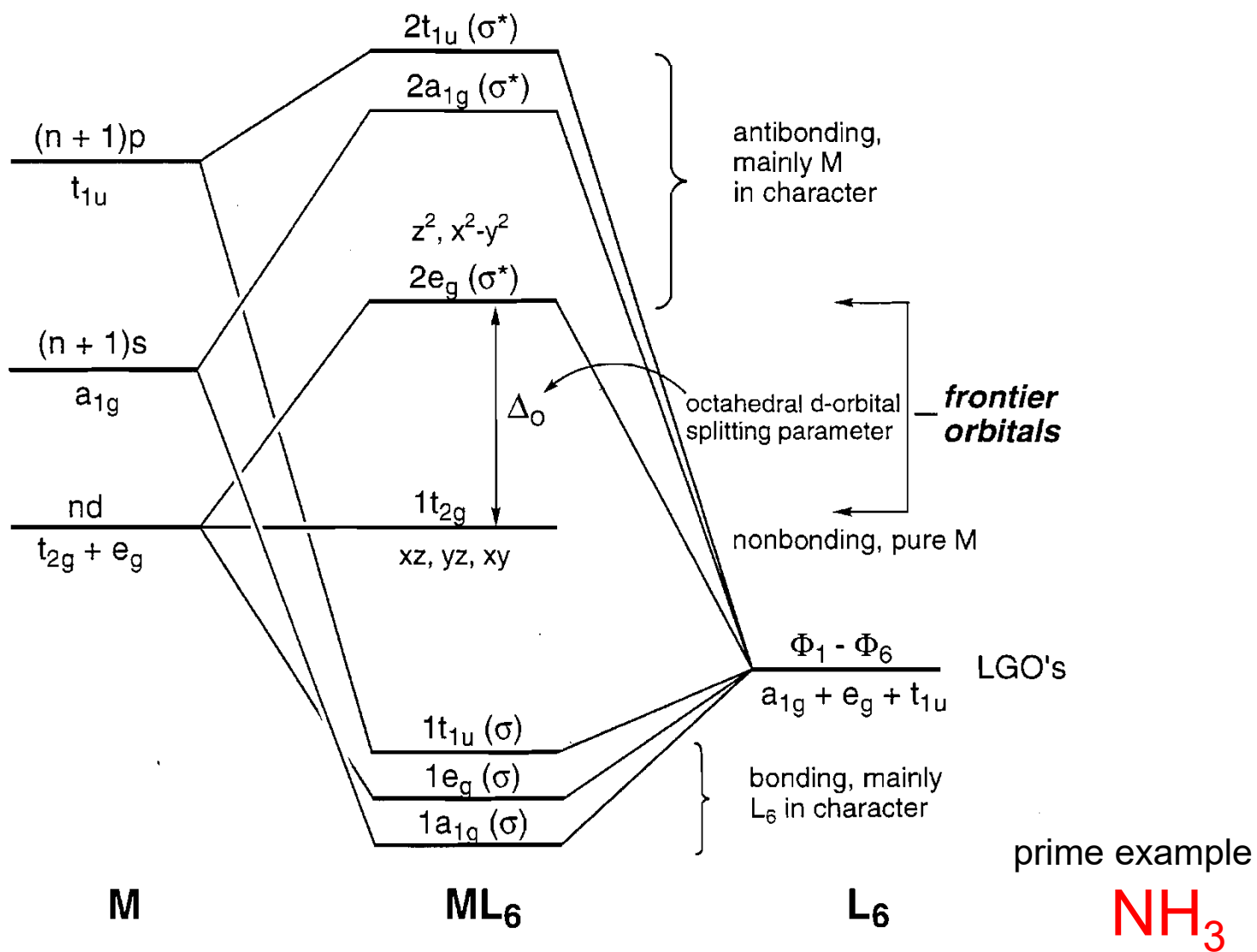
Bonding models: *Valence bond (coordinate covalent bond needs empty orbitals on metal)*

Molecular Orbital Theory (all orbitals defined)

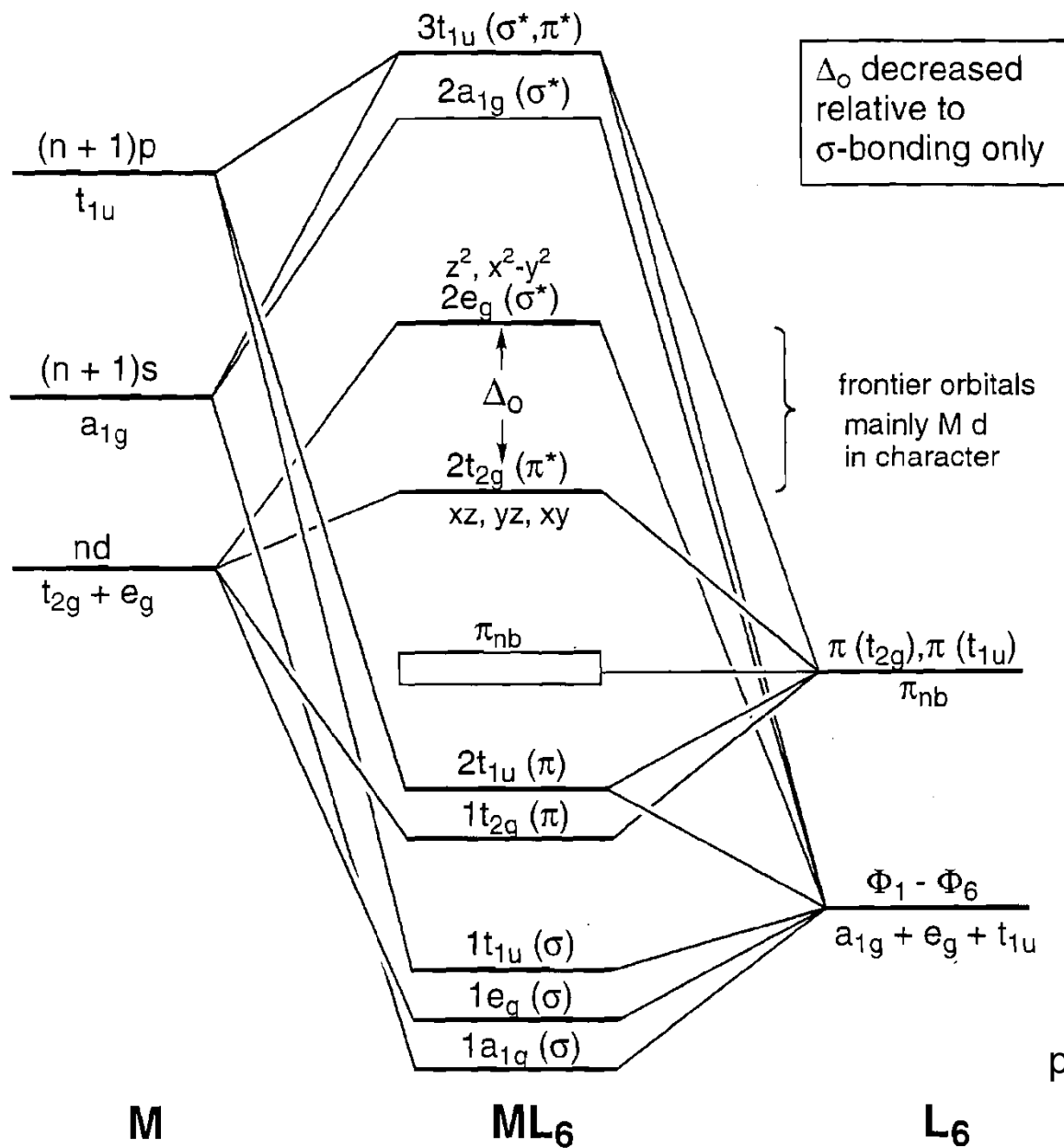
Crystal Field Theory (originally from ionic crystals; influence of ligand lone pair repulsion on d-orbitals)



