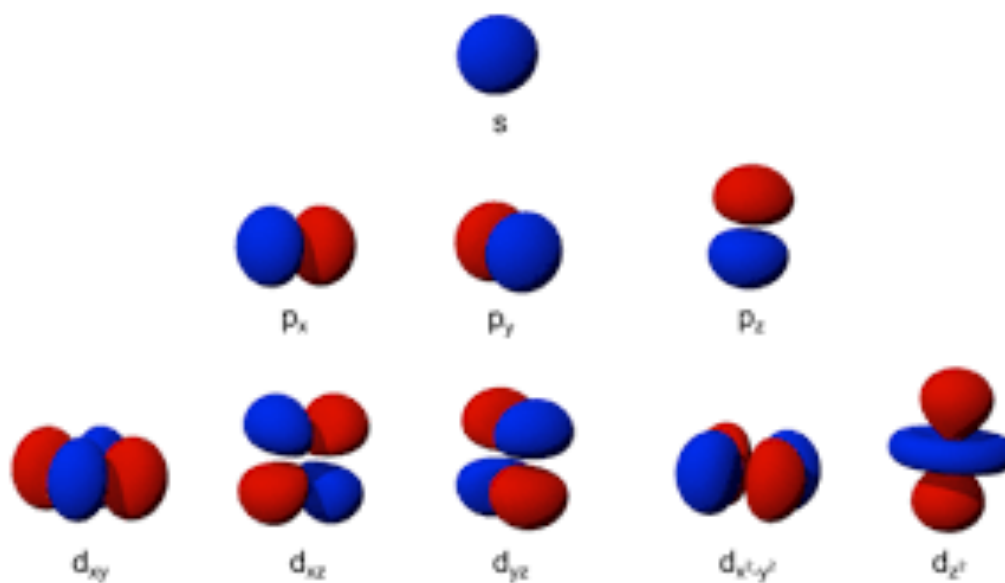


CH2501 – Coordination Chemistry of Complexes

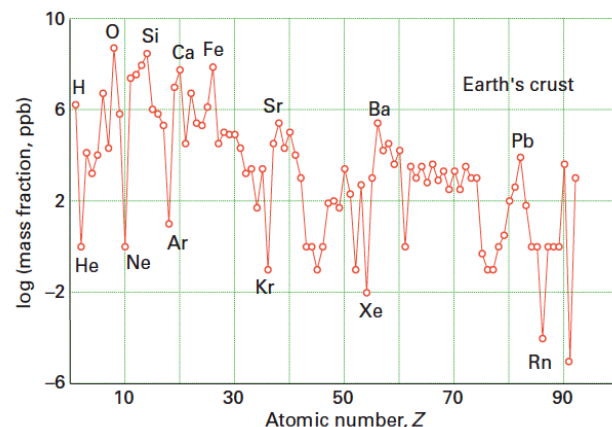
Eli Zysman-Colman (ezc)



1. INTRODUCTION: Coordination Chemistry of Complexes

The goal of this module is to provide an introduction to transition metal chemistry. This includes an outline trends within the d-block of the periodic table along with a particular focus on the chemistry and properties of 3d-metal complexes. Crystal field theory is reviewed and how it can be used to rationalize optical and magnetic properties of transition metal complexes. A detailed background to molecular orbital theory of diatomic and triatomic molecules is provided to provide a framework for how lessons learned there can be adapted towards an understanding of ligand field theory.

1																		18	
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2																		10	
Li																		Ne	
3																		18	
4																		36	
5																		54	
6																		86	
7																		118	
8																		150	
9																		182	
10																		210	
11																		238	
12																		266	
13																		294	
14																		322	
15																		350	
16																		378	
17																		406	
18																		434	
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25																		630	
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28																		714	
29																		742	
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49																		1302	
50																		1330	
51																		1358	
52																		1386	
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68																		1834	
69																		1862	
70																		1890	
71																		1918	
72																		1946	
73																		1974	
74																		2002	
75																		2030	
76																		2058	
77																		2086	
78																		2114	
79																		2142	
80																		2170	
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150																		4130	
151																		4158	
152																		4186	
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166																		4578	
167																		4606	
168																		4634	
169																		4662	
170																		4690	
171																		4718	
172																		4746	
173																		4774	
174																		4802	
175																		4830	
176																		4858	
177																		4886	
178																		4914	
179																		4942	
180																		4970	
181																		4998	
182																		5026	
183																		5054	
184																		5082	
185																		5110	
186																		5138	
187																		5166	
188																		5194	
189																		5222	
190																		5250	
191																		5278	
192																		5306	
193																		5334	
194																		5362	
195																		5390	
196																		5418	
197																		5446	
198																		5474	
199																		5502	
200																		5530	



D-block elements can be found all over the Earth. Some, like iron and titanium are highly abundant but others, particularly the 5d elements are some of the rarest elements naturally found on Earth, with iridium being the most rare of the element with an atomic weight up to 94.

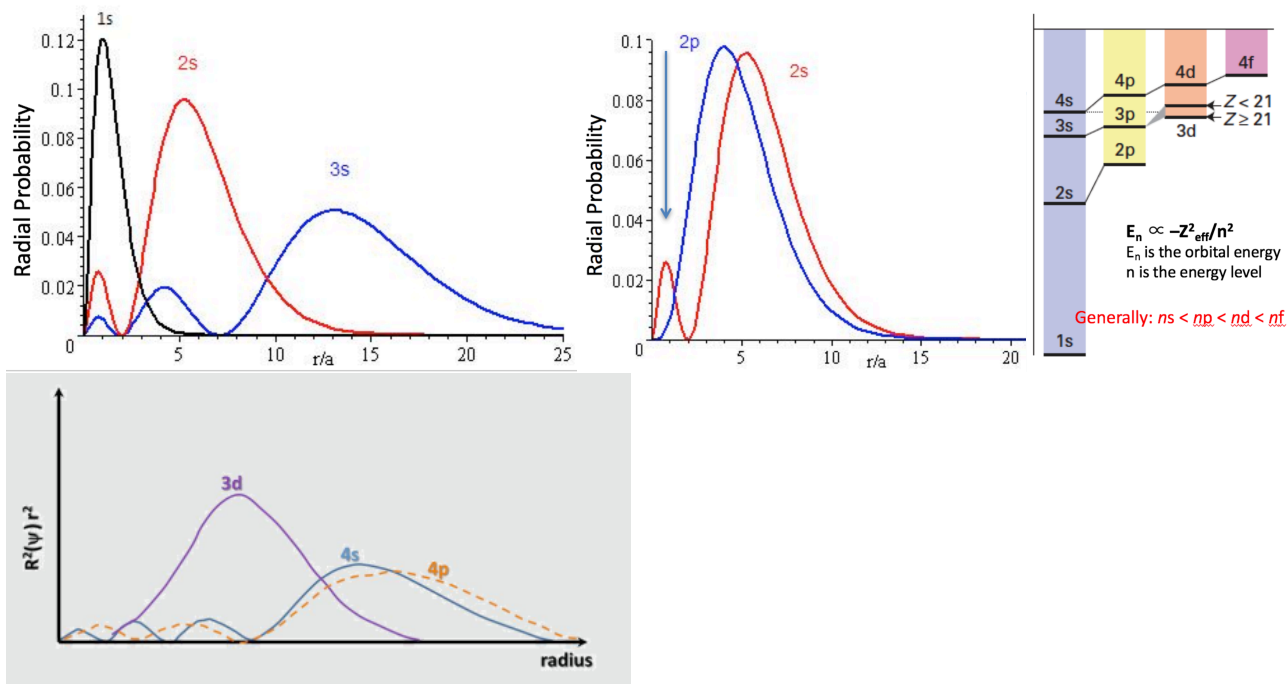
3	4	5	6	7	8	9	10	11	12
21	22	23	24	25	26	27	28	29	30
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] 4s ² 3d ¹	[Ar] 4s ² 3d ²	[Ar] 4s ² 3d ³	[Ar] 4s ¹ 3d ⁵	[Ar] 4s ² 3d ⁵	[Ar] 4s ² 3d ⁶	[Ar] 4s ² 3d ⁷	[Ar] 4s ² 3d ⁸	[Ar] 4s ¹ 3d ¹⁰	[Ar] 4s ² 3d ¹⁰
39	40	41	42	43	44	45	46	47	48
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
[Kr] 5s ² 4d ¹	[Kr] 5s ² 4d ²	[Kr] 5s ¹ 4d ⁴	[Kr] 5s ¹ 4d ⁵	[Kr] 5s ² 4d ⁵	[Kr] 5s ¹ 4d ⁷	[Kr] 5s ¹ 4d ⁸	[Kr] 4d ¹⁰	[Kr] 5s ¹ 4d ¹⁰	[Kr] 5s ² 4d ¹⁰
57-71	72	73	74	75	76	77	78	79	80
lanthanoids	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	[Xe] 6s ² 5d ²	[Xe] 6s ² 5d ³	[Xe] 6s ² 5d ⁴	[Xe] 6s ² 5d ⁵	[Xe] 6s ² 5d ⁶	[Xe] 6s ² 5d ⁷	[Xe] 6s ¹ 5d ⁹	[Xe] 6s ¹ 5d ¹⁰	[Xe] 6s ² 5d ¹⁰

The electronic configuration of the elements in the d-block of the periodic table evidently implicate d-electrons in their valence shell. Frequently, the s-block is filled first, followed by sequential addition of d-electrons along the period. Exceptionally, a more stable electronic configuration of the element occurs to half-fill both the s- and d-blocks, as is the case with chromium or molybdenum, which have electronic configurations of [Ar] 4s¹3d⁵ and [Kr] 5s¹4d⁵. A similar situation happens to ensure a completely filled d-shell, as is the case with copper, which is [Ar] 4s¹3d¹⁰.

2. PENETRATIONS AND SHIELDING

Recall that the attractive electrostatic force experienced by an electron to the nuclear charge of the atom is reduced as a result of all the electrons that are closer to the nucleus than it. Electrons close to the nucleus are called core electrons while those furthest away are called valence electrons. As the electrostatic force is distance dependent, the closer the electrons are to the nucleus, the more tightly they are bound and the lower in energy they will be. This concept is called **penetration**. Below, you can

see that the electrons in the 1s orbital have a very high probability of being close to the nucleus while those in the 3s orbital are far more likely to be significantly further away. Similarly, electrons in the 2s orbital are lower in energy than those in the 2p orbital as a result of increased probability that the former are closer to the nucleus. A quantification of this effective attractive force experienced by an electron is called the effective nuclear charge, Z_{eff} . The more an electron is **shielded** from the nucleus by electrons closer to the nucleus than it, the lower Z_{eff} will be. Roughly, $Z_{\text{eff}} = Z - S$, where Z is the atomic number and S is the number of core electrons. So for calcium, $Z_{\text{eff}} = 20 - 18 = 2$. The energy of the electron is proportional to Z_{eff}^2/n^2 , where n is the principal quantum number.

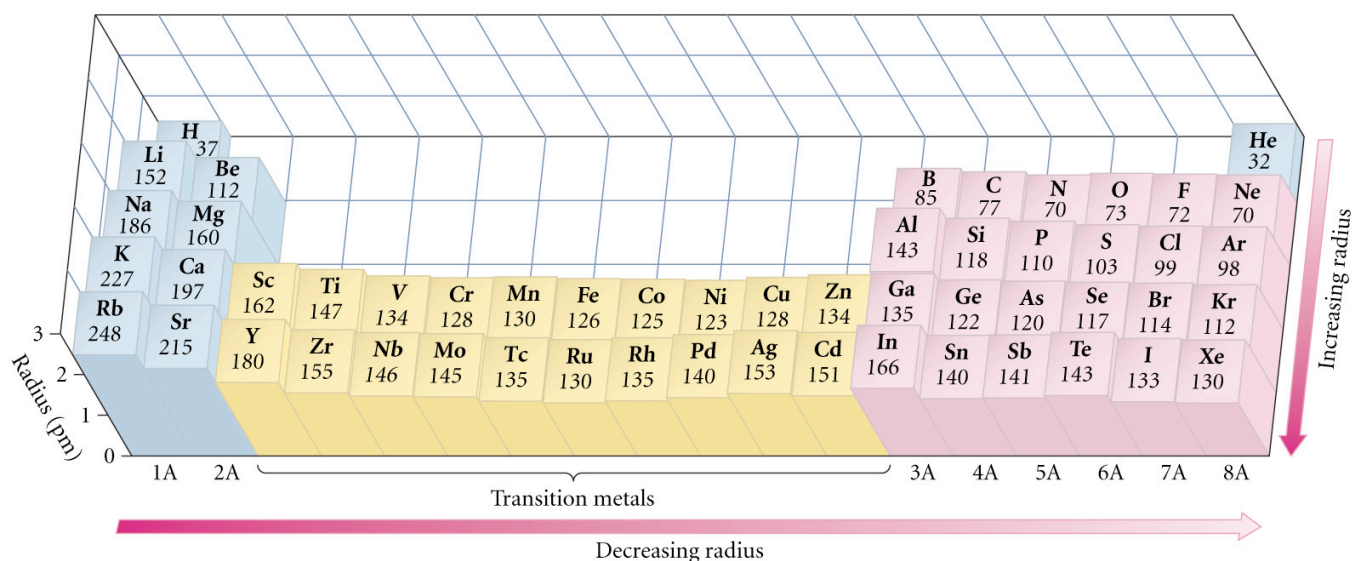


From the image above, we can now see that the 4s electrons penetrate closer to the nucleus than the 3d electrons and so are lower in energy. This is why potassium and calcium precede scandium in the periodic table. However, from scandium through zinc, the 3d electrons actually become lower in energy than the 4s electrons, which helps to explain the reactivity of these elements. In molecular complexes involving d-block metals, all valence electrons are in the d-shell.

3. TRENDS ACROSS THE D-BLOCK

Within the d-block, all the elements are solid at ambient temperature, with the exception of mercury. All d-block elements are naturally occurring with the exception of technetium, which is man-made. Unlike p-block elements, most d-block elements can adopt a wide range of oxidation states. There are many general trends that can be discerned across the d-block of elements. Both atomic and ionic radii tend to decrease upon going from left to right across the period and also up the group. The observed trend is due to an increase in Z_{eff} with increasing atomic number. This trend is commonly known as the **d-block (or scandide) contraction**, which is a result of the poor shielding of the nuclear charge of d-electrons. A similar situation occurs between the 4d and 5d elements, where there likewise the f-electrons in 5d elements are very poorly shielded and therefore there is a **lanthanoid contraction**. This explains the similar atomic radii of the 4d and 5d elements. The observed increase in atomic radii for d^8 , d^9 and d^{10} elements is due to increased electron-electron repulsion.

Trends in Atomic Radius



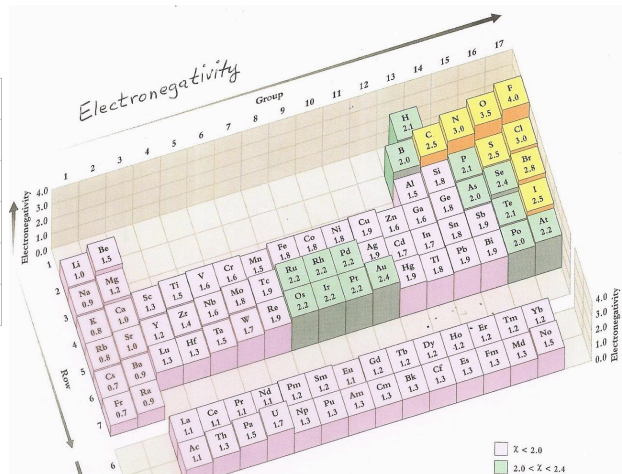
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Ionization potentials (IPs) measures the amount of energy required to remove an electron from an atom or ion. IPs therefore measure how strongly the atom or ion holds onto its electronics. IPs are proportional to $(Z_{\text{eff}})^2/n^2$ (where n is the principal quantum number). Generally, the first IP is smaller than the second, which is smaller than the third (and so on). As one removes electrons it takes more energy to remove the remaining electrons, which are themselves at lower energies as they are core electrons. The effect of increasing Z_{eff} across the period is partially mitigated by the increased shielding of the additional electrons. However, there are much smaller increases observed across the group, which is another manifestation of the lanthanoid contraction.

1	375.7 kJ/mol																2372.3 kJ/mol	
1	H 1312.0											He 2372.3						
2	Li 520.2	Be 899.5											B 800.6	C 1086.5	N 1402.3	O 1313.9	F 1681.0	Ne 2080.7
3	Na 495.8	Mg 737.7											Al 577.5	Si 786.5	P 1011.8	S 999.6	Cl 1251.2	Ar 1520.6
4	K 418.8	Ca 589.8	Sc 633.1	Ti 658.8	V 650.9	Cr 652.9	Mn 717.3	Fe 762.5	Co 760.4	Ni 737.1	Cu 745.5	Zn 906.4	Ga 578.8	Ge 762.2	As 944.5	Se 941.0	Br 1139.9	Kr 1350.8
5	Rb 403.0	Sr 549.5	Y 599.9	Zr 640.1	Nb 652.1	Mo 684.3	Tc 702	Ru 710.2	Rh 719.7	Pd 804.4	Ag 731.0	Cd 867.8	In 558.3	Sn 708.6	Sb 830.6	Te 869.3	I 1008.4	Xe 1170.3
6	Cs 375.7	Ba 502.9	La 538.1	Hf 658.5	Ta 728.4	W 758.8	Re 755.8	Os 814.2	Ir 865.2	Pt 864.4	Au 890.1	Hg 1007.1	Tl 589.4	Pb 715.6	Bi 703.0	Po 812.1	At	Rn 1037.1
7	Fr 393.0	Ra 509.3	Ac 498.8	Rf 580	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
Lanthanides	Ce 534.4	Pr 528.1	Nd 533.1	Pm 538.6	Sm 544.5	Eu 547.1	Gd 593.4	Tb 565.8	Dy 573.0	Ho 581.0	Er 589.3	Tm 596.7	Yb 603.4	Lu 523.5				
Actinides	Th 608.5	Pa 568	U 597.6	Np 604.5	Pu 581.4	Am 576.4	Cm 578.1	Bk 598.0	Cf 606.1	Es 619	Fm 627	Md 635	No 642	Lr 472.8				

Electron affinity (EA) is a measure of the amount of energy gained when a gaseous atom gains an electron. Elements with high EAs can easily accommodate an extra electron where in accommodating that extra electron, the element benefits from a more stable electron configuration. For instance, group 17 elements, in gaining an electron, now would have noble gas configurations. Groups 6 and 11 similarly have higher EAs as upon gaining the electron, they would fill their 4s orbitals (in addition to the half-filled and fully filled d orbitals, respectfully). EA tends to increase from left to right along the periodic table.

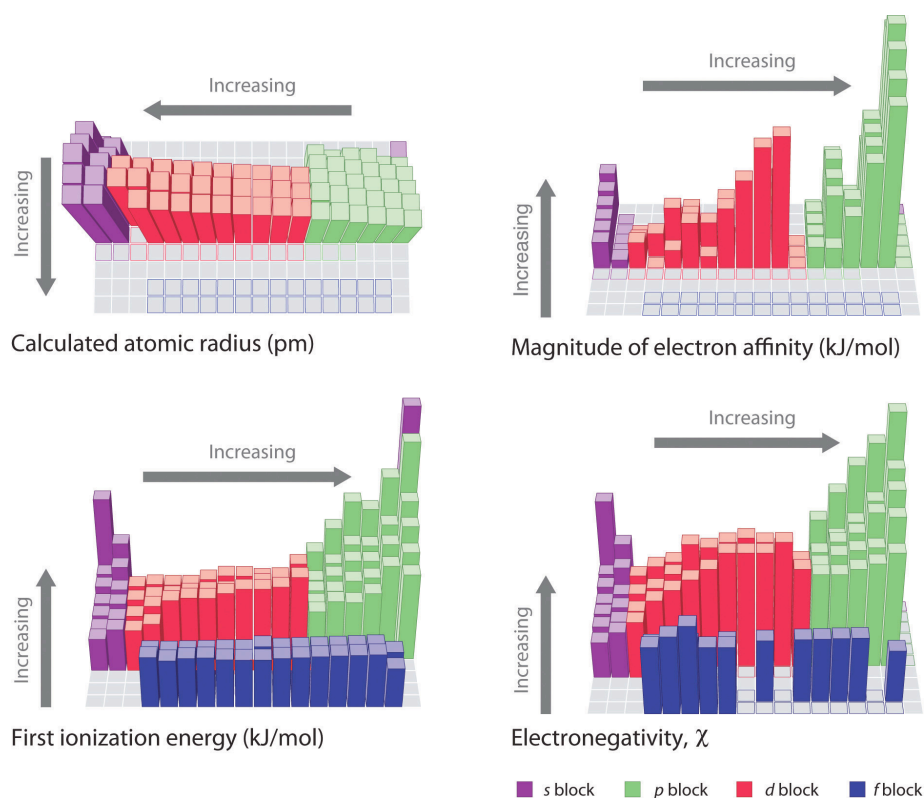
Electron Affinity (kJ/mol)																						
Legend: ≥ 0 kJ/mol (light purple) to -348.6 kJ/mol (dark purple)																						
1																	18					
1	H																He					
2	Li	Be															B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar				
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup							
Lanthanides: Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu																						
Actinides: Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr																						



The electronegativity (X) of an element is the power of an atom of the element to attract electrons to it when it is part of a compound. The most electronegative element is fluorine while the least electronegative elements are cesium and francium. A polarizable atom or ion is one with orbitals that lie close in energy. Large, heavy atoms and ions tend to be highly polarizable and so the trend in polarizability mirror those of atomic radii.