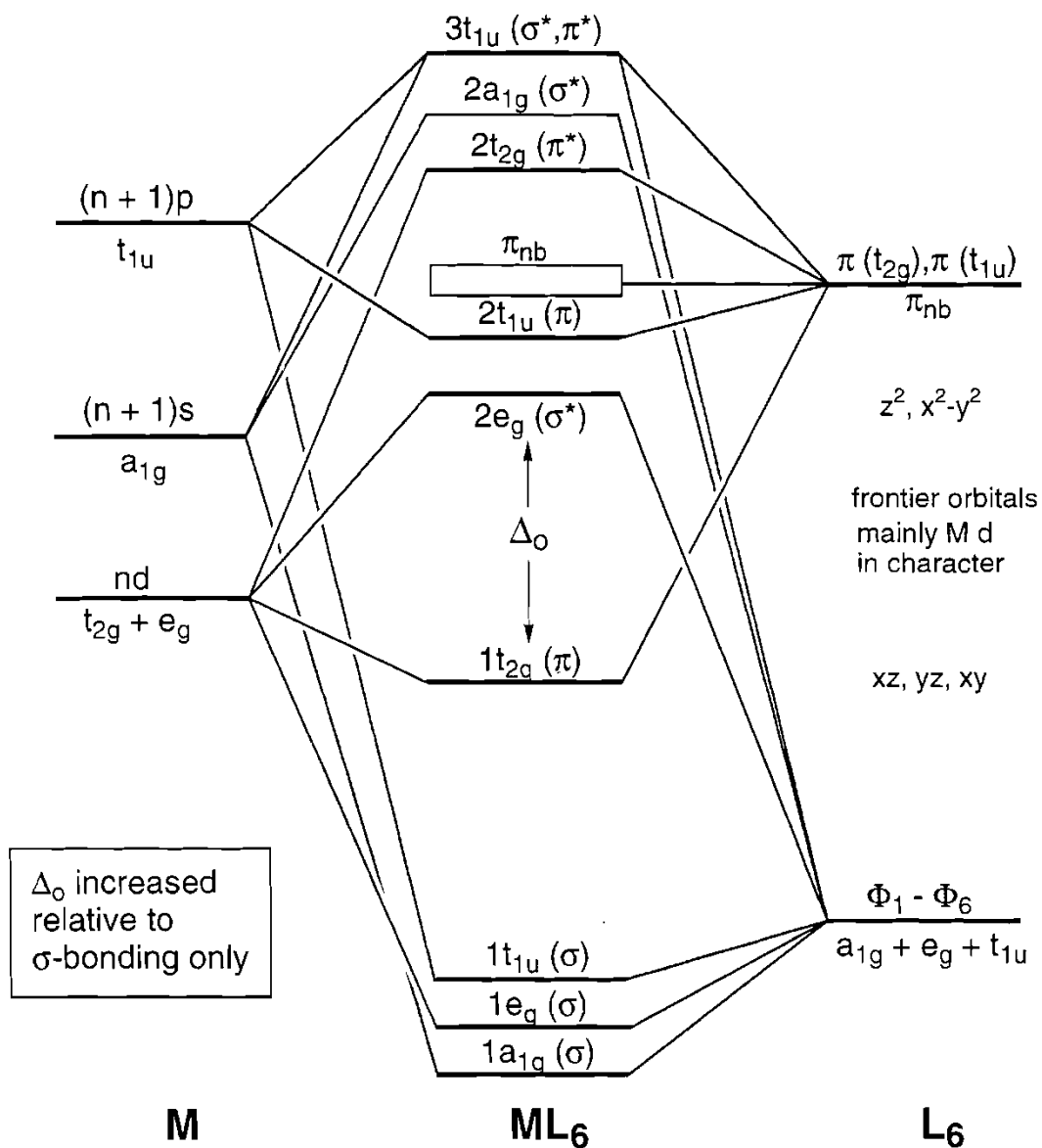
To explain magnetism and colors, need electronic configuration of the Transition Metal Complex



Case 1. $L\pi$ orbitals filled and more stable than $d\pi$ orbitals
(L is a π -donor)



Case 2. $L\pi$ orbitals vacant and less stable than $d\pi$ orbitals
(L is a π -acceptor)