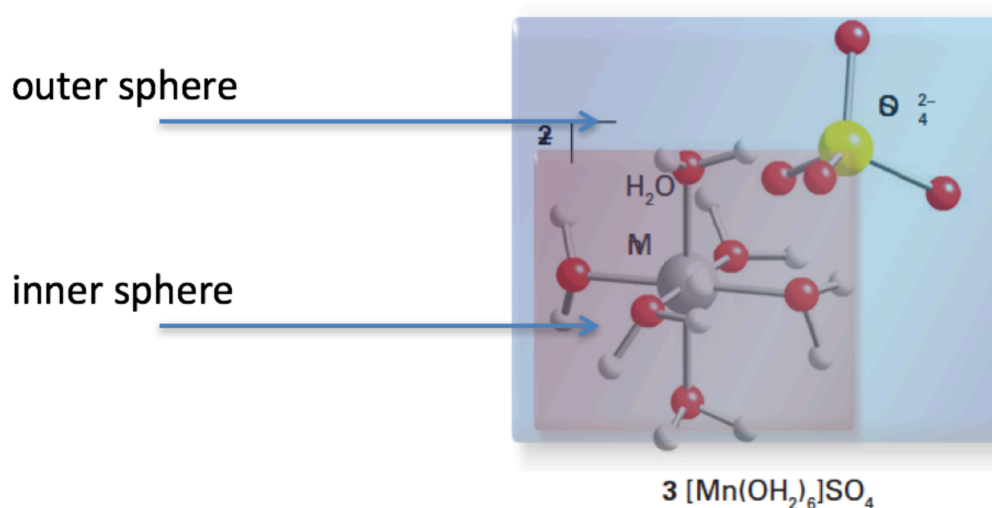
Finally, metallic character is defined as how easily an atom or ion of a particular element can lose an electron. It is therefore not surprising that trends in metallic character are the exact opposite of electronegativity.

Globally, trends are as illustrated below. We have explored explicitly here trends in atomic radius and IP. For a discussion of trends in electron affinity and electronegativity, please refer to your notes in CH2501.



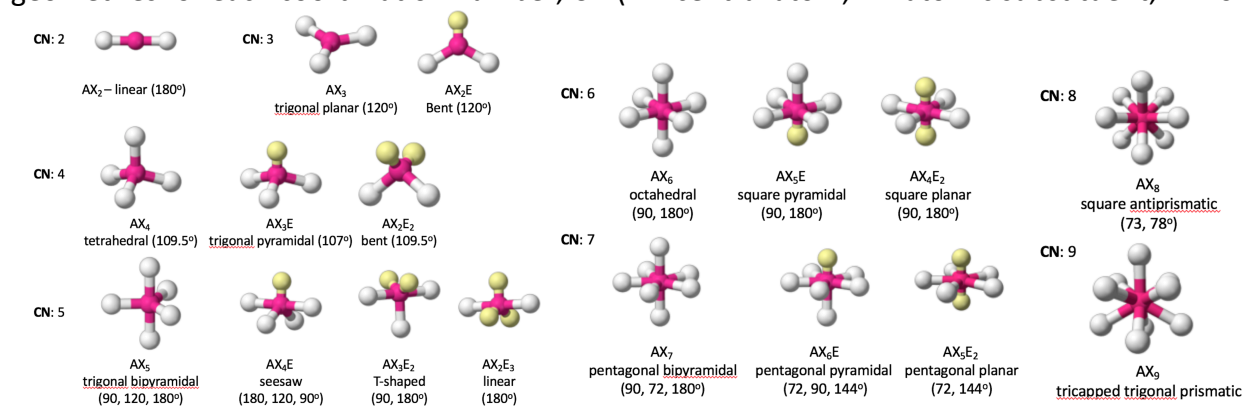
4. COORDINATION CHEMISTRY

Metal complexes, to a first approximation, are held together by electrostatic forces, where the **ligands** are negatively charged/polarized and the metal is positively charged. A coordination complex is composed of a metal, which acts as a Lewis acid and organic ligand molecules, which act as Lewis bases and coordinate to the metal. Those ligand directly bound to the metal are referred to as **inner sphere** whereas those molecules more loosely associated to the metal are termed **outer sphere** (see below).



We can use VSEPR theory to predict which geometries about a central atom, including metals, are most likely. VSEPR theory tells us that ligands about a metal will position themselves to be furthest apart from one another and from any other electron density present, such as from lone pairs. This theory works quite well for p-block molecules but not so well for transition metal compounds (for those Crystal

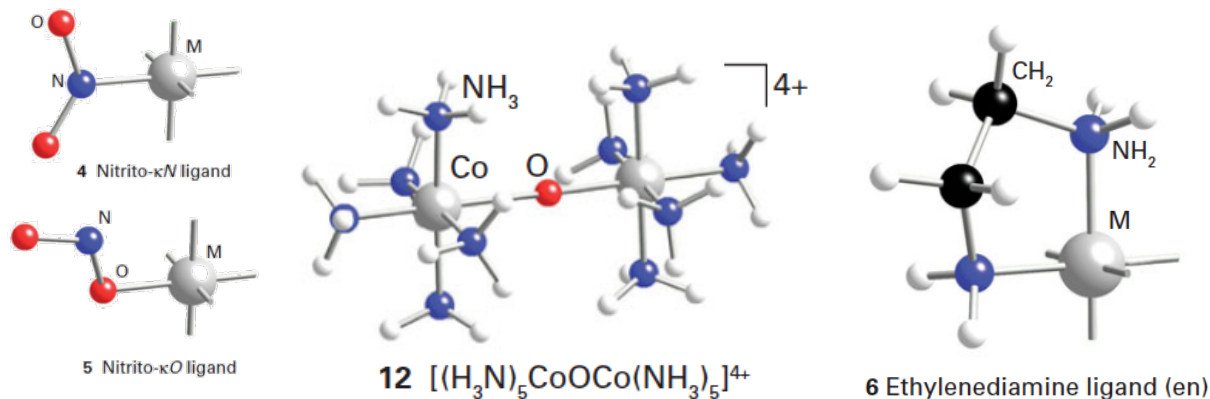
Field Theory does a better job). There are also some other exceptions. Below are the most common geometries for each coordination number, CN (A = central atom; X = atomic substituent; E = lone pair).



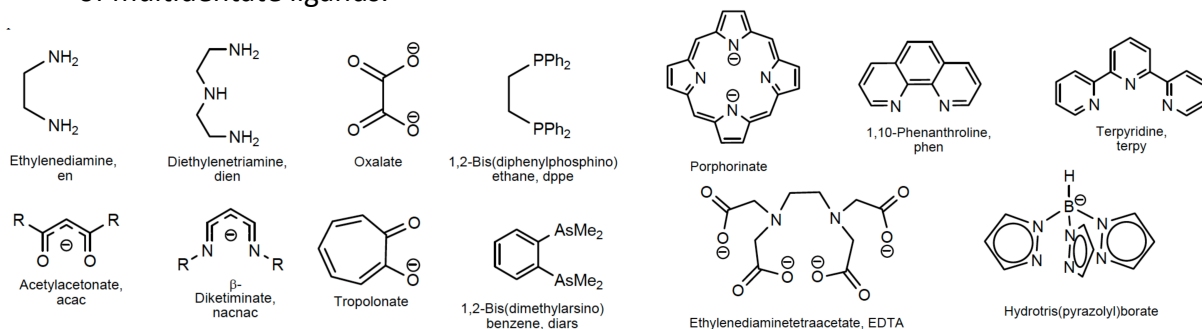
4.1 LIGAND CLASSIFICATION

The ligands that bind to metals can be classified based on their:

- ✓ **charge** – **anionic** (e.g., Cl^- , CN^- , OH^-), **cationic** (e.g., NO^+), **neutral** (e.g., CO , NH_3 , OH_2)
- ✓ **binding mode** – **terminal** (meaning attached to the metal through a single atom), **ambidentate** (meaning ligand can attached to the metal through different atoms), **bridging** (meaning a ligand that attaches to two or more metal centers). Ligands capable of ambidentate binding include NCS^- , CN^- and NO_2 . The Greek letter kappa (κ) is used to denote the atom that binds to the metal (see image below). The Greek letter mu (μ) is used to denote the atom that bridges two or more metals (see image below). If bridging more than two metals then a subscript with the number of metals bridged gets used (e.g., μ_3-O to indicate that the oxygen is bridging to three metals).



- ✓ **Chelate number** – **monodentate** (ligand only binds through one atom to one metal – e.g., NH_3 , H_2O , HS^- , RO^-), **bidentate** (ligand binds to metal through two different atoms – e.g., ethylenediamine, 1,10-phenanthroline, 2,2'-bipyridine)..., **polydentate**. Below is a small sampling of multidentate ligands.

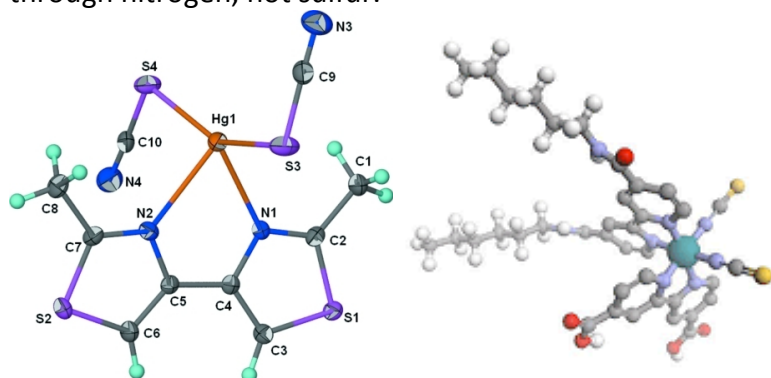


4.2 ISOMERISM IN TRANSITION METAL COMPLEXES

Just as you saw with organic compounds, transition metal complexes with the same molecular formula can exist in one of several different isomeric forms.

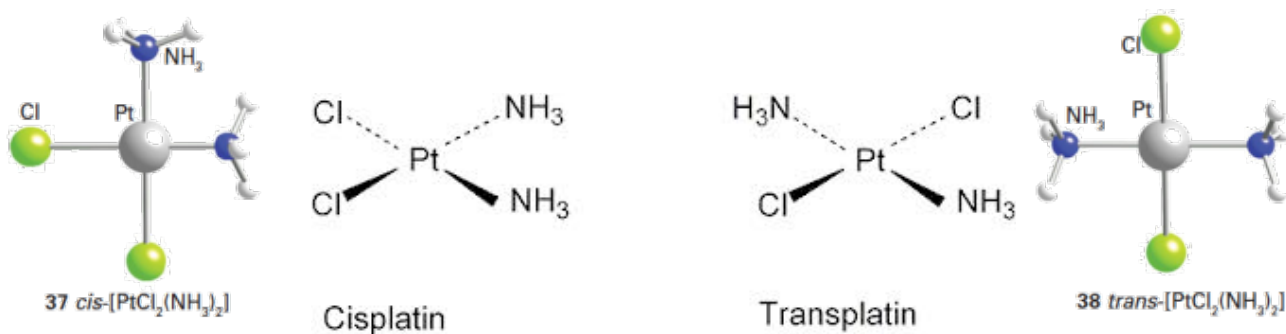
4.2.1 LINKAGE ISOMERISM

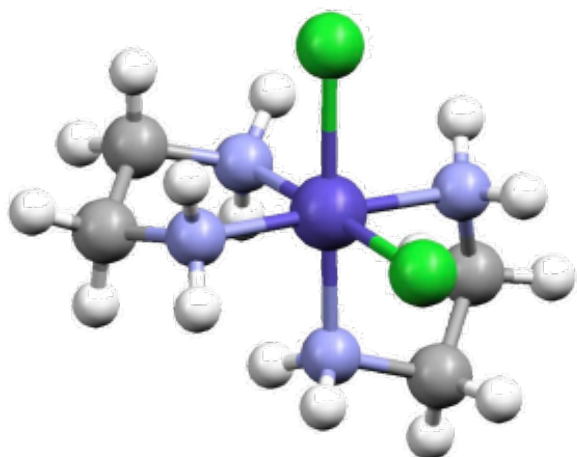
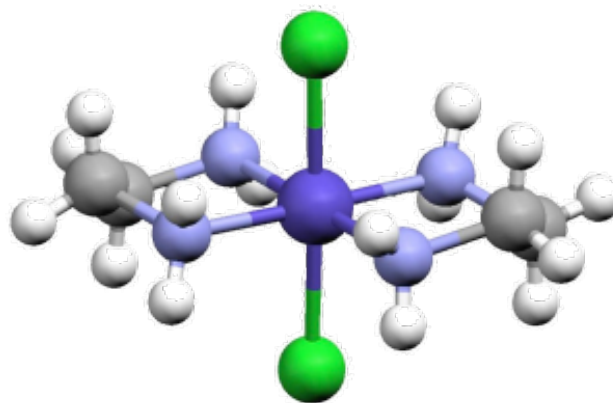
When an ambidentate ligand is used the linkage isomers correspond to the ligand binding through different atoms. For instance, the Hg complex below is the linkage isomer bound through the sulfur but the other linkage isomer would be the same complex with the SCN^- ligand bound through nitrogen. The Ruthenium complex (below, right) is an example of a linkage isomer with the same NCS^- ligand bound through nitrogen, not sulfur.



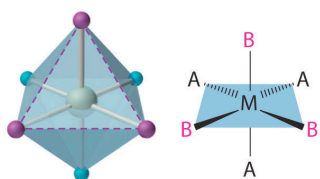
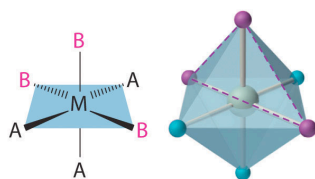
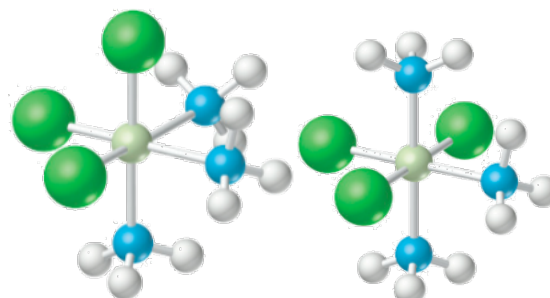
4.2.2 GEOMETRIC ISOMERISM

Geometric isomers differ in the configuration of the ligands about the metal, a concept similar to *cis*- and *trans*-alkenes. A classic example of this is the anti-cancer drug cisplatin and its geometric isomer (and far less potent compound), transplatin. Geometric isomers also exist in other geometries of metal complexes such as octahedral complexes.



 $cis-[Co(en)_2Cl_2]^+$  $trans-[Co(en)_2Cl_2]^+$

An important subset of geometric isomers are facial (*fac*) and meridional (*mer*) isomers. These isomers occur in octahedral complexes possessing two different ligands, each present three times. The facial isomer exists when all three of one ligand type exists on a single face of the octahedron. The meridional isomer exists when all three of one ligand type exists such that the plane generated between the three ligands slices through the metal center.

MA₃B₃ octahedral complex, *fac* isomerMA₃B₃ octahedral complex, *mer* isomer*fac*-[CoCl₃(NH₃)₃]*mer*-[CoCl₃(NH₃)₃]

4.2.3 IONIZATION ISOMERISM

These are isomers that are identical except that an inner sphere ligand(s) has exchanged with an outer sphere counterion(s). An example of this would be CoBr(H₂O)₅Cl vs [CoCl(H₂O)₅]Br.

4.2.4 SOLVATE ISOMERISM

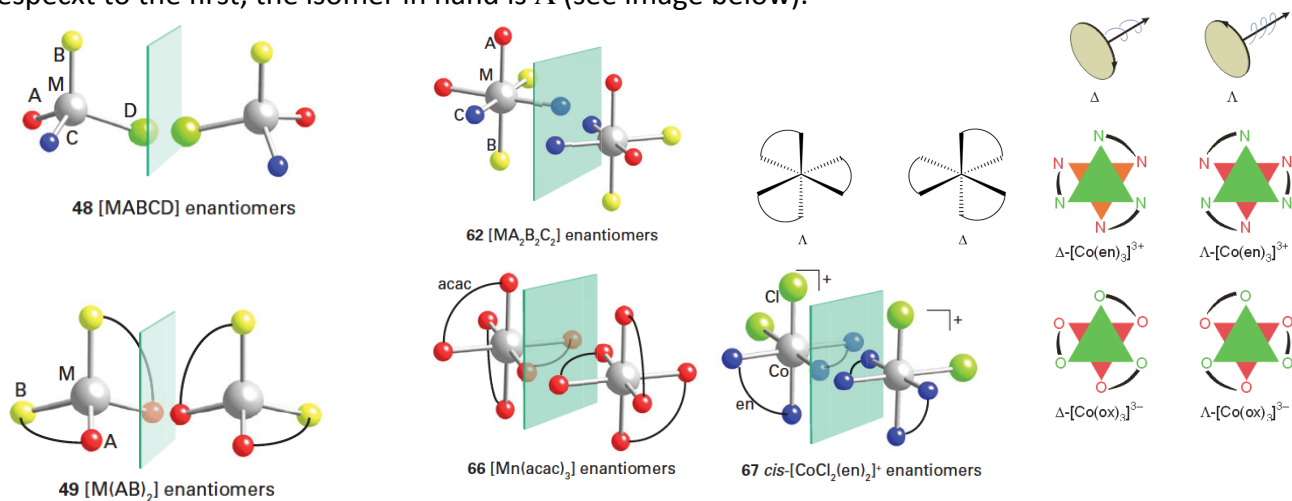
This is a special type of ionization isomerism where a ligand exchanges with a solvent molecule. An example of three different solvate isomers are: [CrCl₂(H₂O)₄]Cl·2H₂O vs [CrCl(H₂O)₅]Cl₂·H₂O vs [Cr(H₂O)₆]Cl₃.

4.2.5 COORDINATION ISOMERISM

These are isomers that contain both complex cations and anions wherein the ligands are exchanged between the two ions. For instance, compare the following three complexes, which are related through coordination isomerism: [Co(bpy)₂(CN)₂]⁺[Fe(bpy)(CN)₄]⁻ vs [Fe(bpy)₂(CN)₂]⁺[Co(bpy)(CN)₄]⁻ vs [Fe(bpy)₃]³⁺[Co(CN)₆]³⁻ (note that bpy here denotes the neutral ligand 2,2'-bipyridine).

4.2.6 OPTICAL ISOMERISM

Similar to organic compounds, non-superimposable mirror images of complexes produce enantiomers. Tetrahedral complexes possess optical isomers where the metal is the stereocenter just as organic molecules do. Octahedral complexes can also possess optical isomerism. Unlike the use of R and S to denote the stereochemistry of a tetrahedral carbon the two configurations of the metal are denoted delta (Δ) and lambda (Λ). These isomers occur when you have at least two (and usually three) of the same bidentate ligands about the metal. The easiest way to visualize which isomer is Δ or Λ is to orient the complex such that one of the atoms of the bidentate ligand is bound to the atom at the 12 o'clock position. Then if the other atom of the bidentate ligand is positioned clockwise with respect to the first the isomer in hand is Δ . If the other atom of the bidentate ligand is positioned counter-clockwise with respect to the first, the isomer in hand is Λ (see image below).

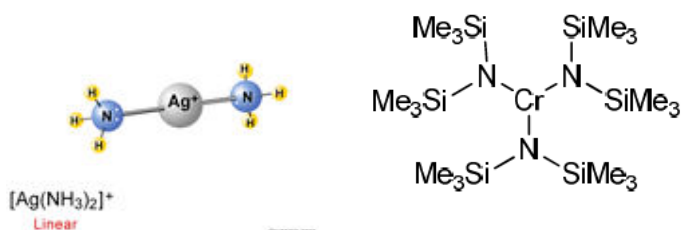


4.3 COORDINATION GEOMETRY

We already surveyed basic geometric modes surrounding a central atom in section 4. In this section, we revisit these concepts, except within the optic of transition metal complexes. For transition metals VSEPR theory does not work well and some geometries do not fit VSEPR theory. Often it is the d-electron configuration that determines the geometry.

4.3.1 2-COORDINATE COMPLEXES

Often found for Group 11 ions such as Cu⁺, Ag⁺ and Au⁺ and other d₁₀ metals such as Pt⁰; frequently with bulky ligands. **Geometry:** linear (see below for Ag example). **Symmetry:** D_{∞h}.

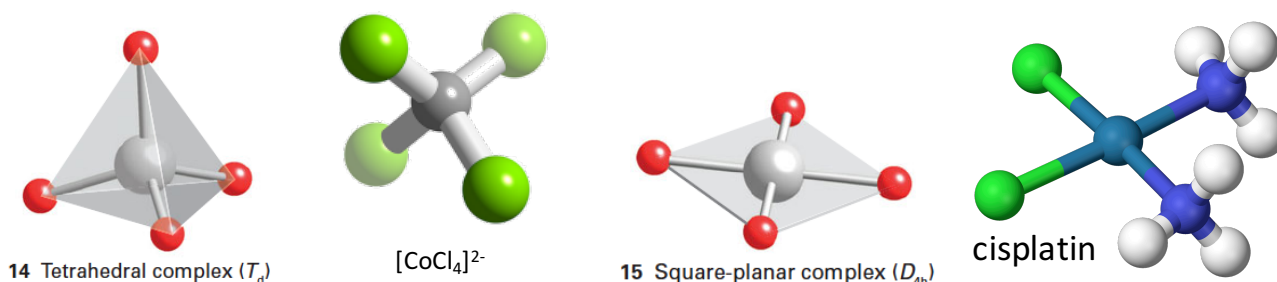


4.3.2 3-COORDINATE COMPLEXES

Rarely found amongst metal complexes and requires bulky ligands. **Geometry:** trigonal planar (see above for Cr example). **Symmetry:** D_{3h} with three identical ligands.