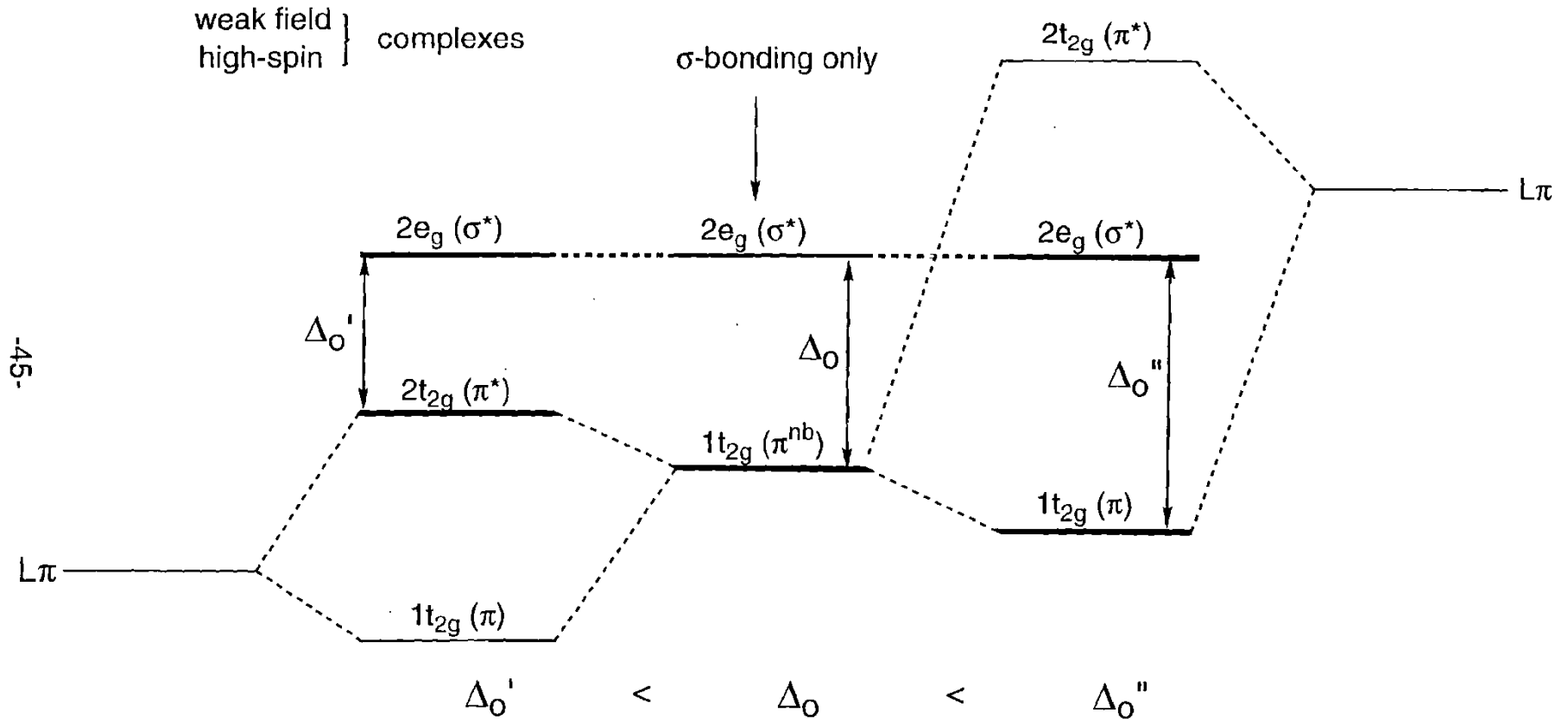


Important Cases of d-Orbital Splittings in Octahedral Complexes

Case 1. $L\pi$ orbitals filled and more stable than $d\pi$ orbitals. L are π -donors.

— mainly M orbitals
 — mainly L orbitals

Case 2. $L\pi$ orbitals vacant and less stable than $d\pi$ orbitals. L are π -acceptors.



$L_{\pi\text{-donor}} = F^-, Cl^-, Br^-, I^-, H_2O, OH^-,$
 $RS^-, S^{2-}, NCS^-, NCO^-, \dots$

(virtually any ligand which, after forming
 M-L σ -bonds, has lone pairs)

$L_{\sigma} = NR_3$

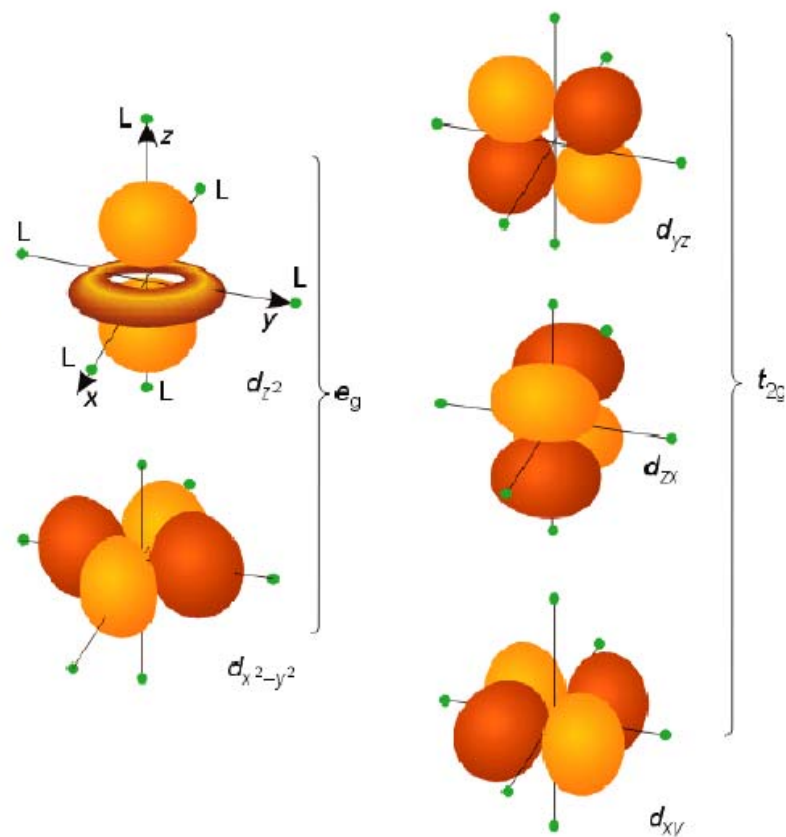
PR_3

$L_{\pi\text{-acceptor}} = CO, NO, CN^-, N_2, \text{bipy}, \text{phen},$
 $RNC, C_5H_5^-, \text{>C=C<}, \text{—C}\equiv\text{C—}$

(virtually any ligand with vacant
 π^* MO's)

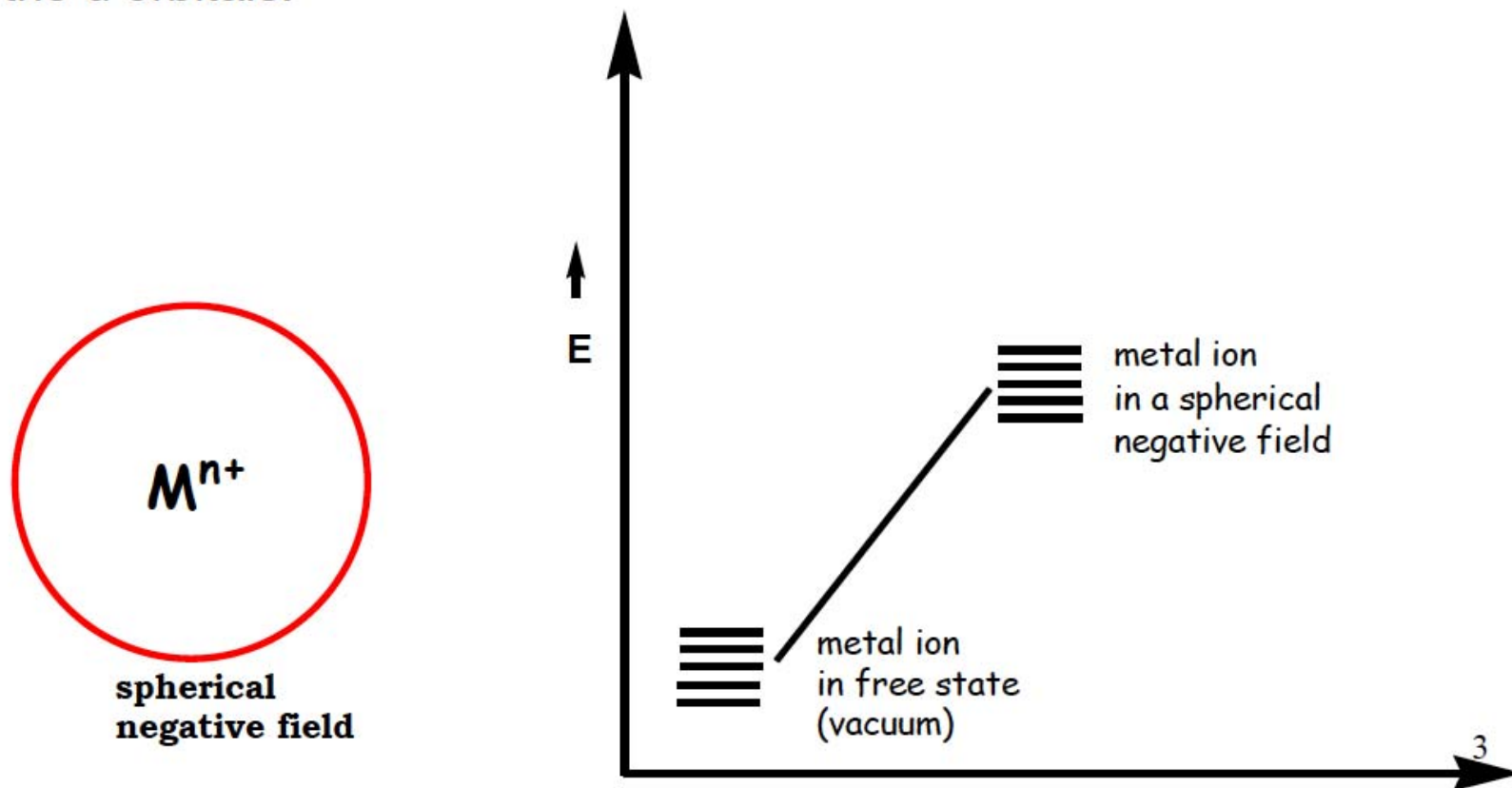
CFT - Assumptions

- The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges
- If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral : ion-dipole interaction
- The electrons on the metal are under repulsive from those on the ligands
- The electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands



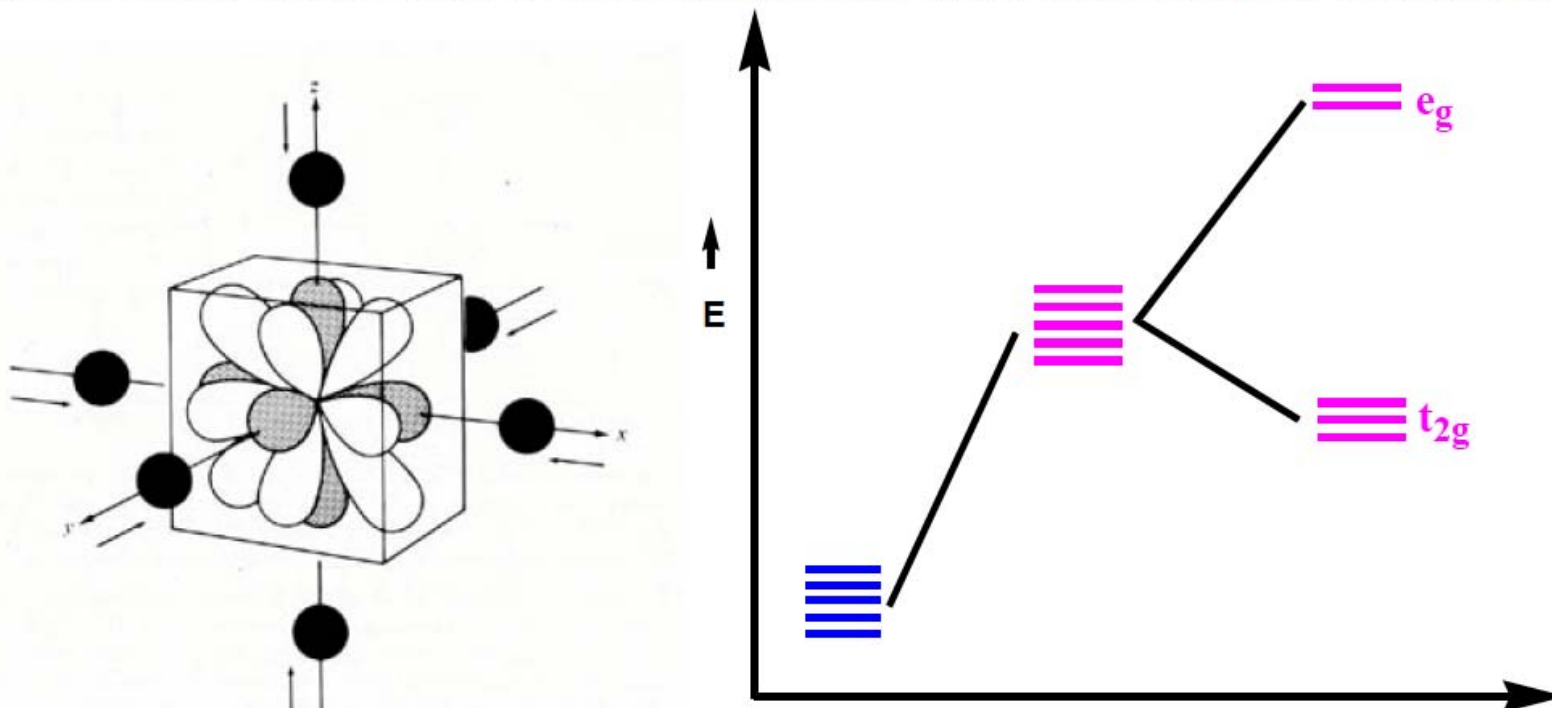
Symmetric Field

- The 5d orbitals in an isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals.



Octahedral Field

• If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.



• Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.

• The orbitals which lie along these axes (i.e. x^2-y^2 , z^2) will be destabilized more than the orbitals which lie in-between the axes (i.e. xy, xz, yz).

CFT-Octahedral Complexes

- For the O_h point group, the x^2-y^2, z^2 orbitals belong to the E_g irreducible representation and xy, xz, yz belong to the T_{2g} representation.
- The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively $10Dq$. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.

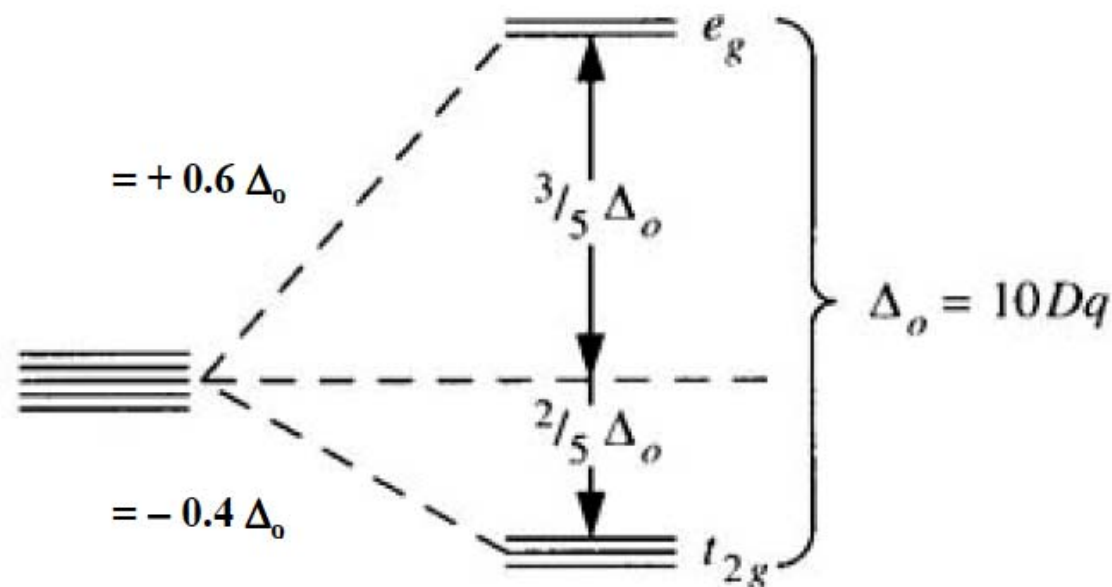
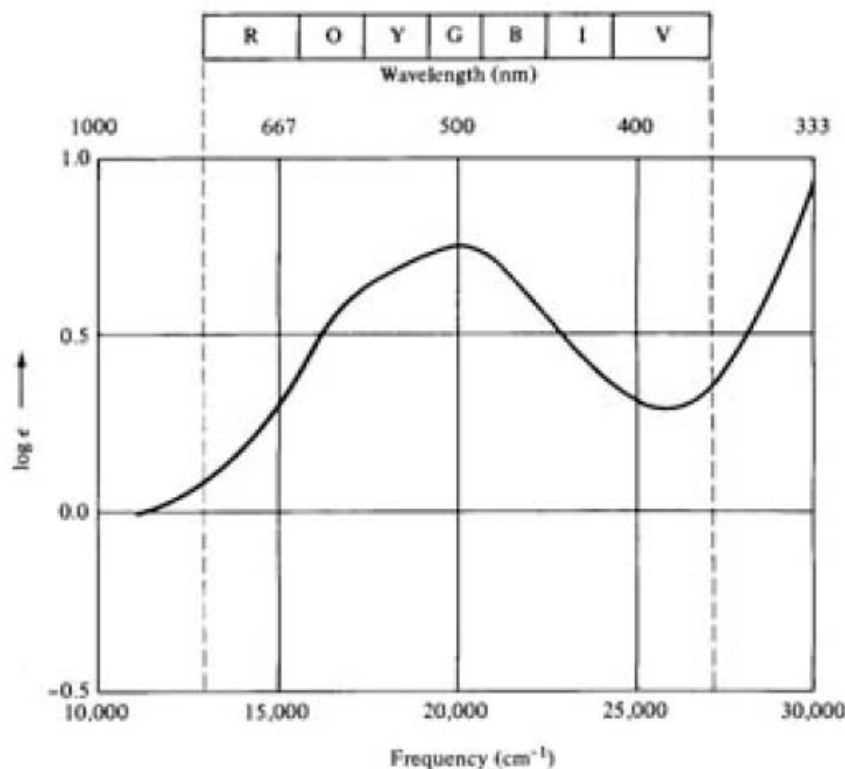


Illustration of CFSE

$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$: a d^1 complex and the e^- occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. The **purple colour** is a result of the absorption of light which results in the promotion of this t_{2g} electron into the e_g level. $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$



The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

($1000 \text{ cm}^{-1} = 11.96 \text{ kJ/mol}$ or
 2.86 kcal/mol or
 0.124 eV.)

Typical Δ_o values are of the same order of magnitude as the energy of a chemical bond.