4.3.3 4-COORDINATE COMPLEXES

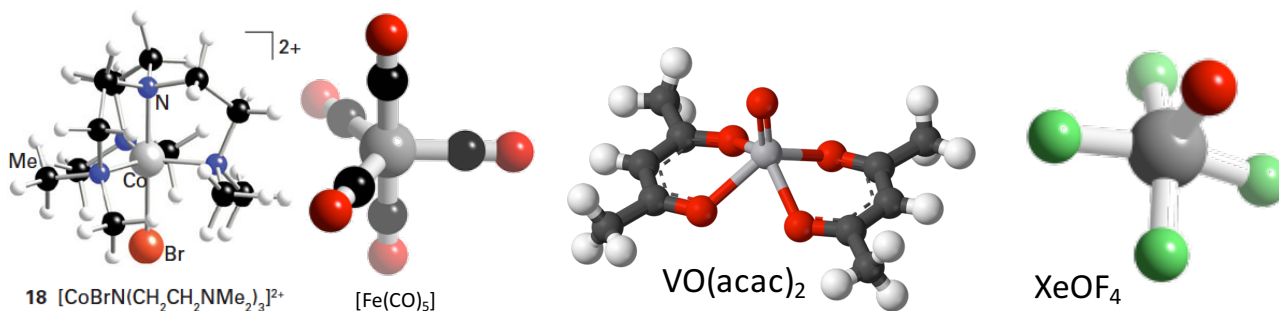
Geometry: tetrahedral. **Symmetry:** T_d . This geometry is favoured over higher coordinate complexes when the metal is small or the ligands are large. Very common geometry and especially common with d^5 and d metal complexes.



Geometry: square planar. **Symmetry:** D_{4h} . This geometry is typically observed for d^8 Group 10 metal complexes such as Pd^{II} or Pt^{II} or d^9 Group 11 metal complexes, especially so for 2nd and 3rd row elements.

4.3.4 5-COORDINATE COMPLEXES

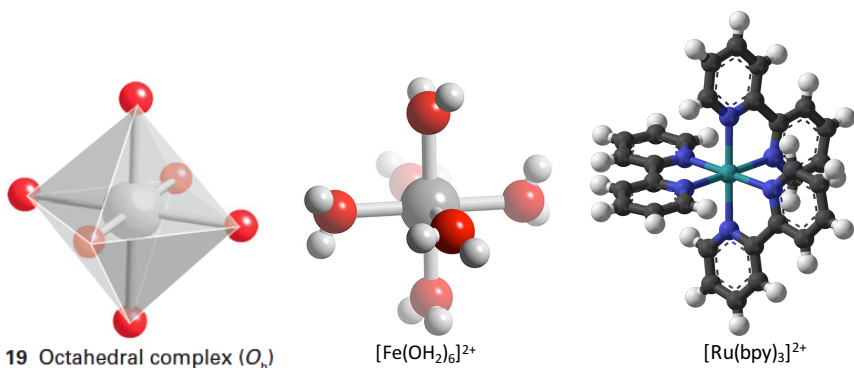
Geometry: trigonal bipyramidal. **Symmetry:** D_{3h} , if all the ligands the same. This geometry is less common than 4- or 6-coordinate complexes. Distortions from this geometry are common. This geometry minimizes ligand-ligand repulsion (see left two examples below).



Geometry: square pyramidal. **Symmetry:** C_{4v} if all the ligands the same. This geometry occurs when conformational constraints exist with multidentate ligands (see right two examples above).

4.3.5 6-COORDINATE COMPLEXES

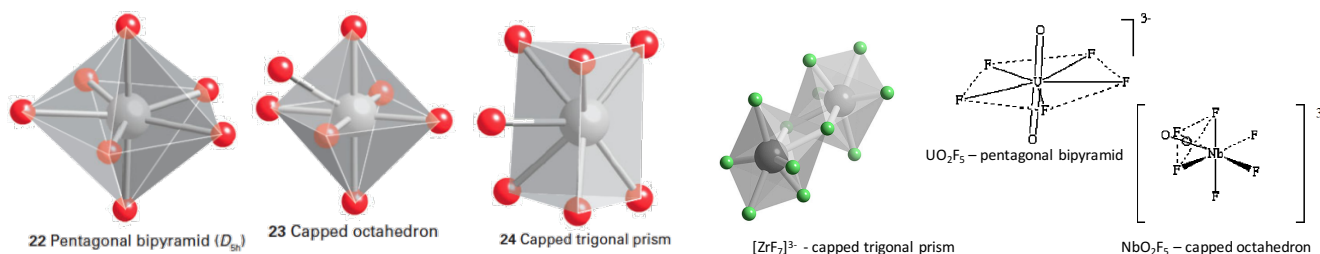
Geometry: Octahedral. **Symmetry:** O_h , if all the ligands the same. This geometry is by far the most common for 6-coordinate complexes. Octahedral complexes are highly symmetric.



Distortions from this geometry lead to complexes of lower symmetry. These include tetragonal (D_{4h}), rhombic (D_{2h}), trigonal (D_{3d}), trigonal prismatic (D_{3h}).

4.3.6 7-COORDINATE COMPLEXES

Geometries: Pentagonal Bipyramidal, Capped Octahedron and Capped Trigonal Prism. These geometries are encountered mainly with larger cations – 4d and 5d complexes.



4.4 NOMENCLATURE OF COORDINATION COMPLEXES

IUPAC governs the rules surrounding the names of chemical compounds. By following the step-by-step instructions below in the right order, you will be able to name any coordination complex.

1. Order of Listing Ions – cation first then anion

- $[\text{Cr}(\text{NH}_3)_6][\text{NO}_3]_3$ hexaamminechromium (III) nitrate
- $\text{K}_2[\text{PtCl}_6]$ potassium hexachloroplatinate (IV)

2. Nonionic complexes are given a one-word name

- $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$ triamminetrinitrocobalt (III)

3. Names of ligands – neutral ligands are named as the molecule; negative ligands end in – o and positive ligands end in – ium

- $\text{C}_5\text{H}_5\text{N}$ – pyridine
- $(\text{C}_6\text{H}_5)_3\text{P}$ – triphenylphosphine
- Cl^- – chloro
- CH_3CO_2^- – acetato
- NH_2NH_3^+ – hydrazinium

4. Order of ligands – alphabetical

- $[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]\text{SO}_4$ tetraamminechloronitroplatinum (IV) sulfate

5. Numerical prefixes – go before ligand to indicate number (di, tri, tetra etc. but bis, tris, tetrakis used before complex names

- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{SO}_4$ dichlorobis(1,2-diaminoethane) cobalt (II) sulfate

6. Termination of names – Anionic complexes end in –ate; otherwise nothing special

- $\text{Ca}_2[\text{Fe}(\text{CN})_6]$ calcium hexacyanoferrate (II)
- $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$ hexaaquairon (II) sulfate

7. Oxidation states – Designated by a roman numeral in () at the end of the name of the complex

Here are some further examples of naming complexes.

diamminesilver(I) chloride, $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$

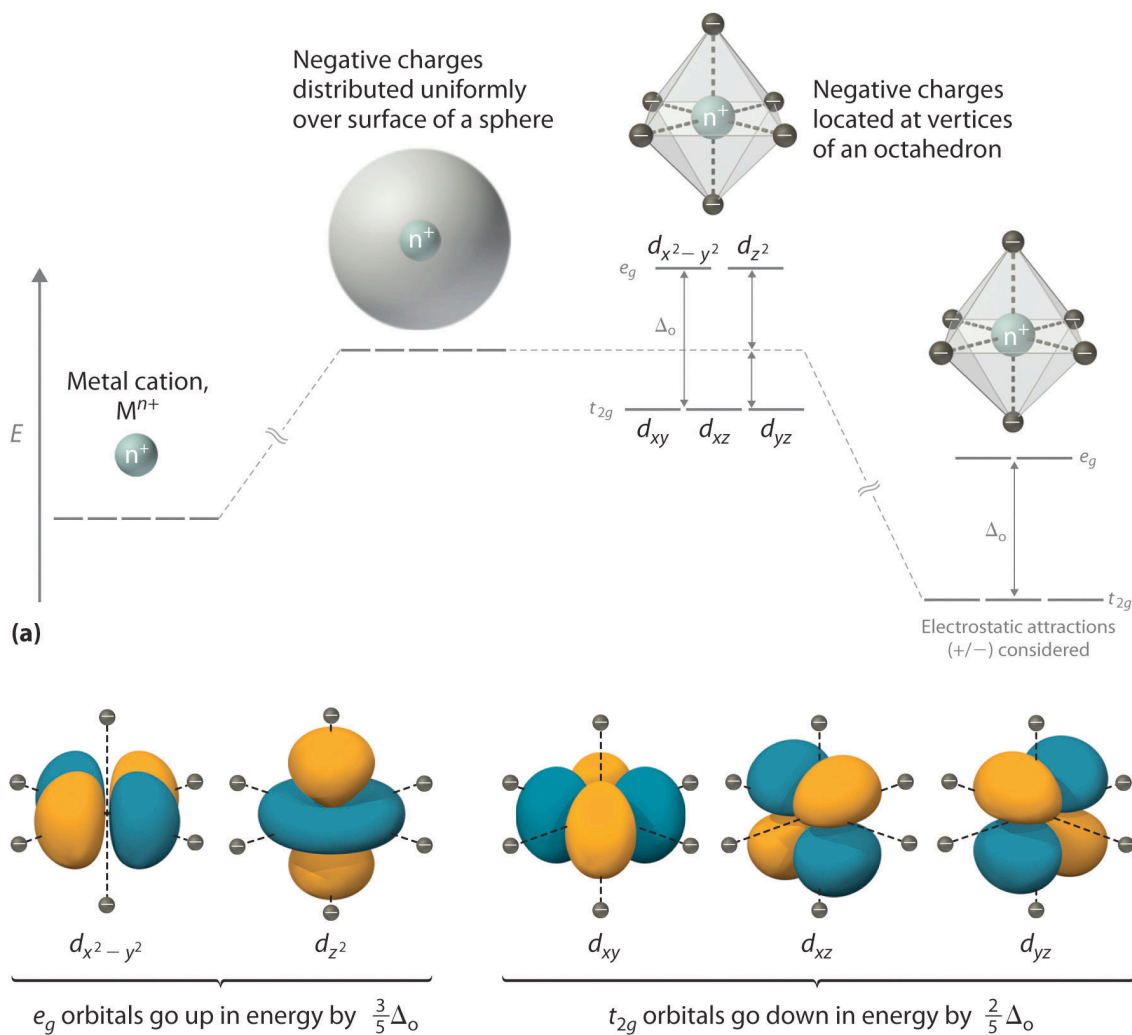
hexaamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

amminebromochloromethylamineplatinum(II), $[\text{Pt}(\text{NH}_3)\text{BrCl}(\text{CH}_3\text{NH}_2)]$

dichlorobis(ethylenediamine)cobalt(III), $[\text{Co}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2\text{Cl}_2]^+$

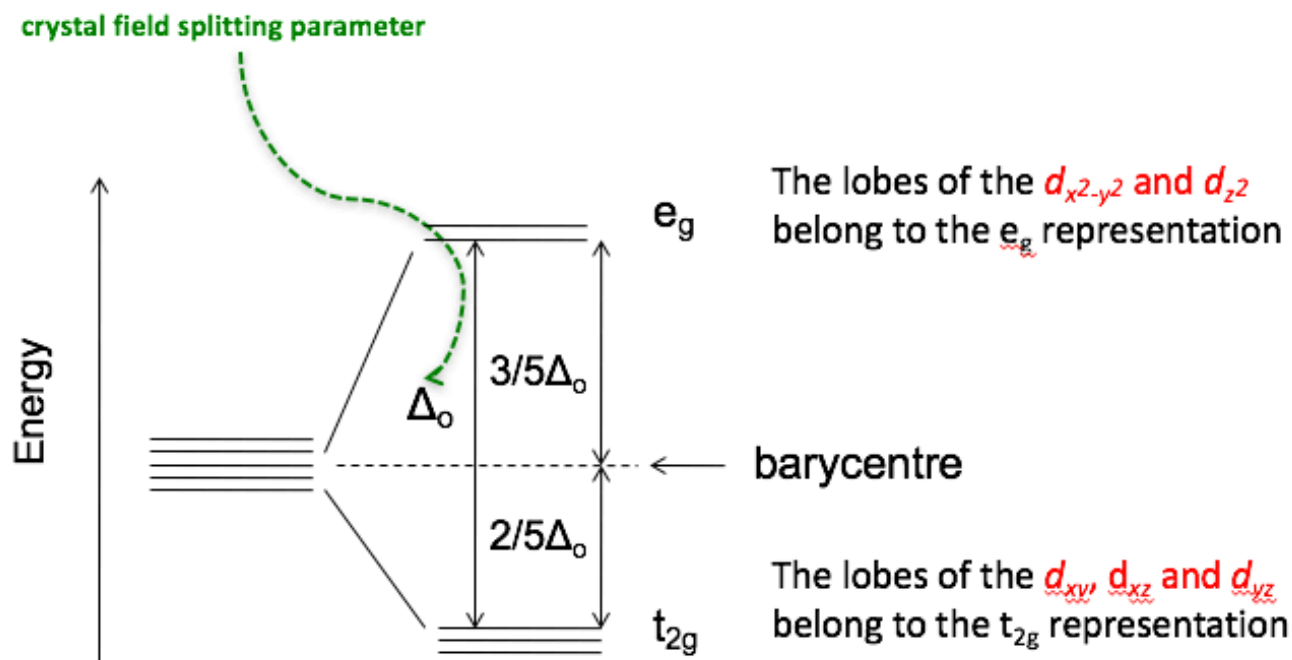
5. CRYSTAL FIELD THEORY

Two theories are commonly used to rationalize the electronic, optical and magnetic properties of complexes. They are: Crystal Field Theory (CFT) and Ligand Field Theory (LFT). We will study both in turn. CFT emerged from an analysis of the spectra of d-metal ions in the solid state. CFT assumes that complexes are held together *via* electrostatic forces between the positively charged metal and the negatively charged or polarized ligands. CFT models these interactions based on electrostatics with the valence electrons of the metal in the d-orbitals and the ligands as negative charges (ion-ion interactions) or dipoles (ion-dipole) interactions (IONIC bonding model). Stronger repulsive interactions between the electrons of the metal and the electrons of the ligands result in greater destabilization of those electrons. The energy difference of d-orbitals correlates with the optical, magnetic and thermodynamic properties of the complex.



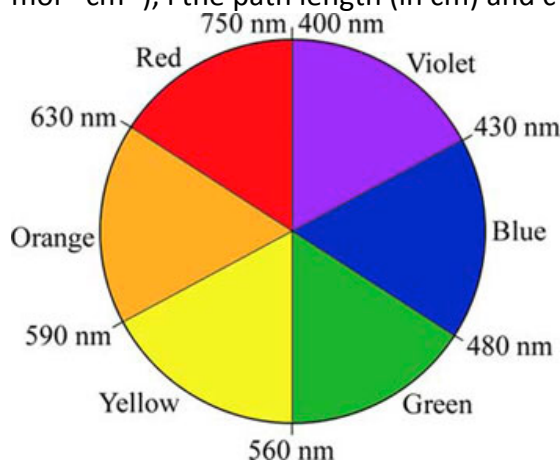
Starting on the left-hand side of the diagram, the metal cation with its d-electrons is at a particular energy. Now assume that the spherically distributed ligands approach the metal and that the metal-based electrons are also spherically distributed. As these negative charges approach, they will be repulsed by the d-electrons of the metal, leading to a destabilization of these d-electrons. Now, if we know that there are six ligands present, the geometry must be octahedral. We further know that the d-electrons of the metal are not spherically distributed but that they reside in one of five d-orbitals, each of certain symmetry. These are shown above and are known as the $d_{x^2-y^2}$, d_{z^2} , d_{xy} , d_{xz} and d_{yz} orbitals. Notice that the electron density distribution of the lobes of the $d_{x^2-y^2}$ and d_{z^2} orbitals are oriented along the axes while those of the d_{xy} , d_{xz} and d_{yz} orbitals are oriented as to bisect the axes. Now, as the ligand negative charges approach along the axes, they will interact more with the $d_{x^2-y^2}$ and d_{z^2} orbitals and these will be destabilized. Within CFT, there must be a compensatory stabilization such that the total energy of the d-electrons remains the same. So as the electrons present in the $d_{x^2-y^2}$ and d_{z^2} orbitals are destabilized, so must the electrons present in the d_{xy} , d_{xz} and d_{yz} orbitals be stabilized. The energy difference between these two sets of orbitals (referred to as the e_g and t_{2g} sets, respectively, based on their relative symmetries, is known as Δ_o (aka 10Dq). To account for the fact that two orbitals are destabilized while three orbitals are stabilized while maintaining the overall energy the same (around what is called the **barycenter**), the e_g set must be destabilized by $0.6\Delta_o$ while the t_{2g} set must be stabilized by $0.4\Delta_o$. Finally, if we now take into account the attractive force of the cationic metal, the overall energy of the d-electrons decreases.

The energy difference between the resulting electron distribution in an octahedral ligand field and that for all electrons within a uniform field is called the **crystal field stabilization energy (CFSE)**. The crystal field stabilization energy (or Ligand Field stabilization energy, LFSE when talking about Ligand Field Theory, below) is a measure of the net energy of occupation of the d orbitals relative to their mean energy.



5.1 CRYSTAL FIELD THEORY: OPTICAL PROPERTIES OF COORDINATION COMPLEXES

In many coordination complexes, including most 3d-metal complexes, the energy difference defined by Δ_o falls coincident with the visible part of the electromagnetic spectrum. This means that if a photon of light is absorbed equivalent to Δ_o in an octahedral complex, one of the d-electrons in the t_{2g} set will be excited into the e_g set and the compound will be coloured. The colour of the complex you would see with your eye will be the complement of the colour absorbed. So, a complex that absorbs green light will appear red to the eye (see colour wheel and table below). The intensity of the colour observed is governed by the Beer-Lambert Law, where $A = \epsilon lc$, with A the absorbance, ϵ the molar absorptivity (in $\text{L mol}^{-1} \text{cm}^{-1}$), l the path length (in cm) and c the concentration (in mol L^{-1}).



Absorbed Color	λ (nm)	Observed Color	λ (nm)
Violet	400	Green-yellow	560
Blue	450	Yellow	600
Blue-green	490	Red	620
Yellow-green	570	Violet	410
Yellow	580	Dark blue	430
Orange	600	Blue	450
Red	650	Green	520

It is important to recall two important selection rules that govern the intensity of the absorption spectra for coordination complexes.

1. $\Delta S = 0$ – The spin selection rule
2. $\Delta l = \pm 1$ – The orbital selection (Laporte Rule) - *Strictly true only if molecule has a centre of symmetry*. Practically speaking, transitions can only occur if there is a change in parity. This means $g \rightarrow g$ or $u \rightarrow u$ transitions are not allowed in an O_h field since an octahedron has a centre of symmetry, which effectively means no $d \rightarrow d$ (or $f \rightarrow f$) transitions are allowed since all d and f derived orbitals have g parity

For a typical spin-allowed but Laporte forbidden transition in an octahedral complex, expect $\epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$. For a typical spin-forbidden and Laporte forbidden transition in an octahedral complex, expect $\epsilon < 10 \text{ M}^{-1} \text{ cm}^{-1}$.

There are three mechanisms that allow ‘forbidden’ electronic transitions to become somewhat ‘allowed’ resulting in some intensity of the color expected.

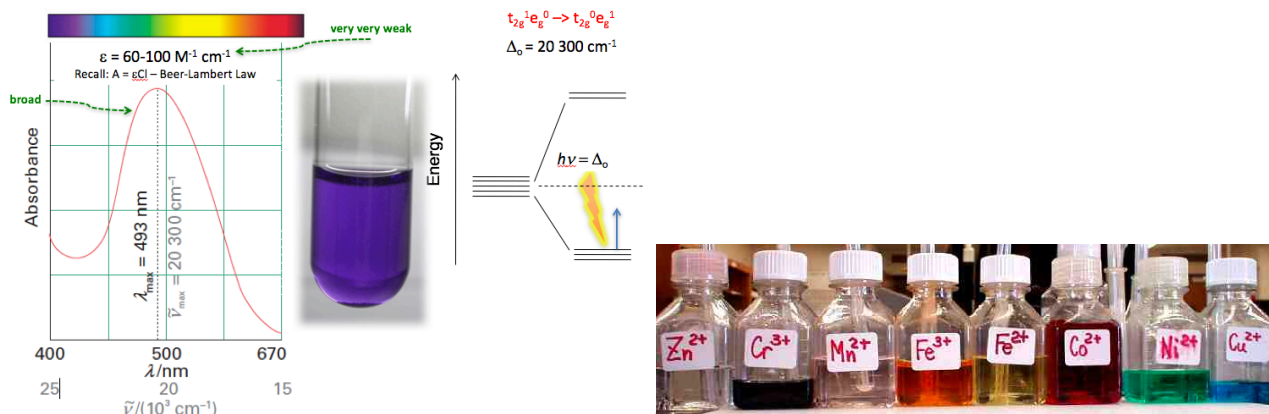
1) Vibronic Coupling: During some unsymmetrical vibrations of a molecule there can be a temporary/transient loss of the centre of symmetry. Loss of center of symmetry helps to overcome the Laporte selection rule. The time required for an electronic transition to occur (lifetime 10^{-18} s) is much less than the time required for a vibration to occur (lifetime 10^{-13} s).

2) Mixing of states: The states in a complex are never pure, and so some of the symmetry properties (g or u) of neighboring states become mixed into those of the states involved in a ‘forbidden’ transition. For example mixing of d (gerade) and p (ungerade) orbitals results in partial breakdown of the Laporte rule.

3) Spin orbit coupling: Partial lifting of the spin selection rule is possible when there is coupling of the spin and orbital angular momentum, known as the spin-orbit coupling (common in heavier transition metals).

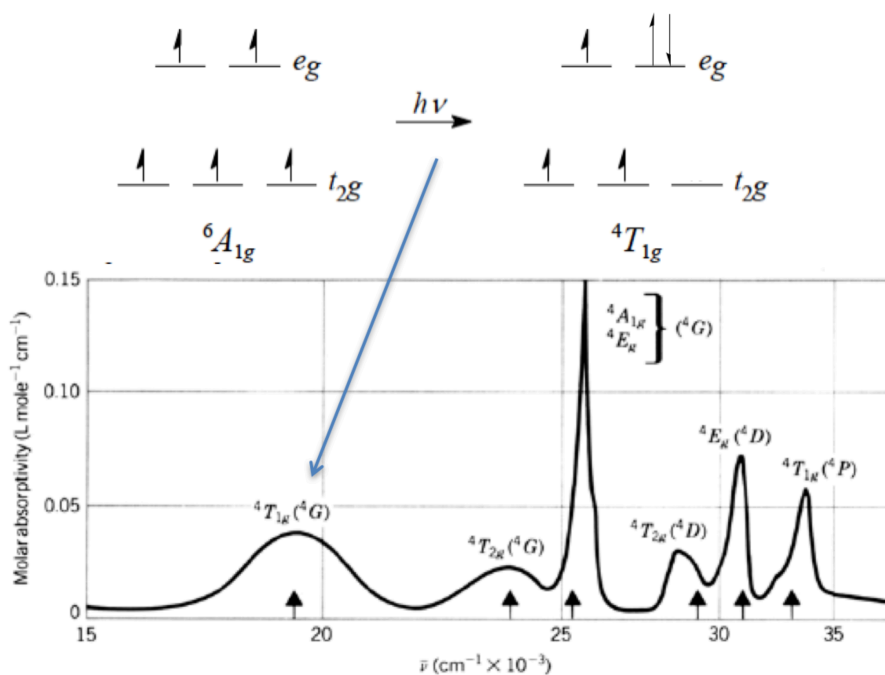
5.1.1 CRYSTAL FIELD THEORY: OPTICAL PROPERTIES OF $[\text{Ti}(\text{OH}_2)_6]^{3+}$

$[\text{Ti}(\text{OH}_2)_6]^{3+}$ contains a Ti^{3+} metal with a single d electron in one of the 3 degenerate t_{2g} orbitals. This complex absorbs blue-green light, equivalent to Δ_o , promoting excitation of the electron to an unoccupied e_g orbital. The absorption is weak (notice the molar absorptivity values) as this absorption is Laporte forbidden (d - d transition). The absorption is broad as the ligands vibrate about the metal. This means their distance from the metal center varies so that Δ_o will also vary. This means the energy of light absorbed will vary hence the broadness of the absorption.



5.1.2 CRYSTAL FIELD THEORY: OPTICAL PROPERTIES OF $[\text{Mn}(\text{OH}_2)_6]^{2+}$

$[\text{Mn}(\text{OH}_2)_6]^{2+}$ is a d^5 high-spin octahedral complex with a very pale pink colour, owing to a series of weak spin-forbidden transitions (in addition to Laporte forbidden) – *notice magnitude of ϵ !* The fact that there is > 1 d electron in the complex means that the absorption spectrum becomes complicated because of the presence of multiple electronic transitions (not just the d-d transition, which is the lowest energy transition).



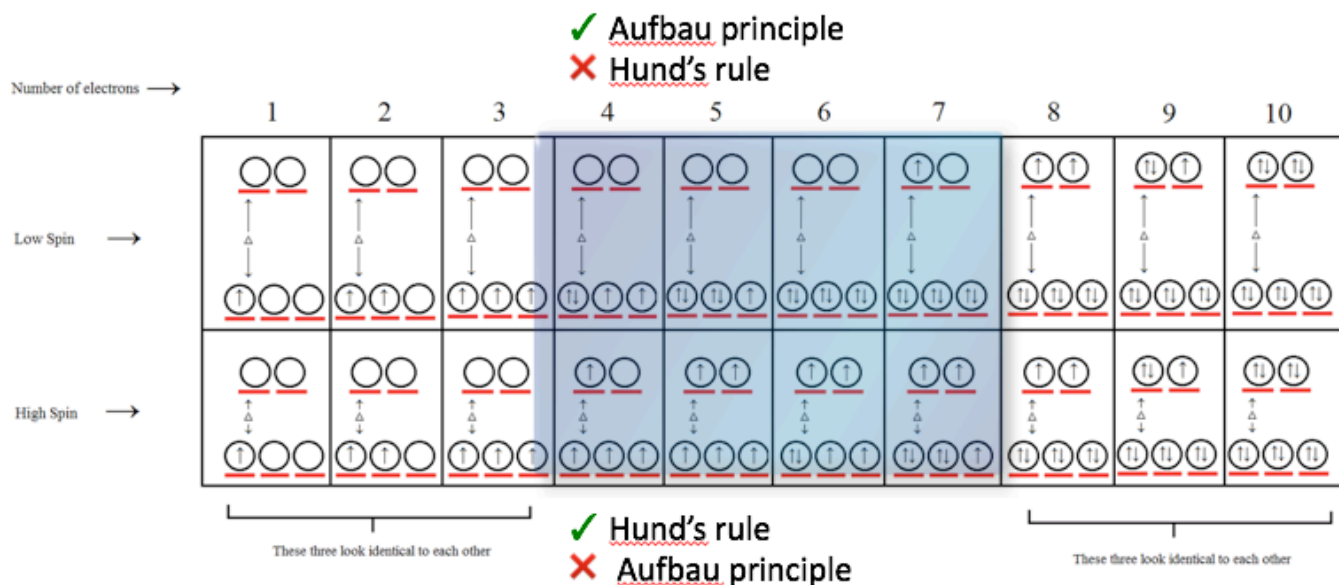
5.2 CRYSTAL FIELD THEORY: RULES FOR FILLING d ORBITALS

There are three rules that must be adhered to when filling orbitals (any orbital) with electrons.

Rule 1: The Pauli exclusion principle: No two electrons can have all four quantum numbers the same. i.e. two electrons in the same orbital **MUST** have opposite spin

Rule 2: The Aufbau Principle: Electrons populate the lowest energy orbitals first

Rule 3: Hund's rule: Electrons occupy degenerate orbitals as to maximize the number of parallel spins



These three rules are easy to follow until one is in a situation where there is a d^4 - d^7 metal complex. In these cases, if Hund's rule is prioritised then the 4th electron would need to be placed in one of the e_g orbitals. If the Aufbau principle is prioritised, then the 4th electron would need to be placed in one of the t_{2g} orbitals (of course the electron would have opposite spin to adhere to the Pauli exclusion principle). Both cases do exist and we term these complexes high spin (for filling e_g) and low spin (for filling t_{2g}), respectively. The term **high spin** refers to the larger number of unpaired electrons while the term **low spin** refers to the smaller number of unpaired electrons.

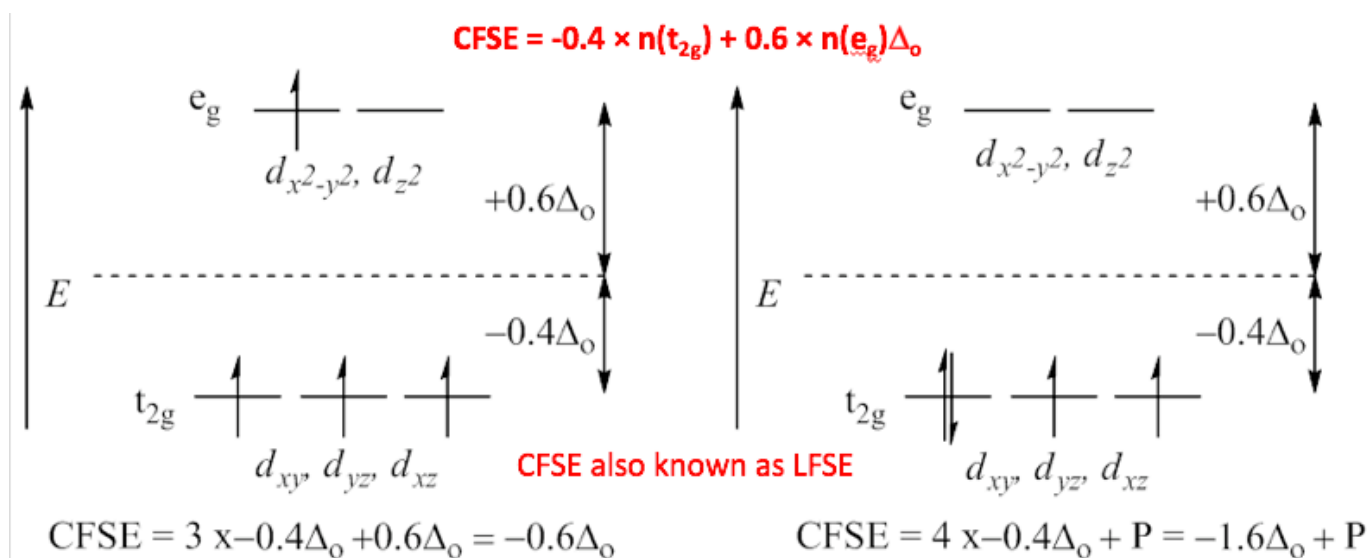
What defines whether a complex is high spin or low spin?

It all comes down to a balance between Δ_o and the pairing energy, P (the energy required to pair two electrons in an orbital)

- ✓ $\Delta_o < P$ – high spin
- ✓ $\Delta_o > P$ – low spin

For 1st row transition elements, P does not vary very much so it all comes down to Δ_o .

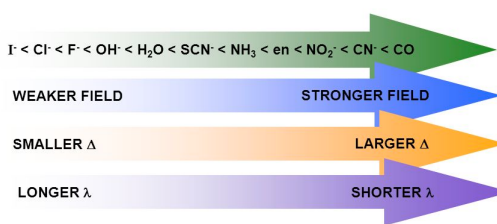
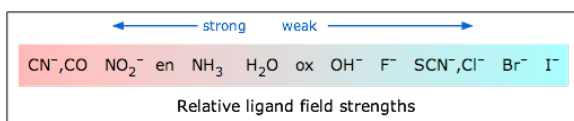
Whether a complex is high spin or low spin will have a dramatic effect on its properties, including the Crystal Field Stabilization Energy (CFSE), the magnetic moment and the heat of hydration.



5.2.1 CRYSTAL FIELD THEORY: RULES FOR FILLING *d* ORBITALS – HIGH SPIN OR LOW SPIN?

So if Δ_o is such an important parameter in determining whether a complex is high spin or low spin, what affects the magnitude of Δ_o ?

- The oxidation state of the metal
As the oxidation state increases, the attractive force between the ligands and the metal increases, which leads to a **larger** Δ_o .
- The row of the metal
As you go down the periodic table the orbitals become more diffuse, which results in greater interactions with the ligands and **larger** Δ_o AND the electrons are further away from each other leading to **smaller** P. For all 2nd and 3rd row complexes $\Delta_o > P$ and are all low spin.
- The nature of the ligand – the spectrochemical series.



5.3 CRYSTAL FIELD THEORY: SPIN-ONLY MAGNETIC MOMENT

Why are complexes called low spin or high spin? It comes from the spin only magnetic moment (μ) differences between the two electronic configurations. μ is a measure of the number of unpaired electrons. When there are unpaired electrons, this gives rise to paramagnetism, else the complex is diamagnetic.

Diamagnetism occurs for all compounds. It is associated with pairs of electrons and is a weak effect in which the compound is repelled by a magnetic field.

Paramagnetism occurs only when there are unpaired electrons. It is a larger effect than diamagnetism and electrons are attracted into a magnetic field.

It is possible to measure μ by comparing the mass difference of a sample weighed outside and within a magnetic field (using an instrument called a Gouy balance). Normally what is measured is the molar magnetic susceptibility, X_m by comparison with a standard sample, which is usually $\text{Hg}[\text{Co}(\text{SCN})_4]_2$

$\mu = 2.83(X_m T)^{1/2}$ with units of Bohr Magnetons (BM or μ_B), where T is the temperature of the sample in Kelvin

μ is based on the overall spin quantum number, S ($S = n/2$, where n = number of unpaired electrons) and the overall angular momentum quantum number, L

$$\mu_{S+L} = [4S(S+1) + L(L+1)]^{1/2}$$

For 1st row transition metal complexes L is normally very small and so the second term can be ignored and so the so-called spin-only magnetic moment can be calculated following:

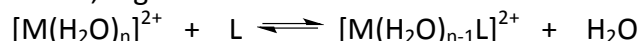
$$\mu = [4S(S+1)]^{1/2} = [n(n+2)]^{1/2}$$

Generally the fit between experiment and this calculation is very good (see table below for examples). For octahedral complexes the fit is good except for high spin d^6 and d^7 and low spin d^4 and d^5 . For tetrahedral complexes the fit is good except for d^3 , d^4 , d^8 and d^9 . In these cases an electron can move from one t_{2g} orbital to another, thus rotating around the metal and generating a magnetic field. This is the origin of the orbital contribution to the magnetic moment so in these cases the L term cannot be ignored.

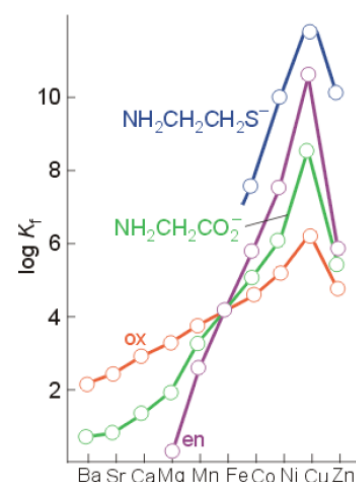
Ion	Number of unpaired electrons	S	$\mu_{s.o.} (\mu_B)$	Experiment
Ti^{3+}	1	1/2	1.73	1.7-1.8
V^{3+}	2	1	2.83	2.6-2.9
Cr^{3+}	3	3/2	3.87	~3.8
Mn^{3+}	4	2	4.90	4.8-4.9
Fe^{2+}	4	2	4.90	5.1-5.5
Fe^{3+}	5	5/2	5.92	~5.9

5.4 CRYSTAL FIELD THEORY: THE IRVING-WILLIAMS SERIES

The Irving-Williams Series (IWS) describes an empirical increase in stability of high spin M^{2+} octahedral complexes as a function of atomic radius, regardless of the nature of L for the following reaction:



The formation constant, K_f , varies along: $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$. The trend reflects the relative electrostatic effects felt by the complex. The smaller the metal with same charge = greater charge density and so the more tightly bound the incoming ligand, L. Based purely on electrostatics, we would expect

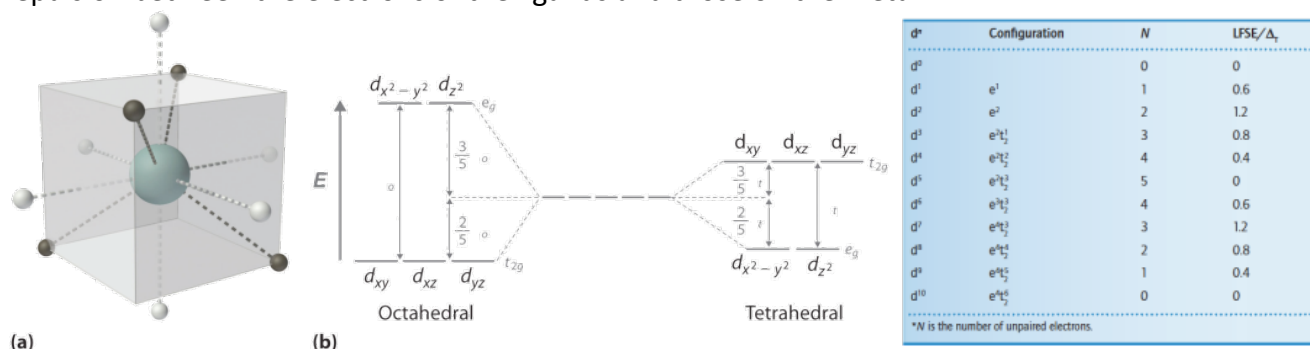


stabilities to vary as $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$, accordance with their respective ionic radii.

However, exceptionally Cu^{2+} is more stable than Ni^{2+} . This exception is due to the Jahn-Teller distortion, which effectively weakens the bonding of one of the departing water ligands while simultaneously strengthening the bonding of the incoming L ligand (see section 5.6 for a more detailed discussion on the Jahn-Teller distortion).

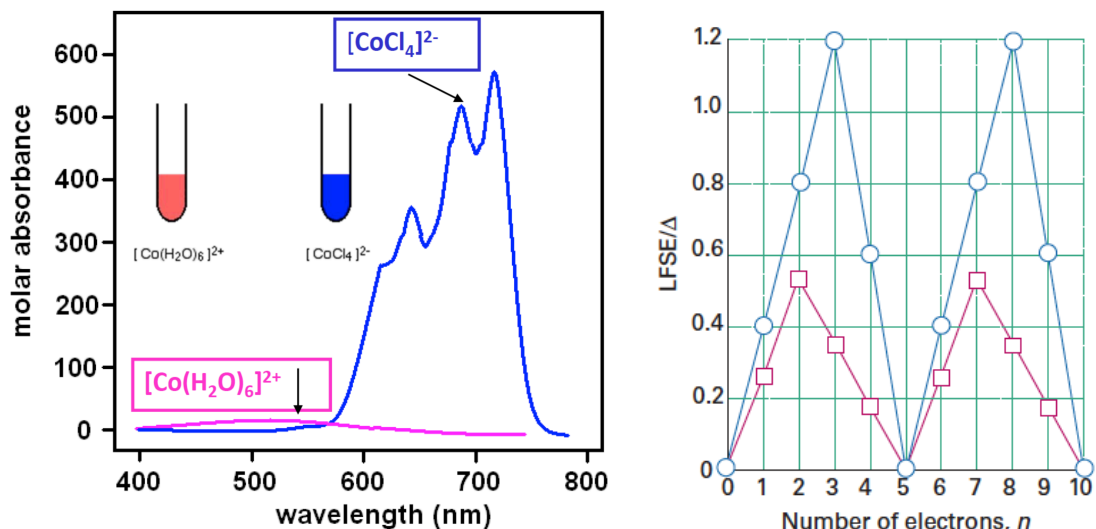
5.5 CRYSTAL FIELD THEORY: TETRAHEDRAL COMPLEXES

In tetrahedral complexes the d_{z^2} and $d_{x^2-y^2}$ point towards the centres of the faces of the cube while the d_{xy} , d_{xz} , and d_{yz} all point towards the centres of the edges of the cube. **No** orbitals point directly at ligands, however d_{xy} , d_{xz} and d_{yz} interact more strongly. This generates a crystal field diagram that looks like the inversion of the one observed for octahedral complexes. However, in this case, the energy difference Δ_t is smaller than Δ_o ($\Delta_t = 4/9\Delta_o$). Δ_t is smaller than Δ_o as there are four ligands rather than six and the ligands do not point at any of the orbitals, both resulting in a smaller destabilizing electrostatic repulsion between the electrons of the ligands and those on the metal.



Tetrahedral geometries occur when the ligands are large and so only four can fit around the metal (reduction in ligand-ligand repulsion). This is the case for $[\text{MX}_4]$ complexes where $X = \text{Br}, \text{I}$. This geometry also occurs with metal ions with zero CFSE (d^0, d^5, d^{10}) or small CFSE (d^1, d^2, d^6 and d^7), such as $[\text{MnO}_4]^-$ (see figure to right).

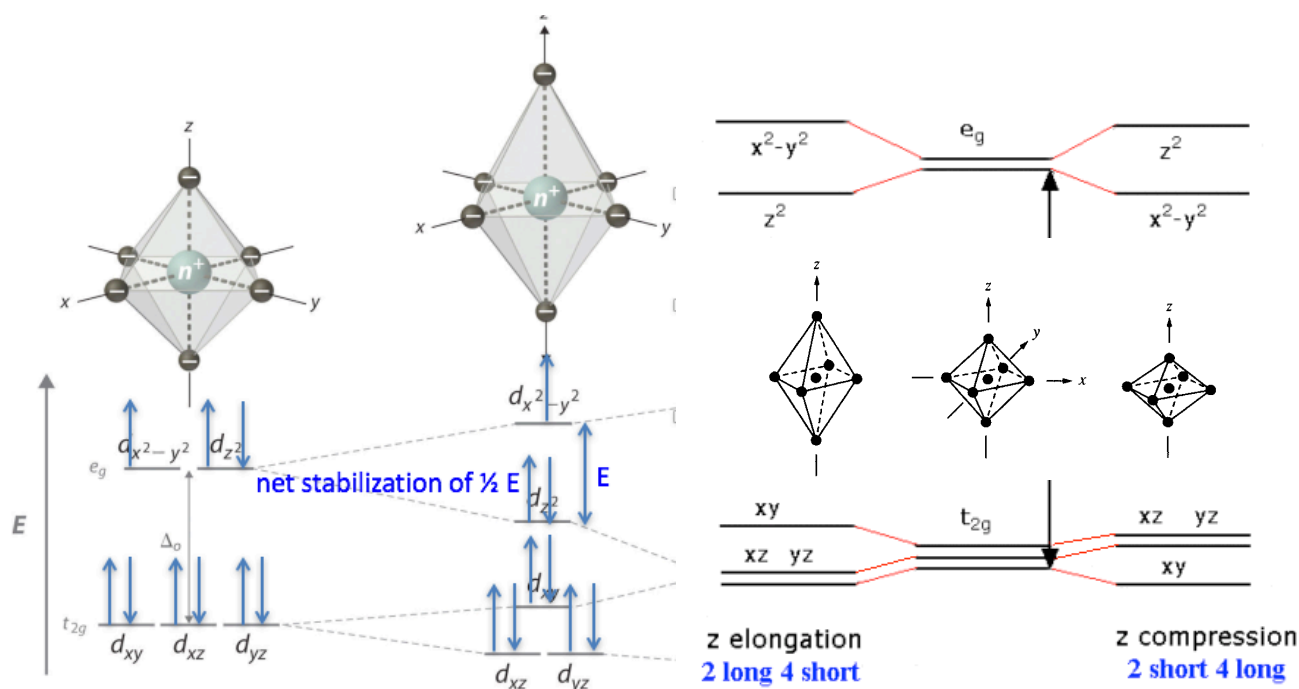
Tetrahedral complexes of the form $[\text{ML}_4]$ absorb light more strongly than many octahedral complexes of the form $[\text{ML}_6]$ as they do not possess a center of symmetry. This means that there is no Laporte selection rule to take into account. Generally molar absorptivities in tetrahedral complexes are about 100x greater than octahedral complexes.