- **What happens for more than 1 electron in d orbitals?**
- **The electron-electron interactions must be taken into account.**
- **For d^1 - d^3 systems:** Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set.
- **For d^4 - d^7 systems** (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation**).
- Therefore, there are two important parameters to consider: **The Pairing energy (P)**, and **the $e_g - t_{2g}$ Splitting (referred to as Δ_0 , $10Dq$ or CFSE)**
- For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE**.

For an octahedral complex, CFSE

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

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. $CFSE > P$)

If CFSE is rather small, no pairing occurs (i.e. $P > CFSE$)

d^5 system



Case I results in LS complex

Case II results in HS complex

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands which cause a small splitting are *Weak field ligands* (CFSE in the range 7000 - 30000 cm^{-1}) and those cause a large splitting are *Strong field ligands* (CFSE typically > 30000 cm^{-1})

Spectrochemical Series

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{N}_3^-, \text{F}^- < \text{urea}, \text{OH}^- < \text{ox}, \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{CH}_3^-, \text{C}_6\text{H}_5^- < \text{CN}^- < \text{CO}.$

$[\text{CrCl}_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	314
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	213
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	314

Tetrahedral Field- Considerations

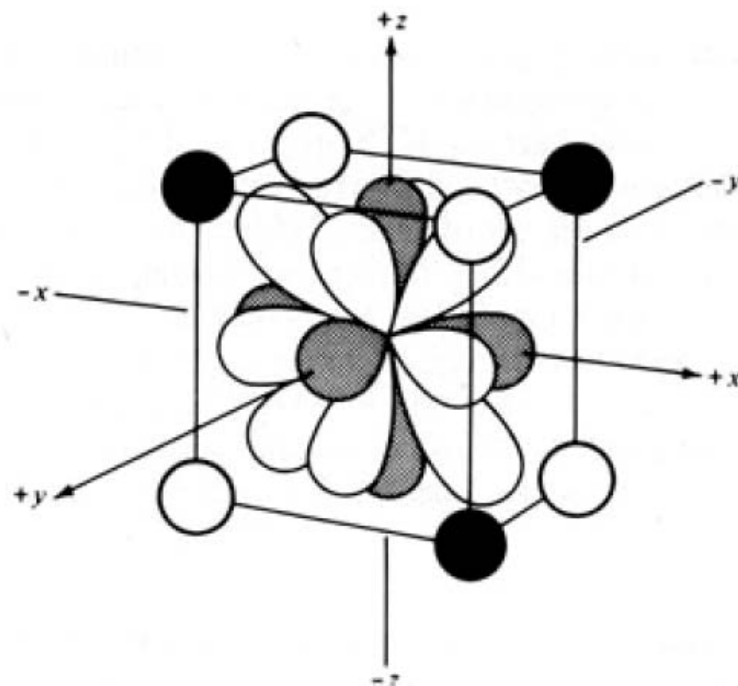
Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two 'e' orbitals point to the center of the face of the cube while the three 't₂' orbitals point to the center of the edges of the cube.

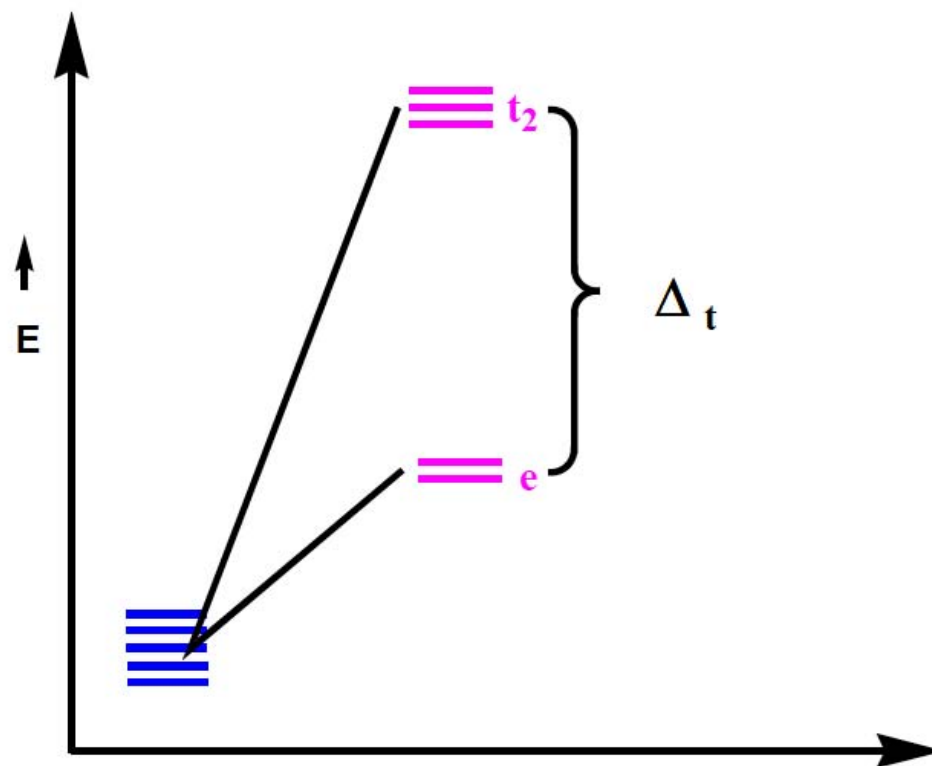
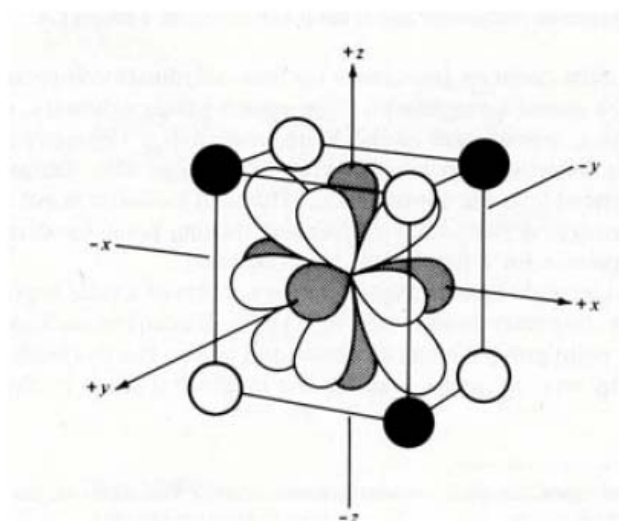
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedral angle, i.e. $109^{\circ}28' / 2 = 54^{\circ}44'$. But the angle between the t₂-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. $109^{\circ}28' / 3 = 35^{\circ}16'$.