5.5 CRYSTAL FIELD THEORY: JAHN-TELLER DISTORTION

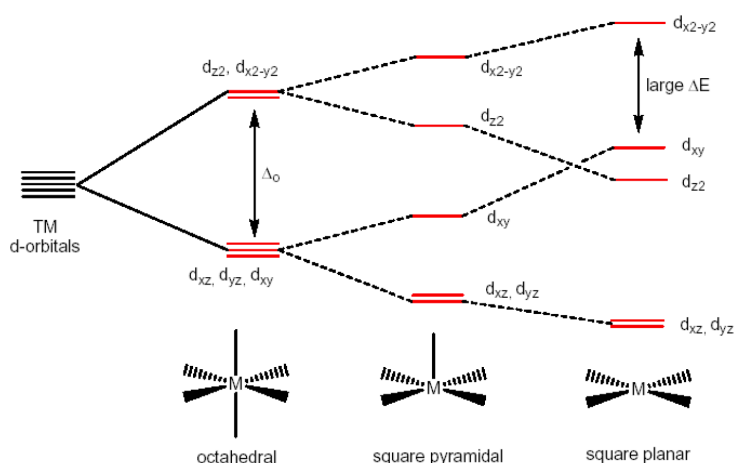
The Jahn-Teller Theorem states: “Any non-linear molecular system in a degenerate electronic state will be unstable and will distort to form a system of lower symmetry and lower energy, thereby removing the degeneracy”

Jahn-Teller (JT) distortion occurs when one can asymmetrically fill orbitals that are degenerate in a complex of non-linear geometry. The geometry of the complex then distorts to reach a more stable electronic configuration. For octahedral complexes, this occurs readily in high spin $d^4 t_{2g}^3 e_g^1$ and low spin $d^7 t_{2g}^6 e_g^1$ or $d^9 t_{2g}^6 e_g^3$. Let's look at the case for LS $d^9 t_{2g}^6 e_g^3$. If there are 2 electrons in the d_{z^2} orbital and 1 electron in the $d_{x^2-y^2}$ orbital then there will be greater repulsion along the z-axis. This will result in elongation of the two M-L bonds along the z-axis to compensate, leading to stabilization of the d_{z^2} orbital. There will be a compensatory contraction of the four M-L bonds along the x- and y-axes. This type of distortion of an octahedral complex, which is the most common distortion, is called **tetragonal distortion**. If there are 2 electrons in the $d_{x^2-y^2}$ orbital and 1 electron in the d_{z^2} orbital then greater repulsion is felt along the xy-plane with elongation of the four M-L bonds, resulting in effective compression of the M-L bonds along the z-axis to compensate, leading to stabilization of the $d_{x^2-y^2}$ orbital.



The JT theorem applies to all non-linear complexes where there is degeneracy of the electronic configurations. The JT theorem does not predict the type of distortion. There are ONLY 5 non-degenerate octahedral configurations. For JT distortion in octahedral complexes the distortions are normally more pronounced if the degeneracy occurs in the e_g orbitals. Remember that the driving force for the JT distortion is to stabilize the system.

5.6 CRYSTAL FIELD THEORY: SQUARE PLANAR COMPLEXES



If one imagines tetragonally distorting an octahedral complex infinitely along the z-axis such that the ligands along that axis are essentially not bound, one would have a square planar geometry complex. In a square planar geometry, the $d_{x^2-y^2}$ is maximally destabilized as the ligands lie on the x- and y-axes. The d_{xy} is also destabilized as it feels the electrostatic repulsion, albeit less so, given the poorer electrostatic interaction. The d_{z^2} orbital is only mildly destabilized due to the interaction of the ligands with the

doughnut part of the d_{z^2} orbital. The other two orbitals are therefore deeply stabilized to compensate for the first three orbitals being destabilized.

d^8 Complexes are frequently square planar, as extra stabilization of the electrons is gained in this configuration. In fact many d^8 complexes are frequently 16 electron complexes so as not to populate the $d_{x^2-y^2}$ orbital. Essentially all 2nd and 3rd row group 10 metal complexes elements already generate a strong field and so if tetracoordinated, they adopt a square planar geometry. For tetracoordinated Ni complexes, one of the only ones with monodentate ligands that adopts a square planar geometry is

$[\text{Ni}(\text{CN})_4]^{2-}$ as here the CN⁻ ligand is sufficiently strong field to influence the geometry to be square planar.

6. LIGAND FIELD THEORY (LFT)

Crystal field theory is very useful for predicting many different properties of metal complexes. However, it has limitations. It cannot answer for instance the following questions.

- Why is KMnO_4 , with Mn^{7+} and no d-electrons, coloured?
- Why is OH^- a weaker field ligand than H_2O ?
- Why are neutral ligands like CO, which are otherwise very poor Lewis bases, such strong field ligands?
- Why in the EPR spectra of high spin complexes is there hyperfine splitting, indicating that the spin is delocalized onto the ligands?

Ligand Field theory treats the electron density on the ligands not as point charges but takes into account the molecular orbital (MO) picture of the entire ligand and looks not only at the d-orbital splitting within the complex but at all MO combinations between the metal and the ligands.

6.1 AN INTRODUCTION TO MOLECULAR ORBITAL (MO) THEORY

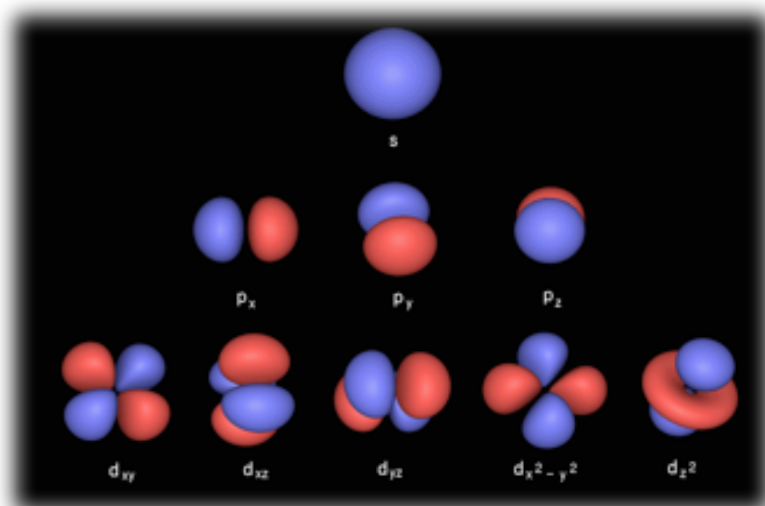
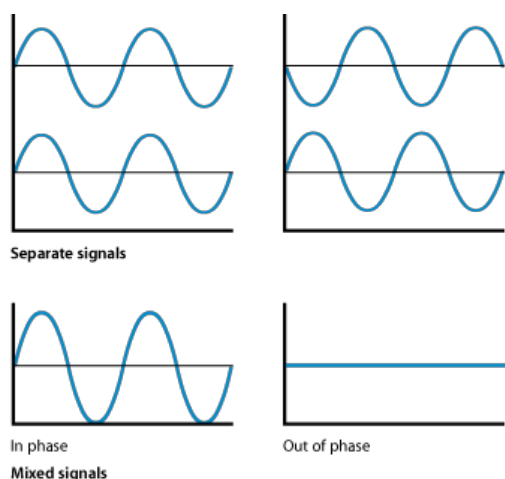
Before we can discuss LFT, we need to establish a background understanding of MO theory.

MO theory considers the **entire molecule** and does not limit the picture of the bonding in molecules to isolated electron pairs. MO theory answers why specific molecules adopt specific geometries and have specific reactivity.

Consequence: An electron pair can be bonding/non-bonding/anti-bonding over more than 2 nuclei.

- Electrons are considered as a standing matter wave in the potential field set up by all the nuclei that make up the molecule.
- There are finite mathematical solutions to these standing matter waves (known as wavefunctions). What this means is that the electron density distribution in a particular MO can only be on the surface of certain shapes (which are really the square of the wavefunction solutions), that we know as molecular orbitals (MO).

A molecular orbital (MO) is composed of a linear combination of atomic orbitals (LCAO) of the form $\Phi_i = c_1\phi_1 + c_2\phi_2 + c_3\phi_3 + \dots + c_n\phi_n$, where c_n refers to the weighting factor of the nth atomic orbital wavefunction ϕ_n and ϕ_n is the nth atomic orbital (such as s, p or d orbitals).



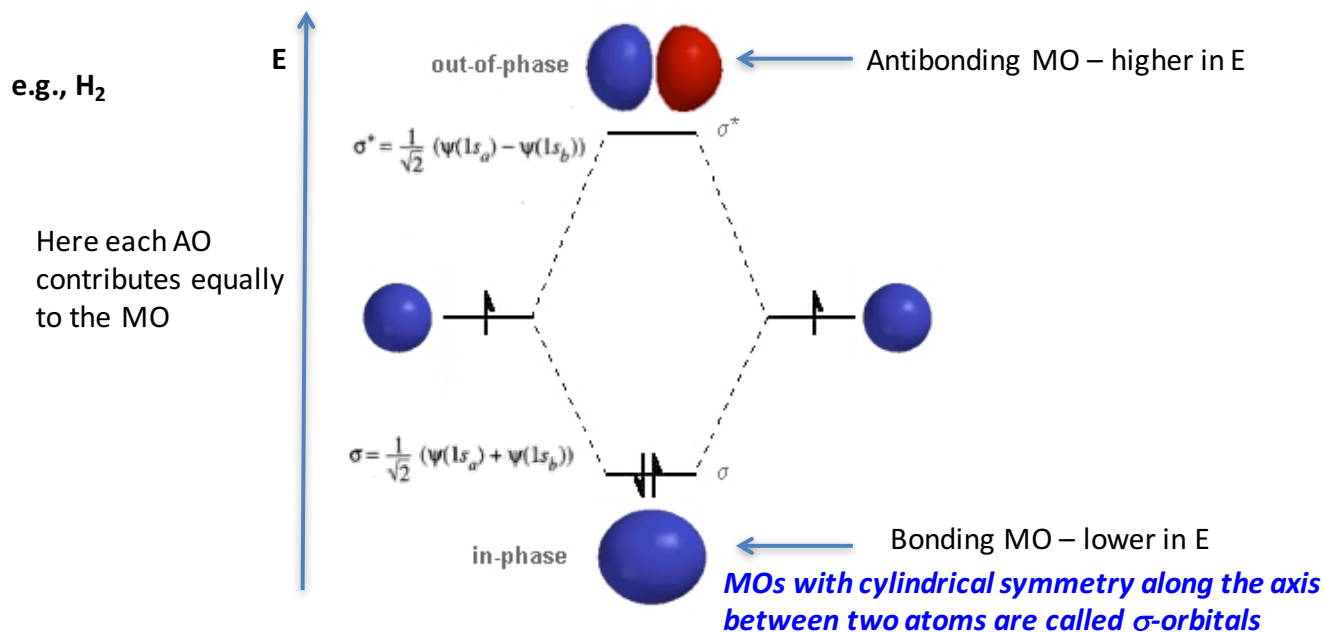
Combinations of wavefunctions can either be constructive when the wavefunctions are in phase (the amplitude increases), which we understand as bonding, or destructive when the wavefunctions are out of phase (the amplitude decreases), which we understand as antibonding.

For n amount of AOs there will be a corresponding n amount of MOs. The shape and phasing of the orbitals (symmetry considerations) defines whether AOs can actually combine to form MOs and whether certain MOs can combine with other MOs to form new MOs. The greater the overlap in space of the AOs, the stronger the interaction. Similarly, the closer in relative energy that the MOs are the stronger the interaction.

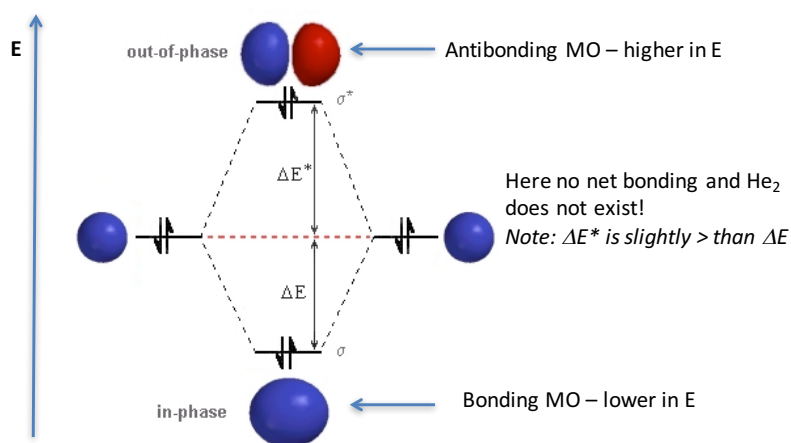
6.1.1 MO OF H_2

Let's look at some examples to illustrate these principles. The simplest molecule is dihydrogen, H_2 , which is formed of two hydrogen atoms. Each hydrogen atom contains an electron in a $1s$ orbital. So there are two atomic orbitals that come together to produce two LCAO solutions, one that is constructive (bonding) and one that is destructive (antibonding). In the diagrams below, a change in colour of the orbital refers to a situation where the phase of MO has changed. One can think of the shape of the MOs as the constructive or destructive superpositions of the atomic orbitals as they are brought together along the bond axis. So for H_2 two $1s$ spherical orbitals come together to form an oval for the bonding combination. When the out of phase orbitals come together the solutions cancel each other out and there is no electron density distribution in those areas. The central point between the two out of phase AOs is called a node. So the in-phase solution has 0 nodes while the out-of-phase solution has 1 node. The electrons populate the MO diagram according to the Aufbau principle, Hund's rule and the Pauli exclusion principle. Therefore, there are two electrons that populate the in-phase MO. The symmetry of this type of head-on bonding interaction is called σ -bonding.

Notice that the bonding combination results in a net stabilization of the MO (this is the driving force for bonding as the molecule gains stability from this process) while the antibonding orbital is destabilized. The stabilization energy is equal in this case to $2 \times \Delta E$, where ΔE is the energy difference between the bonding MO and the AO and the 2 is present as there are two electrons populating that MO.



6.1.1 MO OF He₂



The only difference between H₂ and He₂ is the fact that each 1s orbital now contains two electrons for each He atom. Now when we construct the MO diagram, two electrons now populate the antibonding orbital. It is now important to point out that the antibonding orbital in this (and indeed all MO diagrams) is slightly more destabilized than the bonding orbitals. This implies that He₂ is thermodynamically not stable as the

energy of this molecule is $2 \times \Delta E^* > 2 \times \Delta E$, where ΔE^* is the energy difference between the antibonding orbital and the AOs.

The Bond Order (BO) provides an indication between the strength and length of a bond and serves as a connection to formal Lewis structures, where the number of shared electron pairs is used to indicate single, double or triple bond.

$$BO = (\text{number of bonding electrons} - \text{number of antibonding electrons}) / 2$$

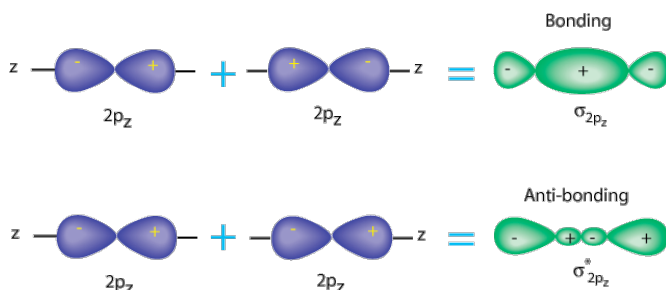
For H₂ the BO = 1, $[(2-0)/2]$, (and so there is a single s bond between H-H)

For He₂ the BO = 0, $[(2-2)/2]$ (and so there is no bond between He-He)

6.1.1 BONDING INVOLVING P-ORBITALS

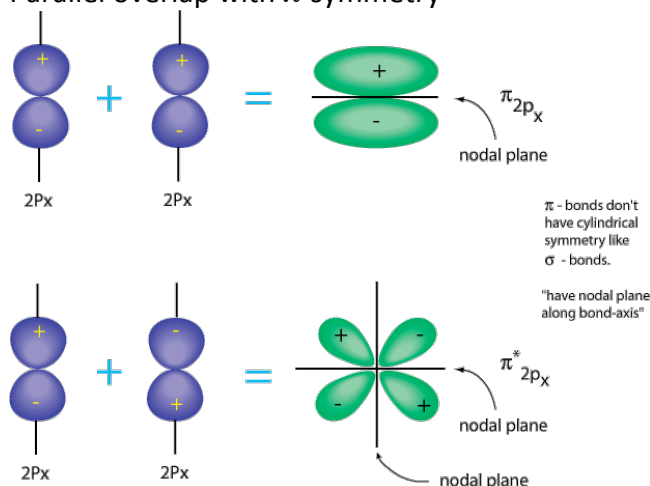
So far, we have looked at two examples involving combinations of 1s orbitals. What about combinations of p-orbitals. There are two possible bonding combinations for p-orbitals interacting with other p-orbitals:

✓ End-on overlap with σ -symmetry



Recall that the p-orbital, which looks like a flower petal or figure eight, has a change in symmetry (node) at the atom center. For σ -bonding, two lobes of the same phase of two p-orbitals come together head-on. The bonding solution looks like a bon-bon.

✓ Parallel overlap with π -symmetry



For π -bonding, two p-orbitals align co-parallel like goal posts and the bonding is side-on. As there is less overlap between the AOs in π -bonding, this bonding is weaker so less stabilization of bonding π -MO and less destabilization of the antibonding π^* -MO than would exist for the σ -bond above.

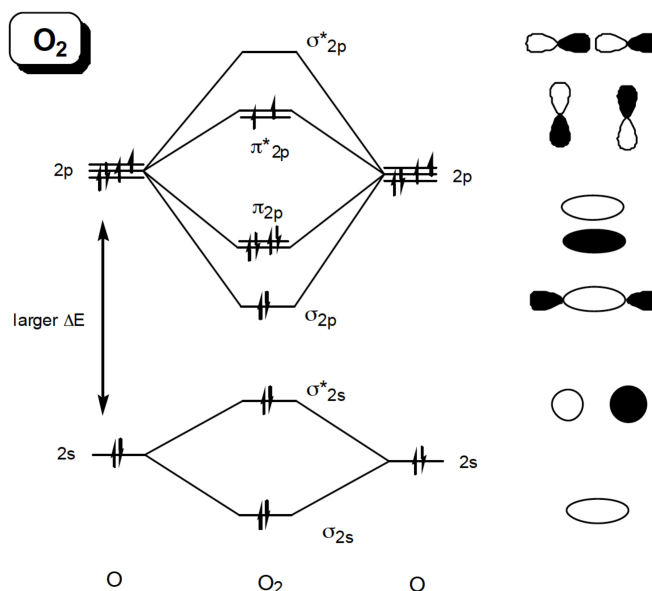
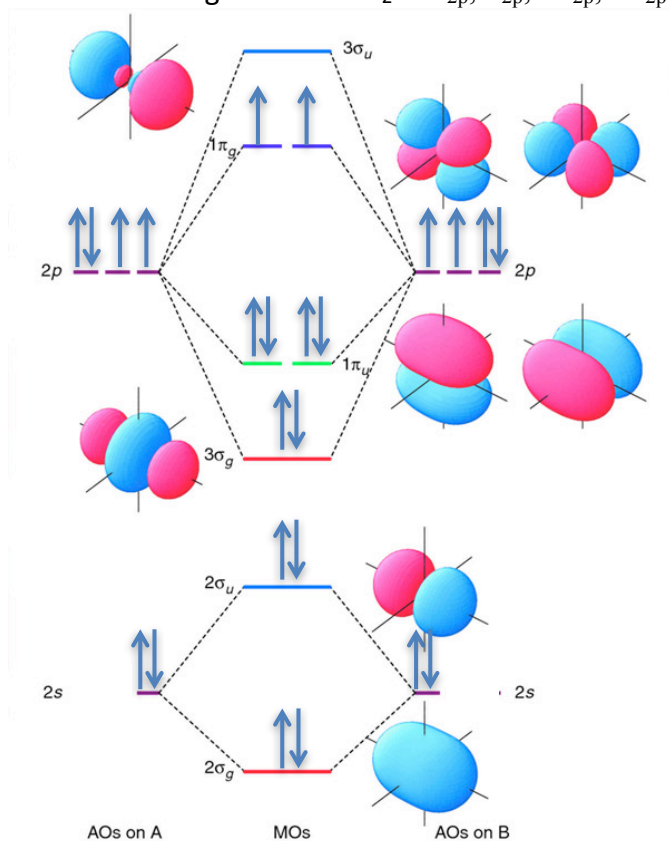
As σ - and π -bonding are orthogonal to each other, they can form simultaneously. This is why the π -bond is drawn as a double bond in stick figure drawings of molecules.

6.1.2 BONDING IN DIATOMIC MOLECULES FROM THE 2ND PERIOD

Let's now look at bonding in 2nd period diatomics (Li_2 , Be_2 , B_2 , C_2 , N_2 , O_2 and F_2), all of which have both 2s and 2p orbitals in their valence shell.

The diagram below is applicable for O_2 and F_2 and the electrons populating it represent O_2 . Notice the following:

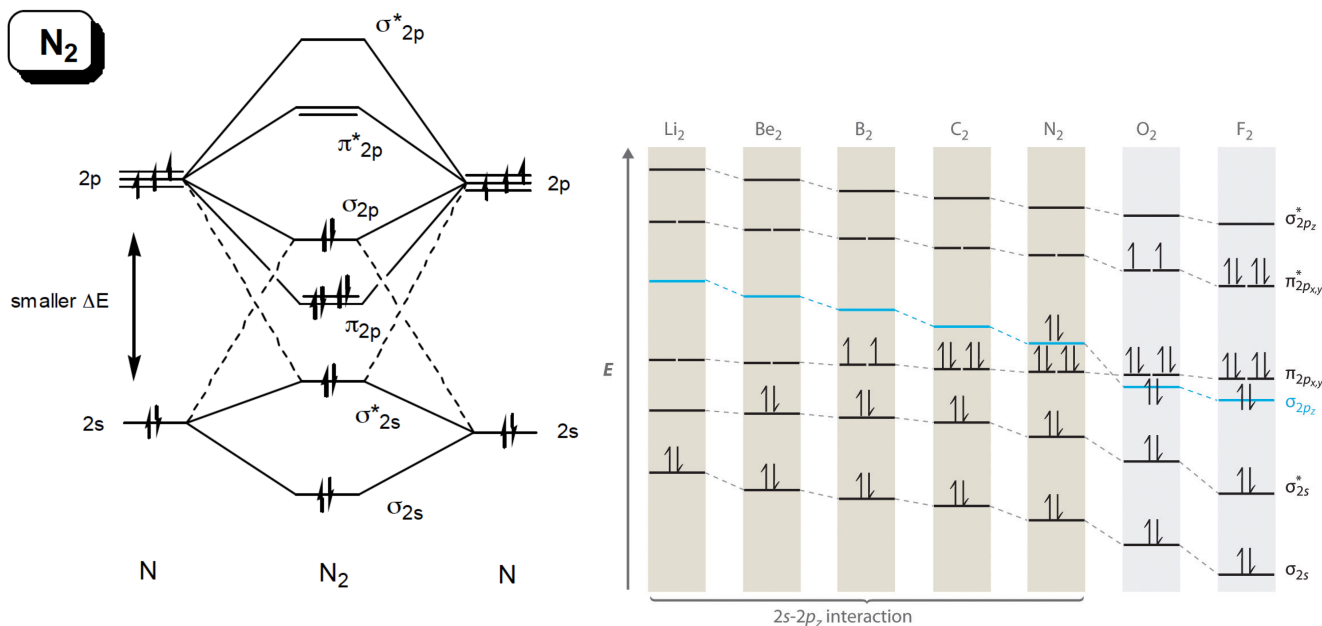
- ✓ The 2s orbitals combine with each other to form a bonding and antibonding MO pair, just like before. The three p-orbitals on each atom combine to form one σ -bonding/antibonding pair.
- ✓ The other two sets of p-orbitals that are oriented orthogonal to the bond (and σ -orbitals) form two sets of π -bonding/antibonding orbitals, which are both of the same energy.
- ✓ There is greater splitting between the bonding/antibonding σ -orbitals than the π -orbitals due to greater overlap.
- ✓ Ordering of MOs in O_2 is σ_{2p} , π_{2p} , π^*_{2p} , σ^*_{2p}



The reason for the ordering of the MOs for O_2 and F_2 are:

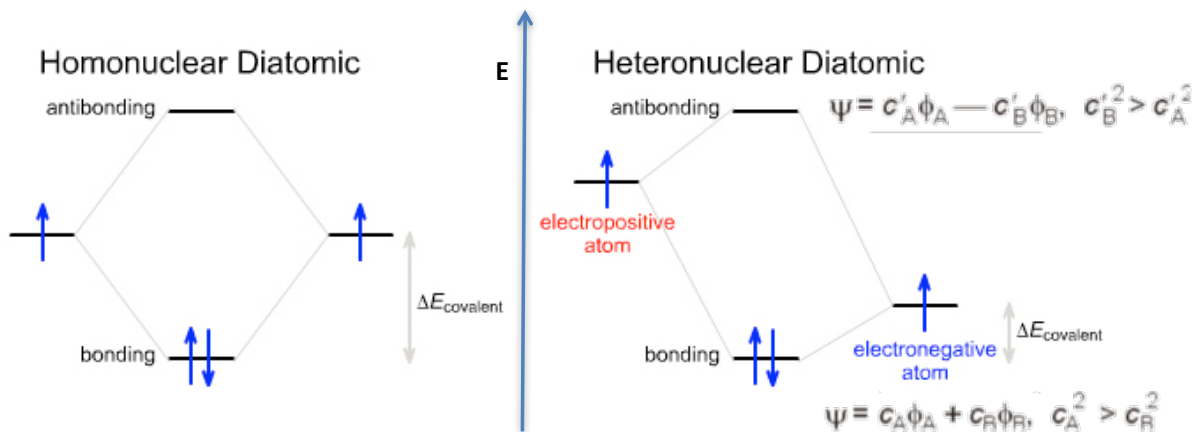
- ✓ Larger ΔE between s and p orbitals, which prevents orbital mixing between the two
- ✓ Larger ΔE because across the period (B,C,N,O,F) more protons added to the nucleus, which pulls the electrons in closer to the nucleus (and lowers the energy of the MOs – this is none other than electronegativity of the atom). This effect is felt more strongly by the s-orbitals than the p-orbitals, so the energy of the s-orbitals drops more rapidly than that of the p-orbitals.

The diagram above does not accurately show the order of MOs for Li_2 , Be_2 , B_2 , C_2 and N_2 (and indeed for other diatomic molecules like CO where one of the atoms is not O or F). In these cases the order is: π_{2p} , σ_{2p} , π^*_{2p} , σ^*_{2p} as exemplified below for N_2 . For Li_2 , Be_2 , B_2 , C_2 and N_2 , ΔE is sufficiently small such that mixing between the σ_{2p} and the σ^*_{2s} orbitals raises the energy of the σ_{2p} above the π_{2p} . In other words, the 2p orbitals found on one of the atoms can linearly combine with the 2s orbital of the other atom, which perturbs both the energy and the LCAO solution, leading to a re-ordering of the MOs. This phenomenon is called **s-p mixing**. Below, right you can see the ordering of the MOs across the series of 2nd row diatomics.



6.1.3 BONDING IN HETERONUCLEAR DIATOMIC MOLECULES

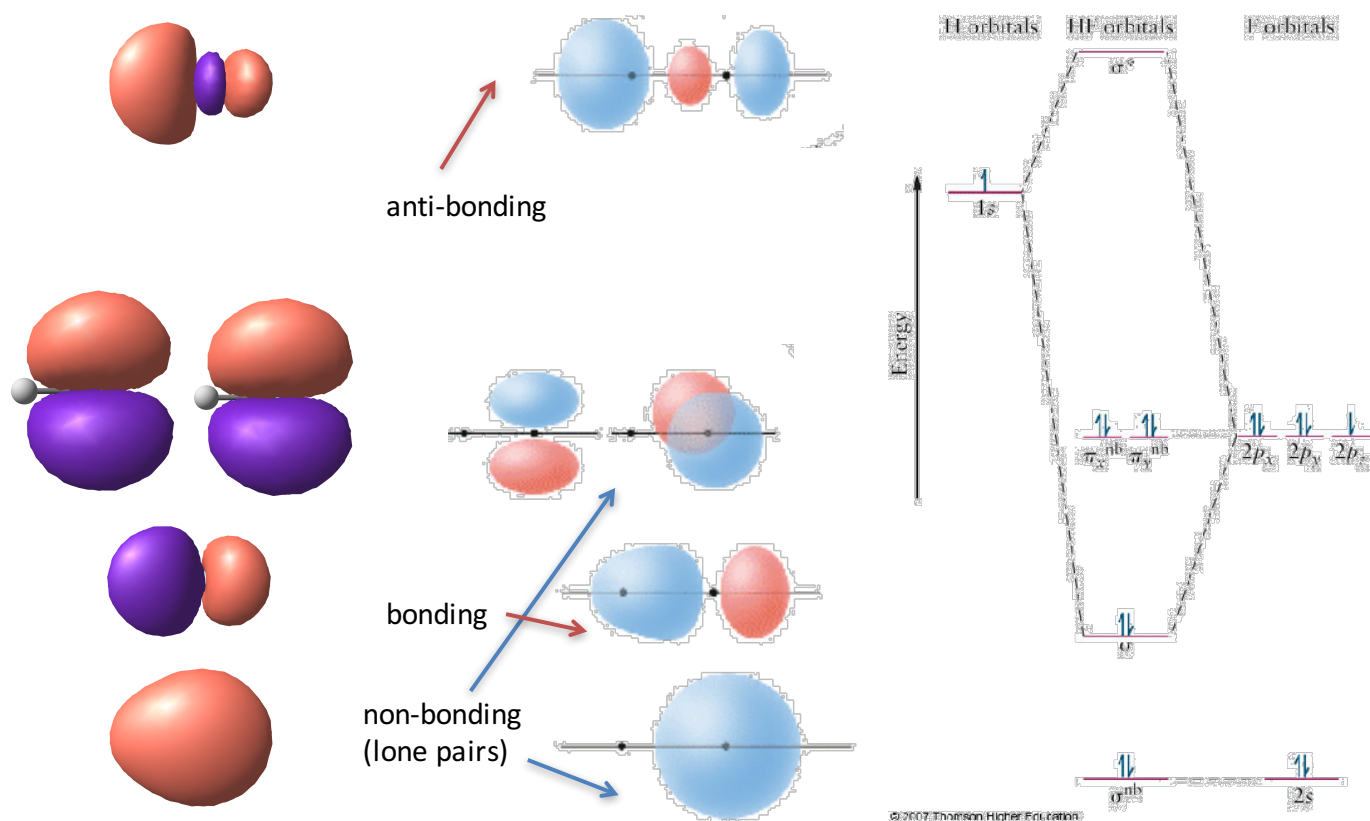
So far we have only considered cases of diatomic molecules where the two atoms are the same. What happens when the two atoms are different? Let's return to the LCAO solution, where now the weighting factor (the c 's in the formulas below) now are no longer equal.



In a diatomic molecule of the form A-B the MO picture now looks like the one above right. The bonding MO will be more like ϕ_A , the AO that is lower in energy (meaning that it will have a lot more character of this AO with the electron density skewed towards this atom) and the antibonding MO more like ϕ_B , the AO that is higher in energy. In other words, the AO closer in E to a MO contributes more to it.

6.1.3.1 BONDING IN HETERONUCLEAR DIATOMIC MOLECULES: HF

Let's look at HF as an example of an A-B system.



For HF

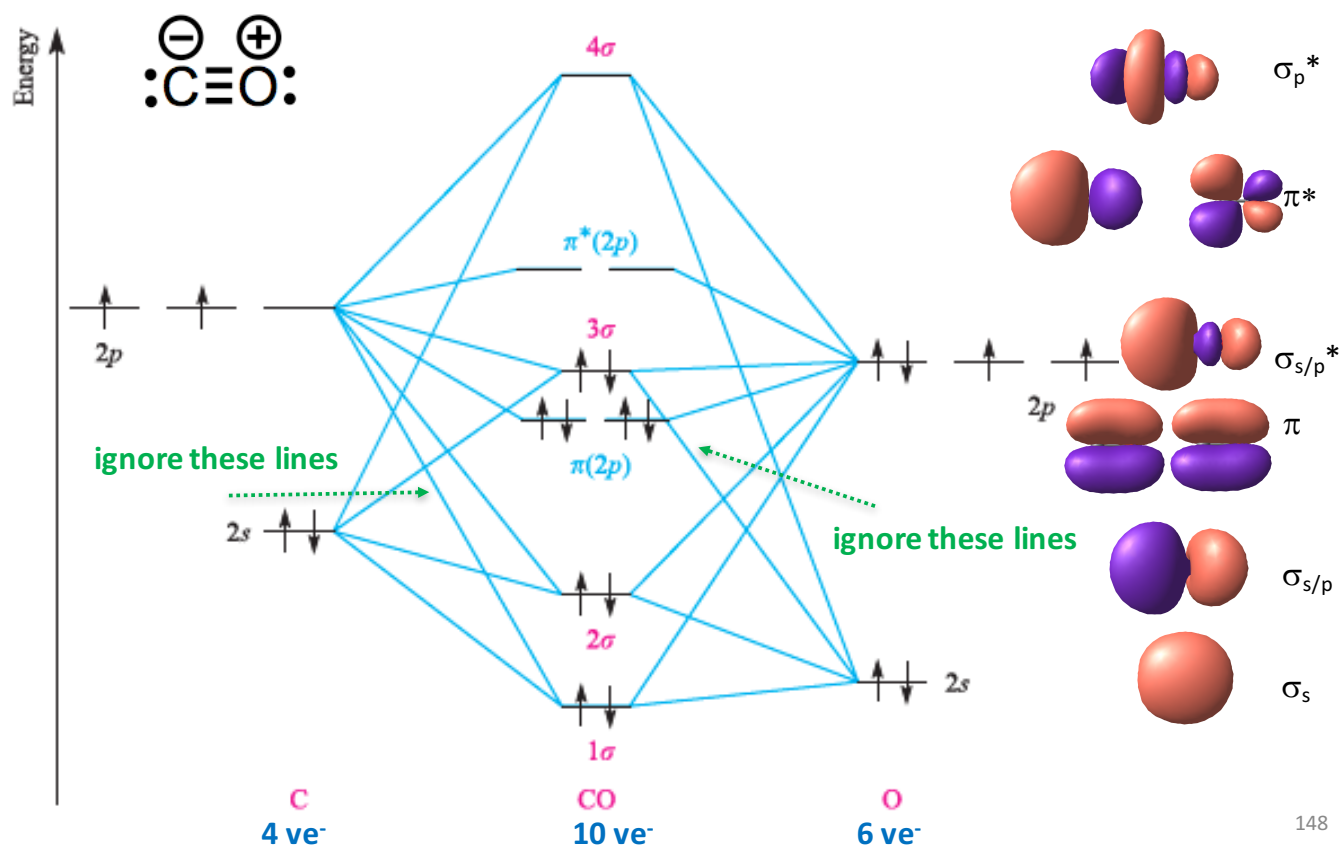
- F is much more electronegative than H so its AOs are much lower in energy
- The 1s orbital of H can only mix with the 2p orbitals of F; the 2s orbital of F is too low in energy to mix.
- Only one combination: H(1s) with F(2p_z) is symmetry-allowed
- As well, as it is F there is no mixing between its s and p orbitals ($\Delta E(2s-2p) > 12 \text{ eV}$ – recall what we observed for O₂ and F₂)

For HF, this means that the F(2s) orbital cannot combine within any AO on H and the resulting MO is non-bonding. Similarly, two of the three F(2p) orbitals are not aligned correctly to permit a bonding interaction with the H(1s) orbital and so are non-bonding. The three non-bonding orbitals actually represent the three lone pairs on F. The H(1s) can interact with the F(2p_z) in a s-bonding fashion to generate a new bonding/antibonding MO pair. The bonding MO (denoted as s above) represents the σ bond between H and F

6.1.3.2 BONDING IN HETERONUCLEAR DIATOMIC MOLECULES: CO

The situation with CO is more complicated in that we now also have to consider π -bonding between the C(2p) and O(2p) orbitals in addition to the σ -bonding.

Notice that O is more electronegative than C and so its AOs are lower in energy than those of C, as we saw with HF. The 2s and 2p orbitals on C will mix with the 2p orbitals of O (the 2s AO of C will also mix with the 2s AO of O), perturbing the MO diagram from what we saw earlier for homodiatom systems. However, the O(2s) is too low in energy to mix with the C(2p) and so cannot mix. Notice also that the order of the MOs is the same as those observed for N₂ due to s-p mixing.



Let's analyse the MOs from lowest energy to highest energy.

The 1σ orbital represents a bonding combination of the C($2s$) with the O($2s$), just like we have seen previously. As O is more electronegative and the 1σ MO is closer in energy to the O($2s$) the MO will have its electron density distributed polarized towards the O.

The 2σ orbital is primarily the antibonding combination of C($2s$) and O($2s$) but C($2p_z$) can also contribute in a bonding fashion as it is close enough in energy to this MO. The result is that the 2σ MO is lower in energy than it would be if the bonding contribution from C($2p_z$) weren't there and the MO adopts some p-character to its distribution.

The $\pi(2p)$ orbitals are formed of the two sets of co-parallel p-orbitals on C and O, just like we observed for N_2 .

The 3σ MO is primarily the bonding combination of C($2p_z$) with O($2p_z$) but C($2s$) also contributes in an antibonding fashion such that overall it is weakly antibonding. The implication of this additional contribution is to raise the 3σ MO higher in energy than the $\pi(2p)$ orbitals and to give this MO greater carbon-containing character than it otherwise would have. Recall that as O is more electronegative than C and the 3σ is closer in energy to the O($2p_z$) orbital, we would assume that this MO would have greater oxygen character. As there are to AOs from C contributing to this MO, the weighting of the electron density distribution now becomes skewed towards C. In fact, the MO picture of the 3σ orbital actually reflects the lone pair on carbon in CO.

The next MO, $\pi^*(2p)$, is the antibonding π^* combination of the $2p_x$ and $2p_y$ orbitals from each of the atoms.

Finally, the 4σ MO is the antibonding contribution from $C(2p_z)$ and $O(2p_z)$. Notice that 1σ contains no nodes, 2σ contains 1 node, 3σ contains 2 nodes and 4σ contains 3 nodes.

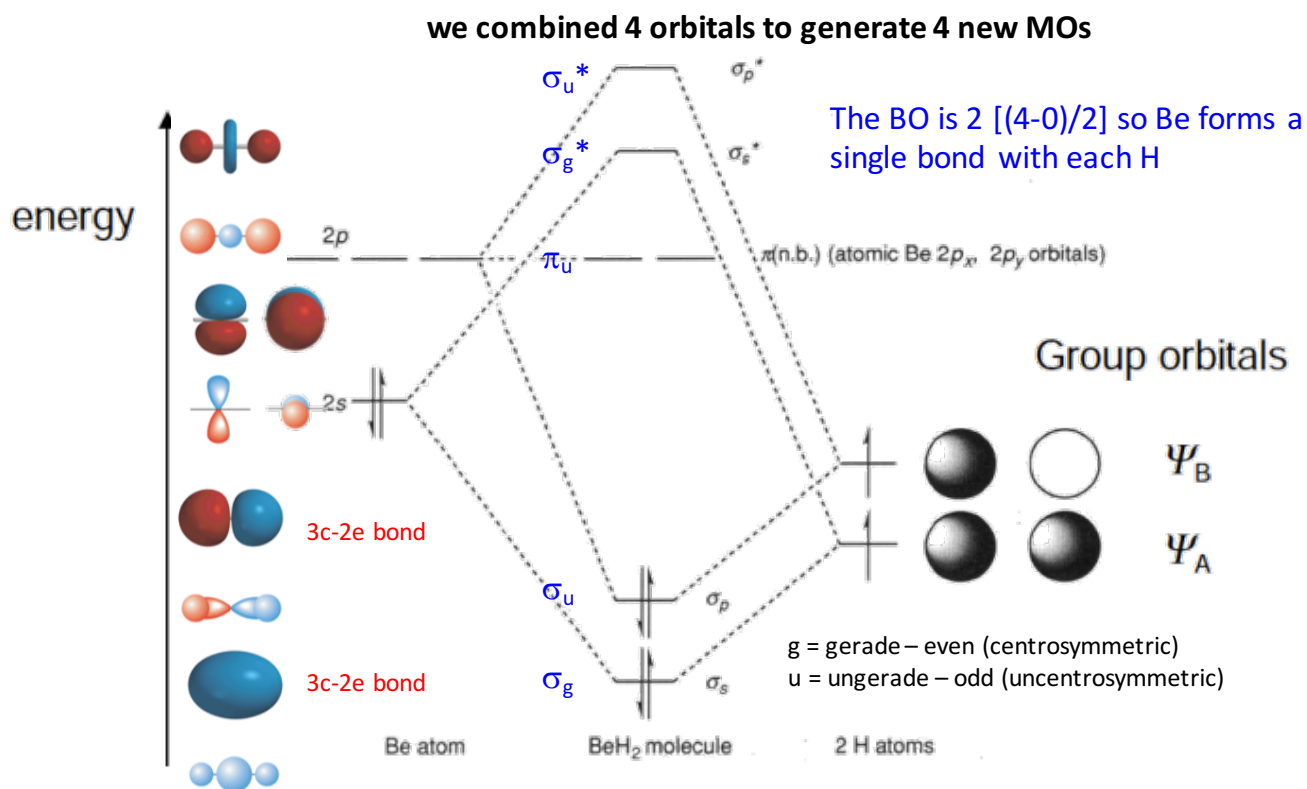
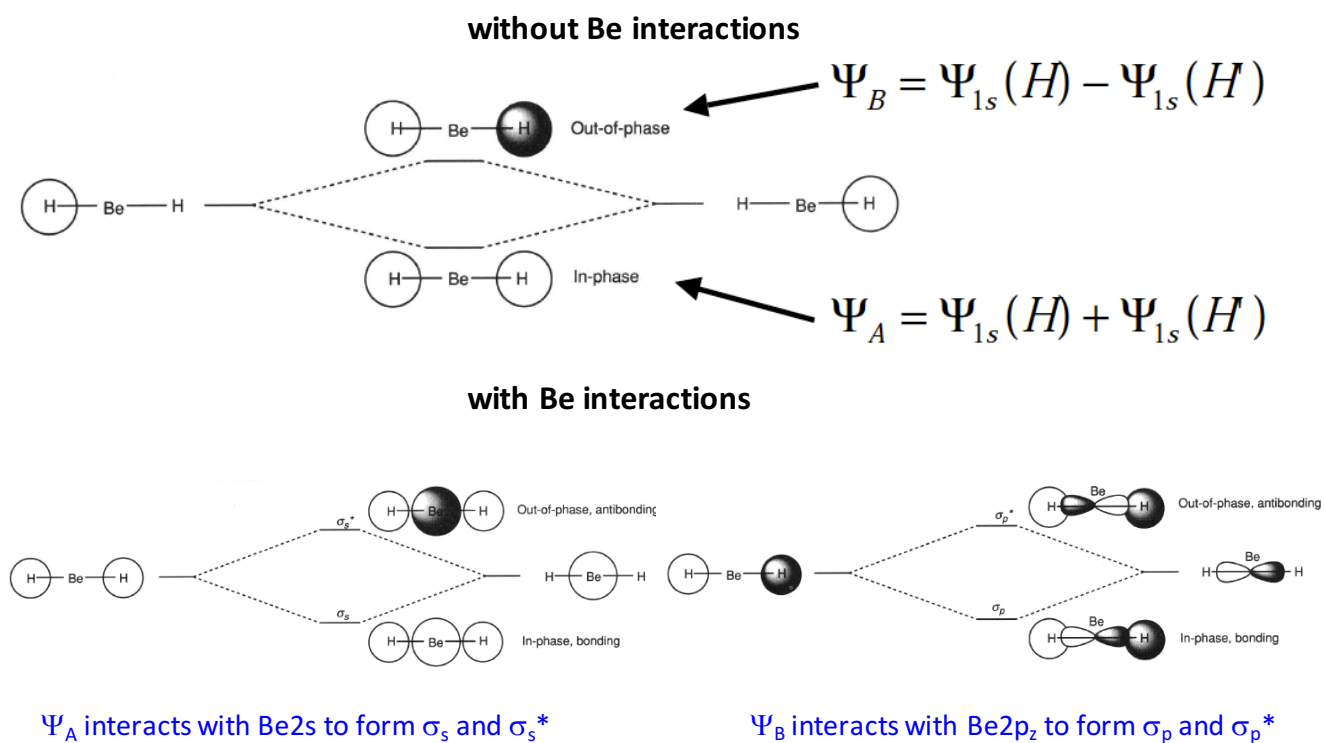
The highest occupied MO, **HOMO**, is the one MO with the highest-energy electrons populating it. In CO this is the 3σ orbital and thus the chemistry of CO, when it is acting as a ligand, is to bond through carbon to the metal. The lowest unoccupied MO, **LUMO**, is the next MO higher in energy, which is $\pi^*(2p)$. Here too the electron density is skewed towards carbon and so when CO is acting as an electrophile, nucleophiles attack at carbon.