Thus the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t₂ orbitals have higher energy compared to e-orbitals



Tetrahedral Field



$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9 \Delta_o$$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly $2/3 \times 2/3 = 4/9$ of Δ_o .

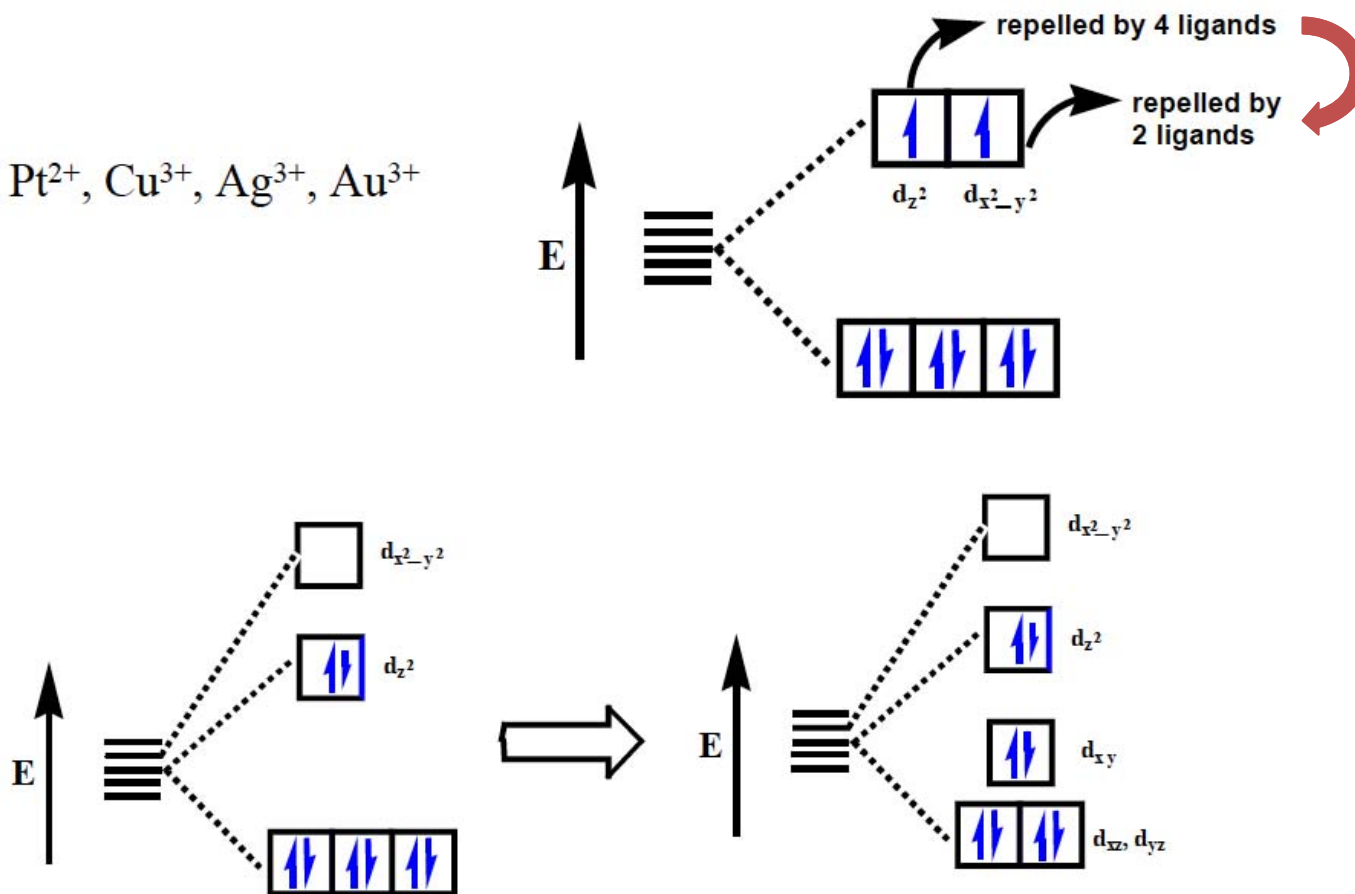
As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the pairing energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Special case of d^8 Octahedral

Examples:

Ni^{2+} , Pd^{2+} , Pt^{2+} , Cu^{3+} , Ag^{3+} , Au^{3+}



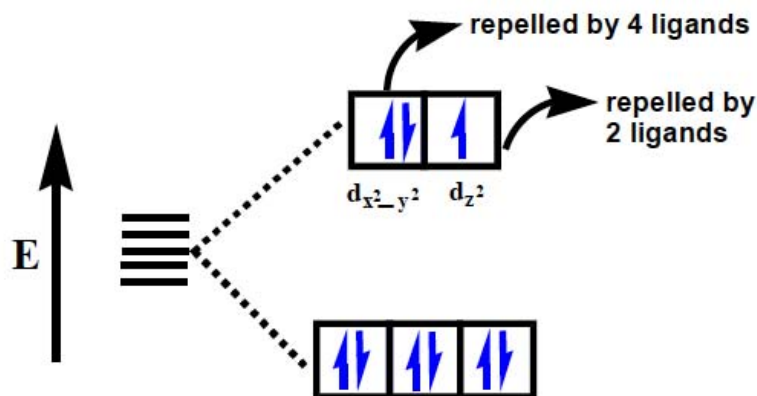
Square-planar complex is formed ; attempts to form octahedral complexes become impossible

Special case II Jahn-Teller Distortion

If both the e_g orbitals are symmetrically filled - all ligands are repelled equally.

Result: regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other. **Result:** Distorted octahedron



Consider e_g configuration: $(d_{z^2})^1 d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the z axis.