6.1.4 BONDING IN POLYATOMIC MOLECULES

So far we have only considered diatomic molecules. How do we handle molecules with more than two atoms? Symmetry analysis by group theory is now required to figure out which MO combinations are bonding, non-bonding and anti-bonding. Basically, what this means is that we consider the symmetry of the molecule and group AOs of similar symmetry in order to simplify the bonding model. These grouped AOs are called **symmetry adapted linear combinations (SALCs)**.

6.1.4.1 BONDING IN POLYATOMIC MOLECULES: BeH_2

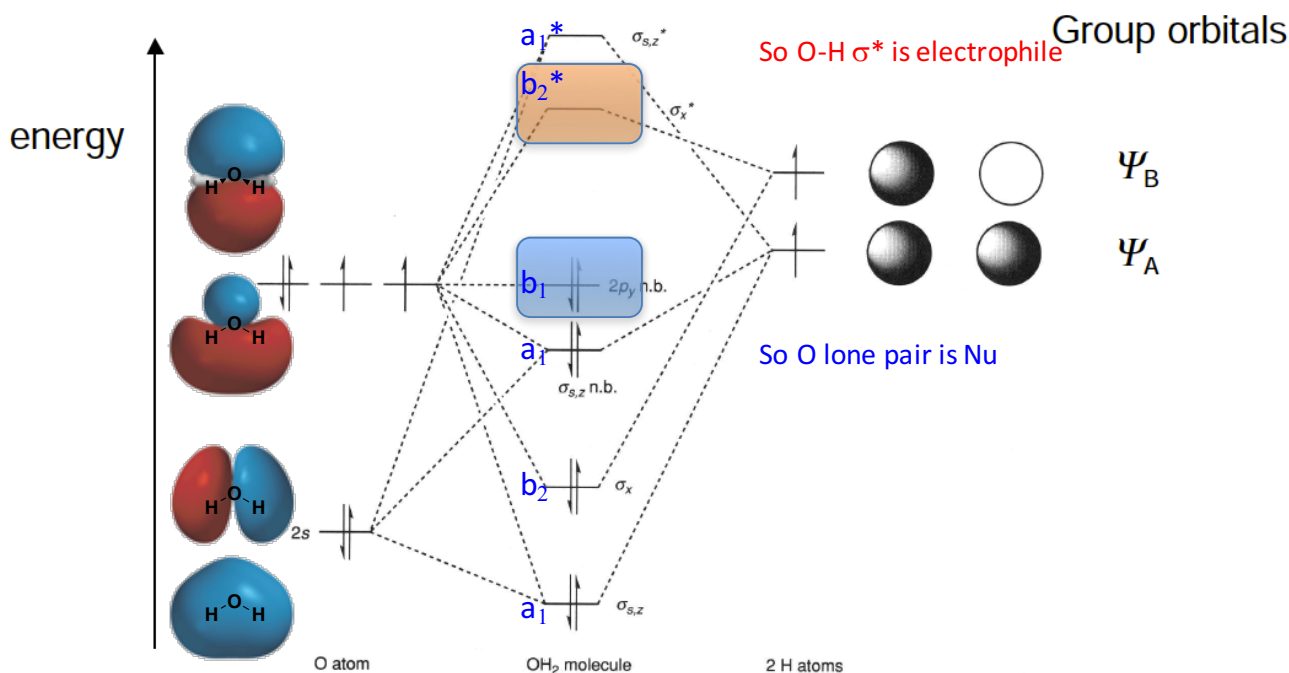
Let's consider BeH_2 , which is a linear molecule. We can now consider the bonding of Be to a SALC of the two H atoms. We already know the solution to the MO combination of two H atoms, which is none other than H_2 . This is what is shown below for Ψ_A and Ψ_B , where in the model below we temporarily ignore the Be atom. With these solutions, we now introduce the $Be(2s)$ and $Be(2p)$ orbitals by inserting Be between the two H atoms. Firstly the $Be(2s)$ orbital can only bond with Ψ_A as Ψ_B does not have the correct symmetry to interact with it. This results in a new bonding/antibonding MO pair, denoted as σ_s and σ_s^* . Analogously, the $Be(2p_z)$ can interact with Ψ_B but not Ψ_A as only Ψ_B has the right symmetry. This interaction produces a second bonding/antibonding MO pair, denoted as σ_p and σ_p^* . The $2p_x$ and $2p_y$ orbitals do not have the appropriate symmetry to interact with either Ψ_A and Ψ_B and so are non-bonding π -MOs.



The MO diagram for BeH₂ is now shown above along with images for the electron density distribution for each of these MOs.

6.1.4.2 BONDING IN POLYATOMIC MOLECULES: H₂O

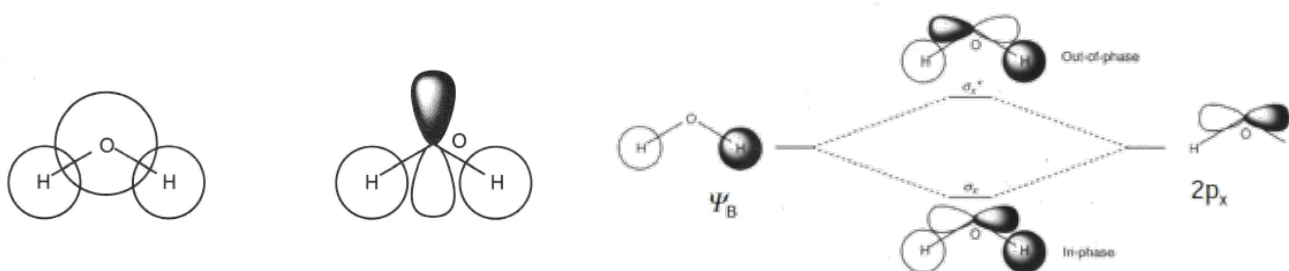
Let's now look at water. H₂O is bent due to the presence of the two lone pairs on O and so we now need to take this into account when formulating our bonding picture.



Ψ_A interacts with O2s and O2p_z resulting in one bonding, one anti-bonding and one non-bonding interactions

The MO diagram above looks a lot like that of BeH₂. There are some differences. The O AOs are lower than the SALCs due to the electronegativity of O. The diagram above defines bonding of the O(2p_x) orbital with the Ψ_B SALC (just an artifact of the bonding coordinate chosen in this case). As the molecule is bent the O(2p_z) O(2p_y) orbitals are not strictly degenerate and do interact differently with the SALCs (see below).

with O interactions



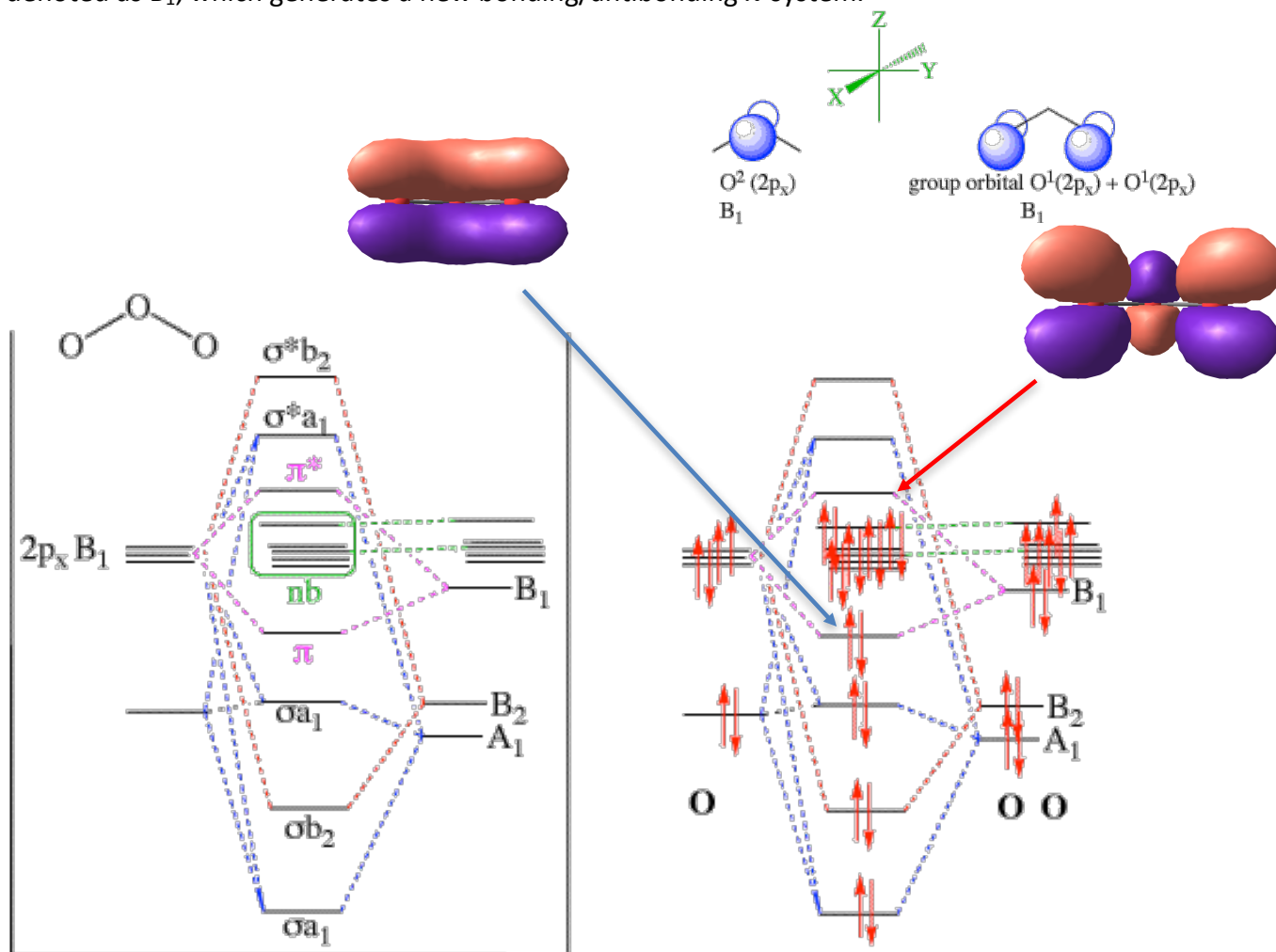
Ψ_A interacts with O2s and O2p_z resulting in one bonding, one anti-bonding and one non-bonding interactions

Ψ_B interacts with O2p_x to form σ_s and σ_s*

As the molecule is bent, there is a mild bonding preference with O(2p_z) with Ψ_A, which is not possible for O(2p_y). This results in a new bonding/antibonding MO pair, denoted as σ_{s,z} and σ_{s,z}*, which effectively lowers the energy of the bonding MO compared to O(2p_y).

6.1.4.2 BONDING IN POLYATOMIC MOLECULES: O₃

Ozone, an important atmospheric gas, is also a bent molecule. Ozone contains the same σ -bonding framework as H₂O but not we must also consider π -bonding where the p-orbitals on all three oxygen atoms are co-aligned. For clarity, the A₁ and B₂ at lower energy represent similar σ -bonding SALC combinations to what we observed previously for BeH₂ and H₂O. These are of course at much lower energy than the previous molecules as oxygen is much more electronegative than H. There is now an additional p-interaction of the central O(2p_x) with the SALC composed of the peripheral O(2p_x) AOs, denoted as B₁, which generates a new bonding/antibonding π -system.



6.2 LIGAND FIELD THEORY (LFT), REVISITED.

Now that we have learned to build MO diagrams of simple molecules, let us revisit LFT.

What is LFT?

LFT is a more complete theory of bonding within complexes, and incorporates aspects of crystal field theory with MO theory. Ligand field theory attempts to incorporate the overlap of metal-based d orbitals with ligand orbitals of suitable symmetry. This approach tries to explain, among other things, the effect of different ligands on Δ_o .

LFT is:

- A **semi-empirical theory** that applies to a *class of substances* (transition metal complexes)
- A **language** in which a vast number of experimental observations can be rationalized and discussed
- A **model** that applies only to a restricted part of reality

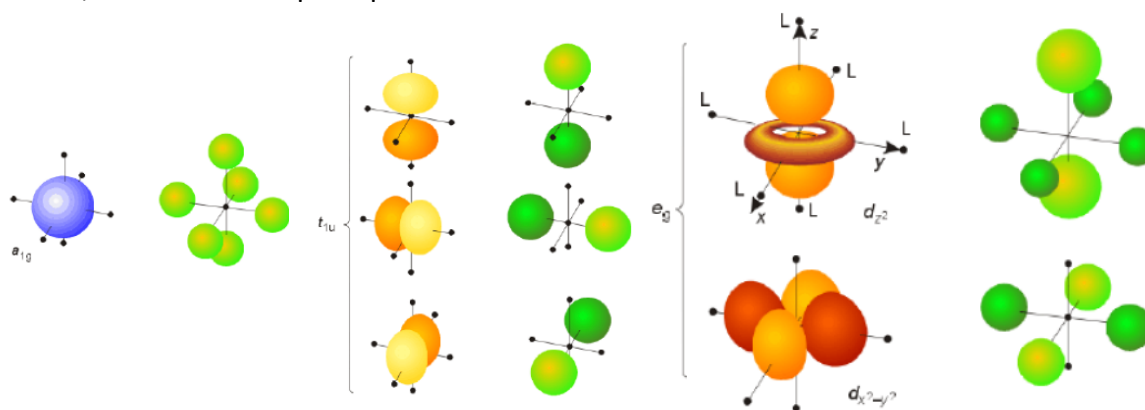
LFT is not:

- An **ab initio theory** that lets one predict the properties of a compound
- A physically rigorous treatment of the electronic structure of transition metal complexes

LFT analyses bonding of metal s, p and d orbitals with SALCs of the ligands, which are usually formed of s and p orbitals. There are two principal bonding bonds, similar to what we have seen previously. They are σ - and π -bonding.

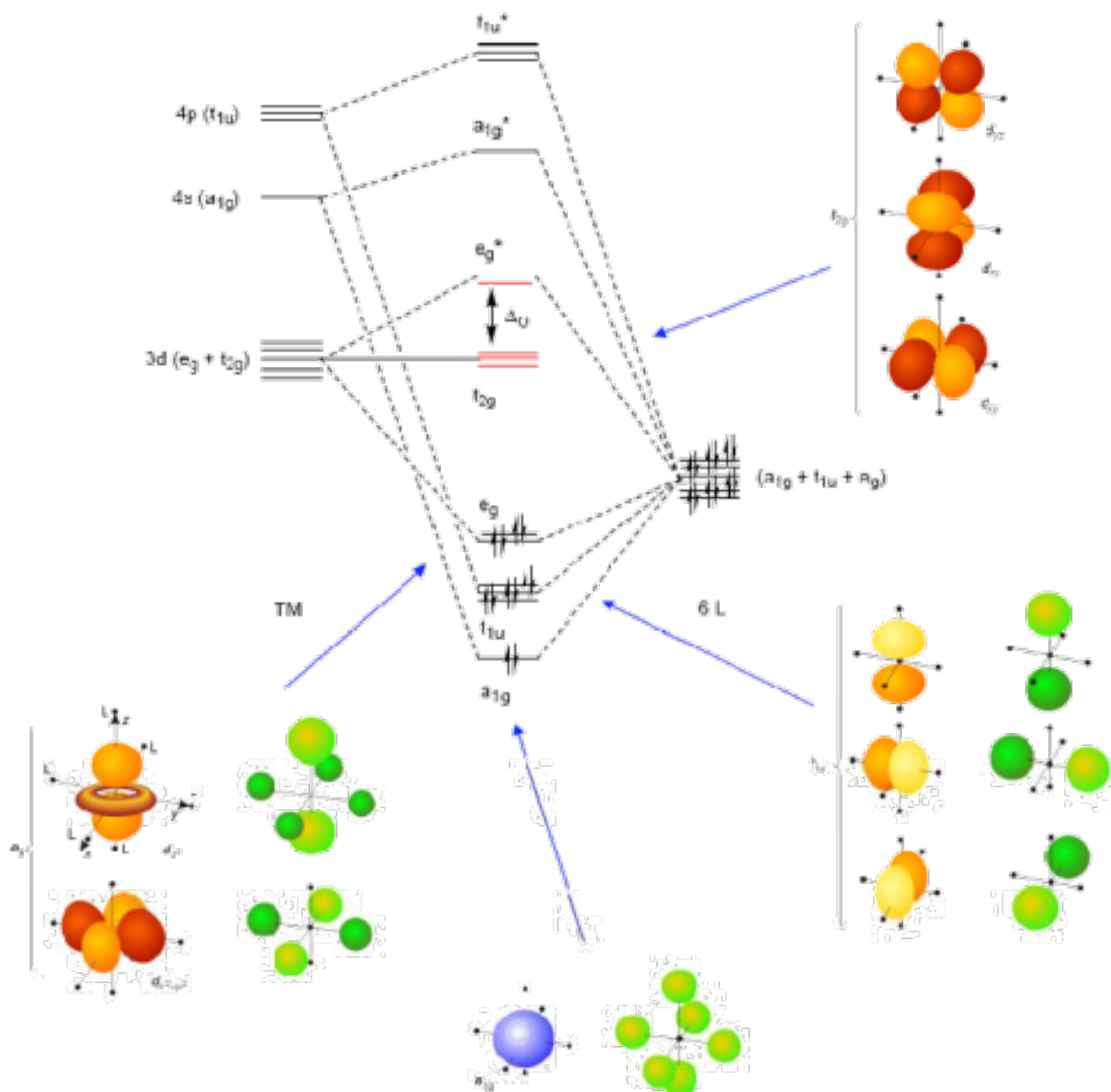
Sigma (σ) bonding

- Neutral ligands (e.g., NH_3) or anionic ligands (e.g., F^-) possess lone pairs that can bond to metal-based orbitals (s, p_x , p_y , p_z , d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, d_{z^2}) with σ -symmetry
- In an O_h complex, 6 symmetry-adapted linear combinations (SALCs) of the 6 ligand σ -symmetry orbitals can be formed
- MOs for the resulting complex are formed by combining the ligand SALCs and the metal-based d-orbitals of the same symmetry type
- With 6 SALCs combined with the metal MOs, we will get 6 bonding and 6 antibonding MOs – now called **ligand group orbitals (LGOs)**
- The resulting MO diagram now gets populated with the electrons according to the Aufbau process, Pauli exclusion principle and Hund's rule



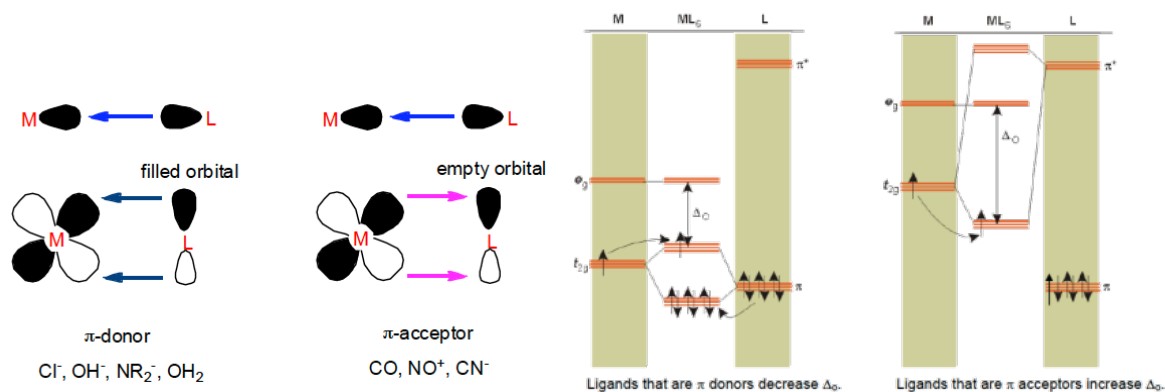
Above you can see the different SALCs interacting with the metal s (left), p (middle) and d (right) orbitals. For the Ligand SALCs, these are composed uniquely of s orbitals. The d_{xy} , d_{xz} and d_{yz} orbitals do not have the appropriate symmetry to combine to form new LGOs.

If we now look at the corresponding MO diagram (below), we now see that the new bonding/antibonding MO combination of the $d_{x^2-y^2}$ and d_{z^2} orbitals are now called e_g and e_g^* . The e_g MO is very ligand based (it is closer in energy to the ligand SALCs) while the e_g^* is more metal based. The three d orbitals constituting the t_{2g} set are now non-bonding. Notice that the d-orbital splitting pattern is exactly the same as was observed in CFT with an energy difference of Δ_o .