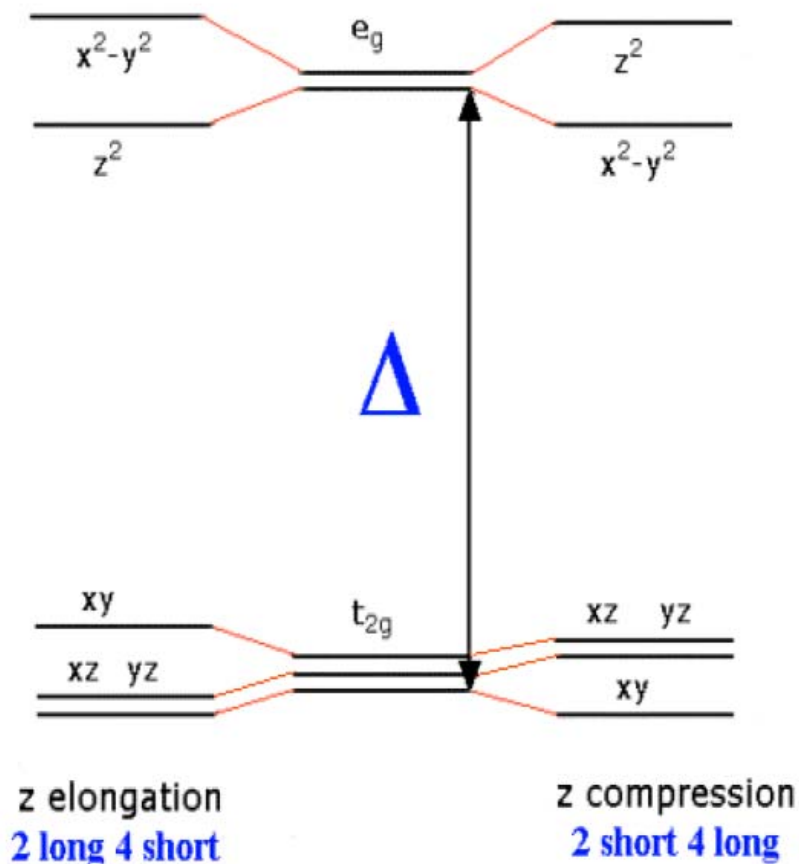
Consider e_g configuration: $(d_{z^2})^2 d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.

The Jahn-Teller Theorem was published in 1937 and states:

"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

The e_g point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



Some examples of Jahn-Teller distorted complexes

CuBr_2	4 Br at 240pm 2 Br at 318pm
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm
CsCuCl_3	4 Cl at 230pm 2 Cl at 265pm
CuF_2	4 F at 193pm 2 F at 227pm
$\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$	4 N at 205pm 1 O at 259pm 1 O at 337pm
K_2CuF_4	4 F at 191pm 2 F at 237pm
CrF_2	4 F at 200pm 2 F at 243pm
KCrF_3	4 F at 214pm 2 F at 200pm
MnF_3	2 F at 209pm 2 F at 191pm 2 F at 179pm

d-orbital splitting diagrams for various geometries

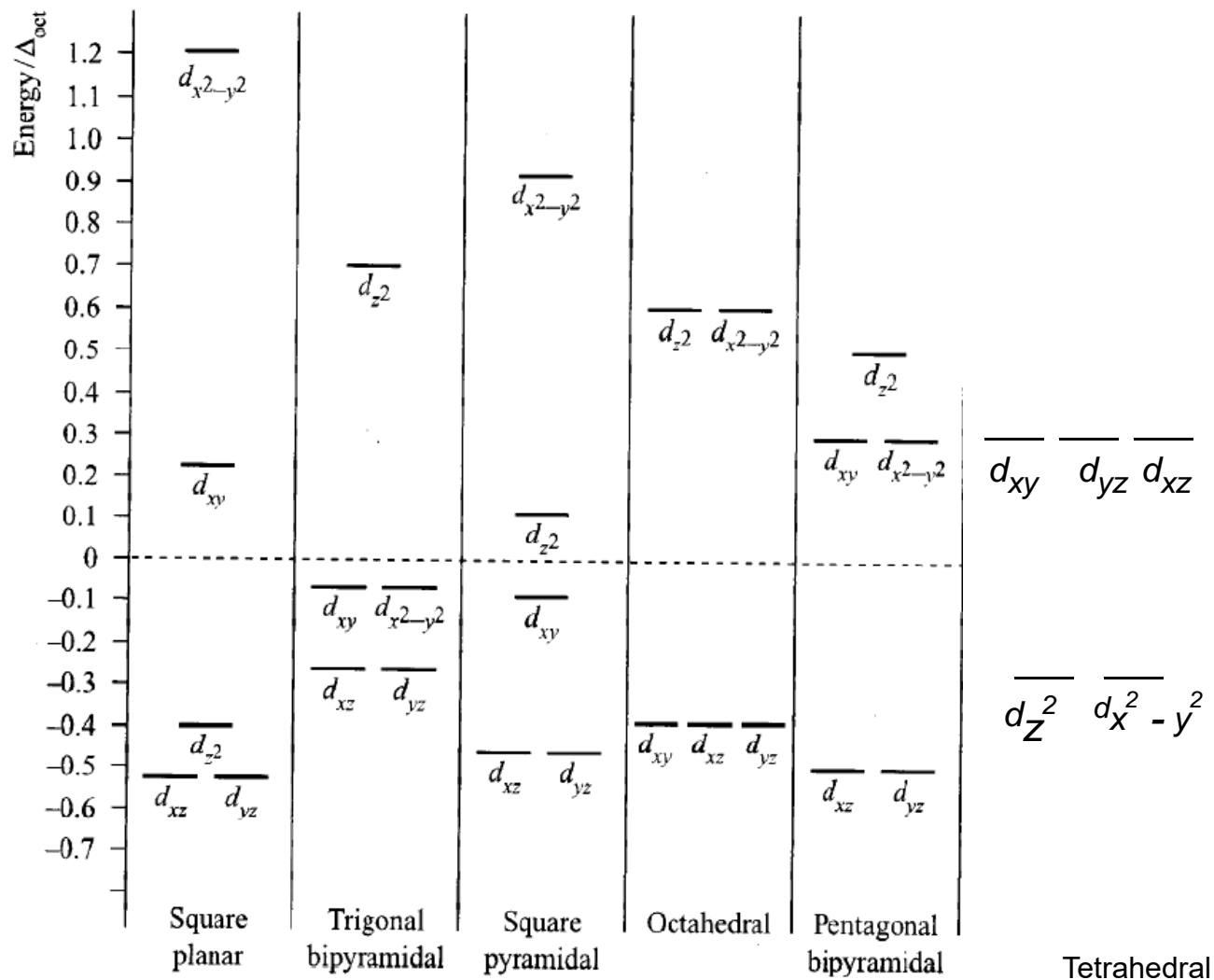


Figure 2 Crystal field splittings of d orbitals