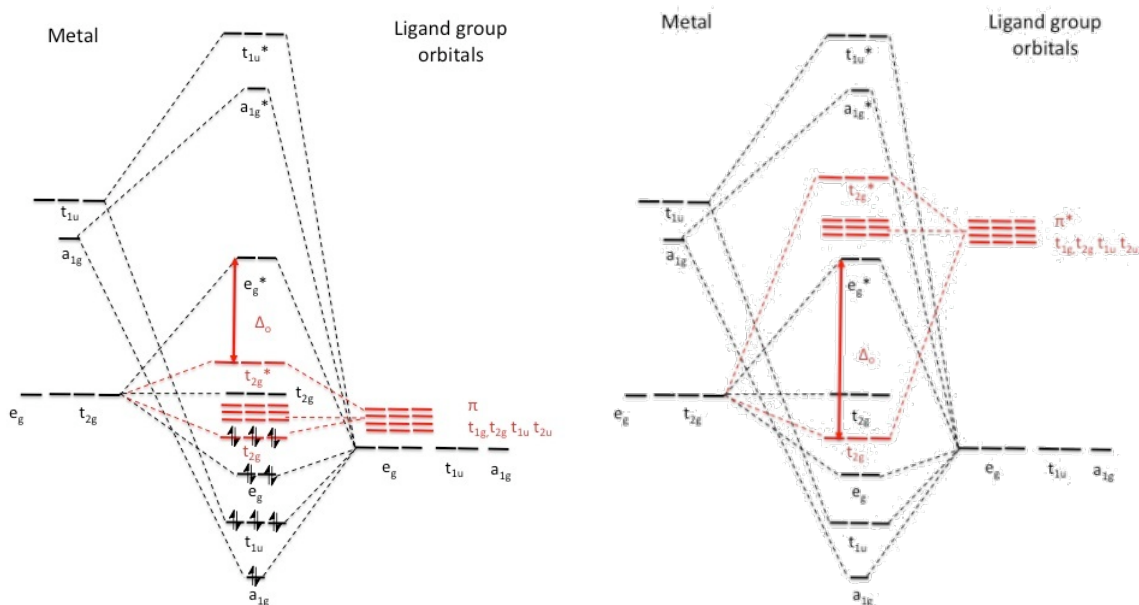


Pi (π) bonding:

- The previous MO diagram ignores π bonding. If the ligands possess orbitals of local π -symmetry then these can interact with the metal d-orbitals with the same symmetry (i.e. the t_{2g} set) to form new LGOs
- These ligand SALCs can act as electron donors (populated) or electron acceptors (vacant)
- The nature of this secondary interaction will affect Δ_o

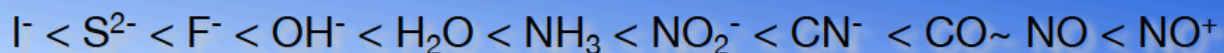
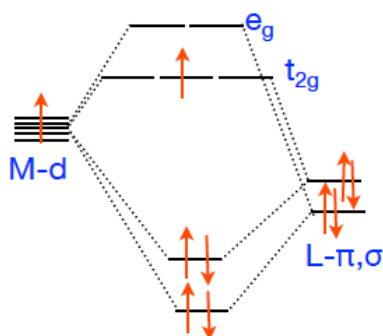
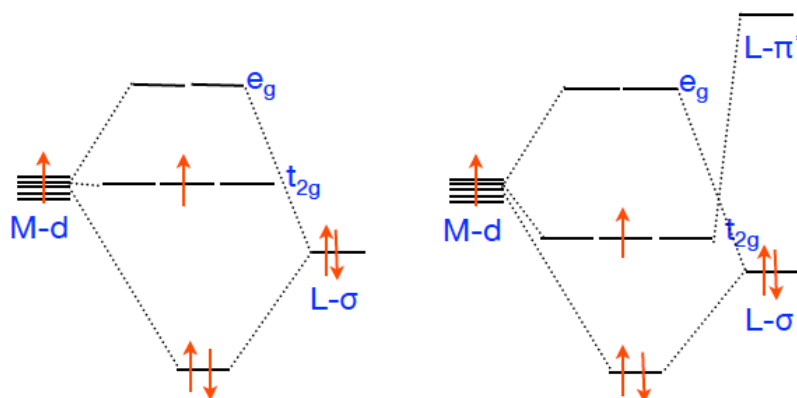


If the π -bond that is formed is composed of unoccupied d-orbitals with occupied p-orbitals on the ligands then this is the case of **π -donor ligands (π -bases)**. Below left is an MO diagram demonstrating the impact of the new bonding/antibonding combination of the ligand SALCs interacting with the metal t_{2g} set. The impact of this new interaction is to destabilize the antibonding t_{2g}^* orbital that contains large metal character, thereby decreasing Δ_o . Complexes with π -donor ligands are frequently high spin due to the smaller Δ_o .



If the π -bond that is formed is composed of occupied d-orbitals with unoccupied p-orbitals on the ligands then this is the case of **π -acceptor ligands (π -acids)**. Above right is an MO diagram demonstrating the impact of the new bonding/antibonding combination of the ligand SALCs interacting with the metal t_{2g} set. The impact of this new interaction is to stabilize the bonding t_{2g} orbital that contains large metal character, thereby increasing Δ_o . Recall that Δ_o refers only to the energy difference between the metal-based MOs. The interaction of the metal t_{2g} orbitals with π -acceptor ligands is frequently called **π -backbonding**. π -Backbonding effectively removes electron density from the metal, which does not like to have too high an electron density. Complexes with π -acceptor ligands are frequently low spin due to the larger Δ_o .

Take home message: π -bonding and π -backbonding modulate the energy of the metal t_{2g} orbitals. This secondary bonding interaction now explains the spectrochemical series.

 Δ SMALL π -DONOR Δ LARGE π -ACCEPTOR

7. THE 18-ELECTRON RULE

It's like the octet rule for inorganic chemists. As with many laws, not always obeyed. Remember that charge of ligands + formal oxidation state of the metal = total charge of the complex

There are two equivalent methods for counting electrons

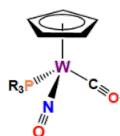
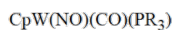
NEUTRAL (COVALENT) METHOD

1. We remove all the ligands from the metal and associate the electrons of the bonds being broken to the ligands in order to make them neutral (So NMe_3 is a $2e^-$ donor and CH_3 is viewed as a radical $1e^-$ donor)
2. We count the d-electrons of the metal, taking into account which group it is in, plus the electrons for each of the ligands as well as the charge of the overall complex

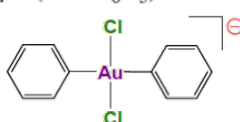
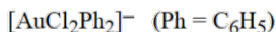
IONIC METHOD (MY PREFERRED METHOD)

1. We remove all the ligands from the metal and associate the electrons of the bonds being broken with the ligand (so CO and NMe_3 are a $2e^-$ donors, Cl^- and CH_3^- are ionic $2e^-$ donors)
2. We increase the oxidation of the metal to compensate for the added electrons in order to maintain charge neutrality
3. We count the d-electrons of the metal plus the electrons for each of the ligands as well as the charge of the overall complex

Below are a couple of examples of how to count the number of electrons on a complex.



W(0)	d6
Cp ⁻	6e ⁻
NO ⁺	2e ⁻
PR ₃	2e ⁻
CO	2e ⁻
Total	18 e ⁻



Au(+3)	d8
2Ph ⁻	4e ⁻
2Cl ⁻	4e ⁻
Total	16 e ⁻

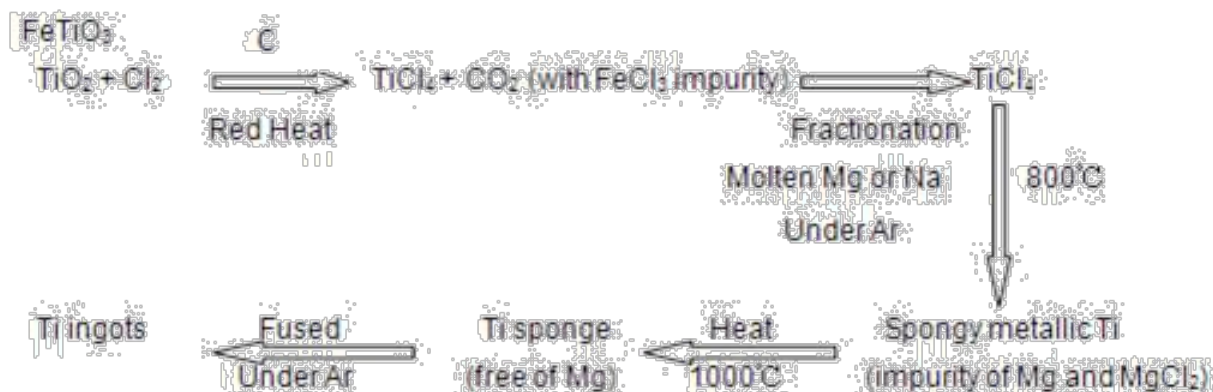
8. DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES

3d-Metal complexes have a rich mix of properties, which are largely based on the nature of the metal and its oxidation state, as exemplified by the photo below. In this section, we will briefly explore the chemistry and properties of a selection of complexes.



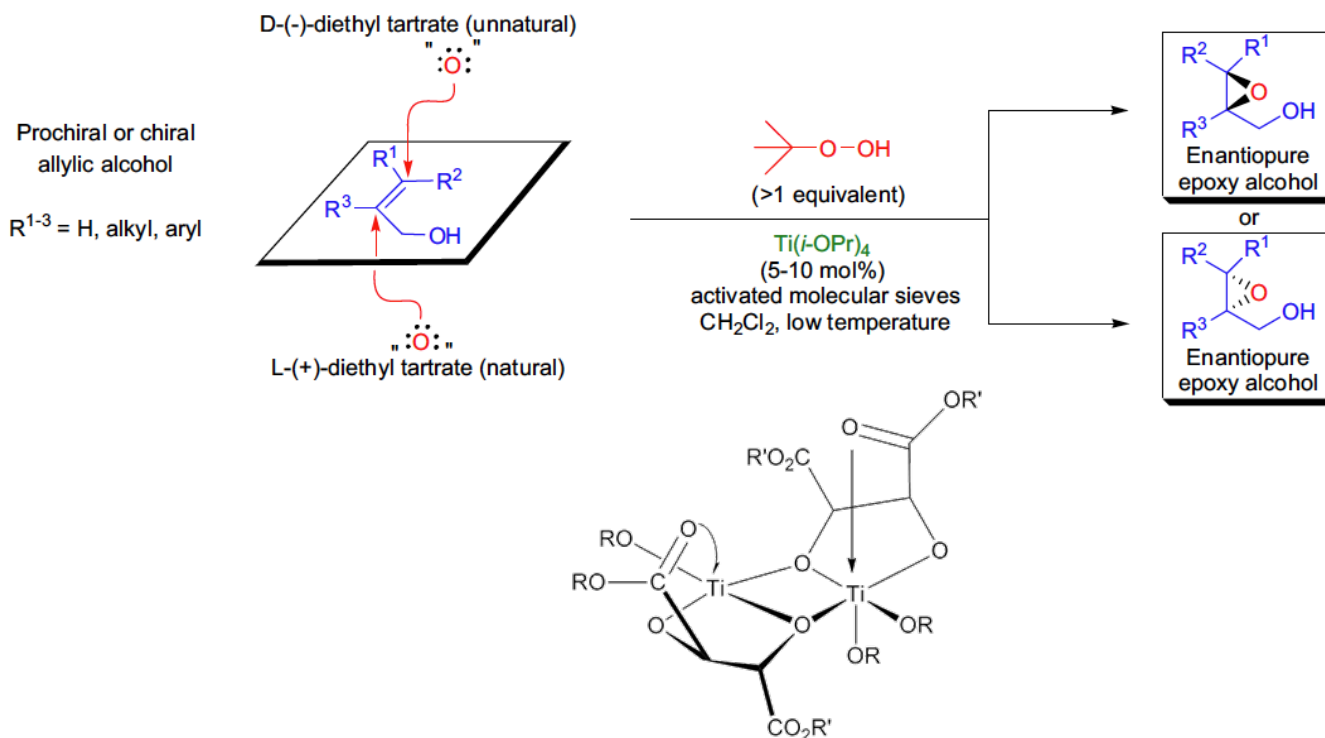
8.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ti

Titanium metal is produced *via* the Kroll process. Titanium is a light weight, robust metal that is quite corrosion resistant.



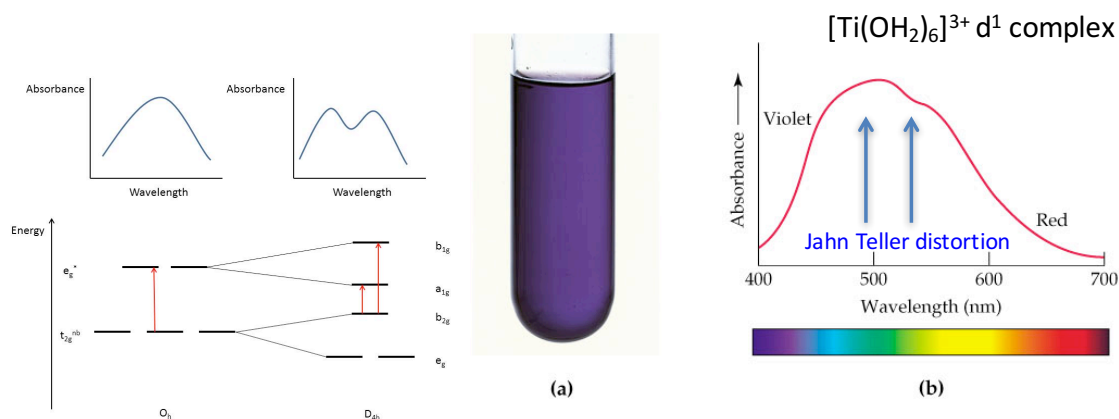
8.1.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ti(IV)

The starting material in the Kroll process is titanium dioxide. TiO₂ comes in two crystalline forms: rutile and anatase. It is used as a white pigment in paint, in sunscreen, as a semiconductor and as a photocatalyst.

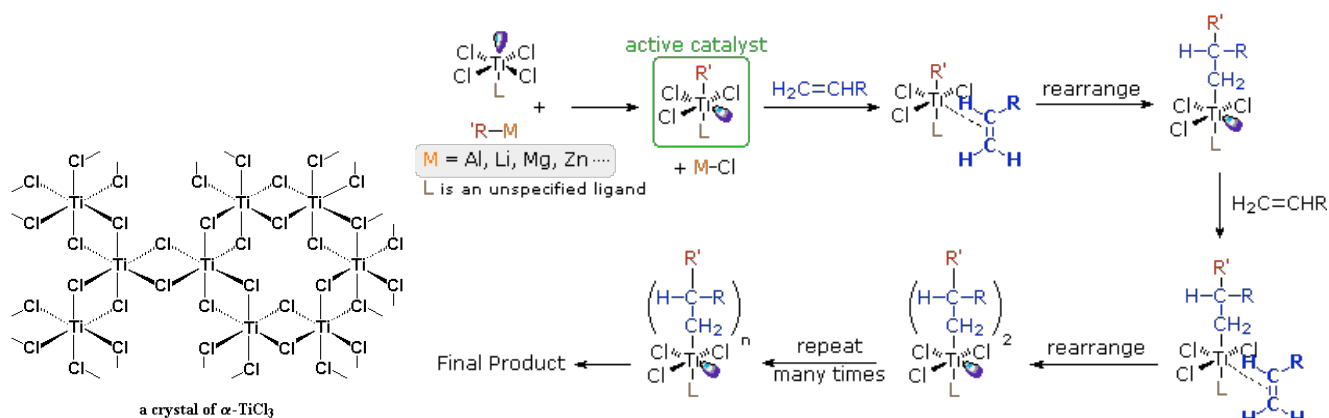


8.1.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: $Ti(III)$

We had previously discussed the absorption profile of $[Ti(OH_2)_6]^{3+}$ as being a purple solution. We can now understand why there are several peaks in the absorption spectrum. This is due to Jahn-Teller distortion of the d^1 system, which causes additional transitions to appear as a result of the tetragonally distorted octahedral structure (see below).



An important reaction involving $Ti(III)$ is the Ziegler Natta polymerization of alkenes, the reaction responsible for the production of many plastics, including poly(acetylene) and poly(styrene). The mechanism is shown below. The starting titanium source is $TiCl_3$, which has an extended structure, shown below.

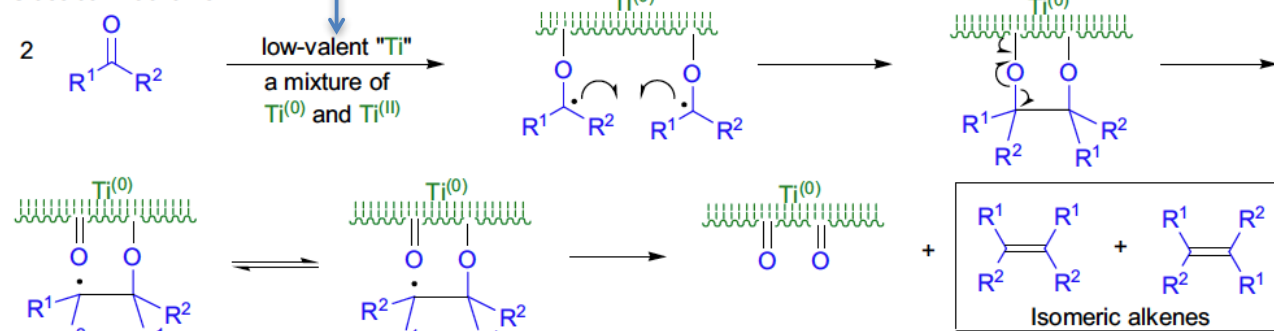


8.1.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ti(II)

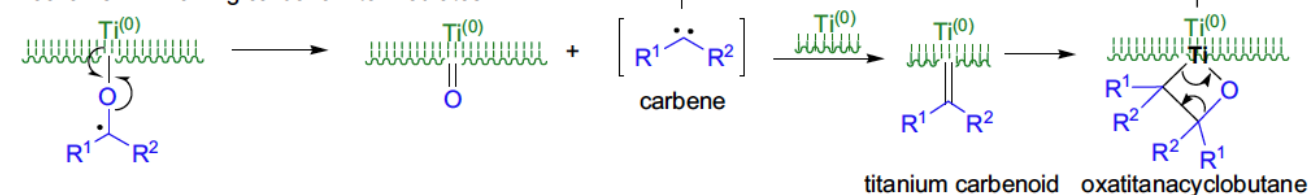
McMurry coupling reactions are mediated by in situ generated low valent titanium species, which promote the formation of highly substituted alkenes from ketones.

rare: made by disproportionation
from TiCl_3 or TiCl_4

Classical mechanism:



Mechanism involving carbene intermediates:



8.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Va

Vanadium was discovered in 1801 by the Spanish scientist Andres Manuel del Rio. Del Rio discovered the new element in brown lead ore (now known to be the mineral vanadinite, $\text{Pb}_5[\text{VO}_4]_3\text{Cl}$) in New Spain (Mexico). He named his new element panchromo or panchromium meaning 'all of the colors' because of the wide range of colors he had found when investigating the element's salts. He then renamed the element eritrono or erythronium, from the Greek word eruthros, meaning red. The new name was inspired by the red colour which was seen when Group 1 or Group 2 oxide salts of the new element – for example sodium vanadium oxide – were heated or acidified.

In 1805 the French chemist Hippolyte-Victor Collet-Descotils examined the lead ore and announced that erythronium was actually impure chromium – an analysis that, unfortunately, del Rio accepted.

In 1830, Nils Gabriel Sefström in Stockholm, Sweden, found a new metal in a Swedish iron ore. He called this new element vanadium after 'Vanadis' the Scandinavian goddess of beauty because of the beautiful multicolored compounds formed by the metal. In the same year, German chemist Friedrich Wöhler reinvestigated the Mexican lead ore and found that vanadium was identical to del Rio's erythronium.

The metal was first isolated by Sir Henry E. Roscoe in 1867, in Manchester, England, by reducing vanadium chloride with hydrogen. The vanadium mineral roscoelite was named in honor of Roscoe's work.

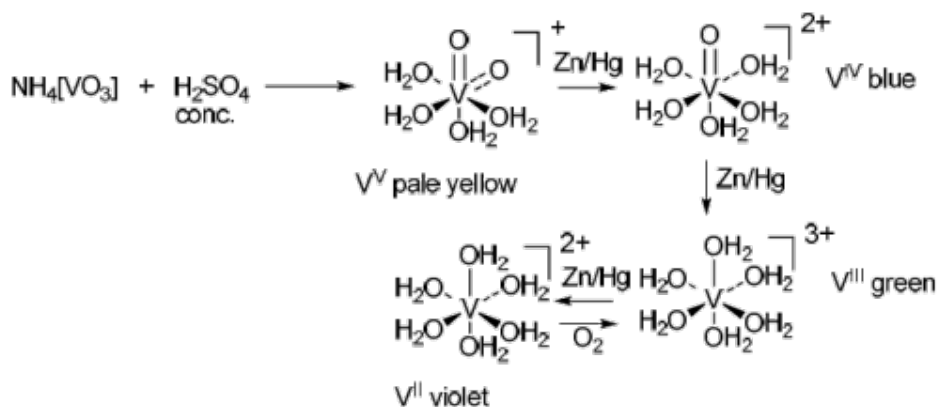
World vanadium manufacturers produced around 61 000 tonnes in 2011 and rising at 3% pa. China is the biggest producer. Vanadium is commonly used in steel alloys.

Depending on the oxidation state, aqueous vanadium compounds display a wide range of colours.



8.2.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Va(V)

V₂O₅ is used as a catalyst in the Contact process that converts SO₂ to H₂SO₄. VF₅, VOCl₃, VOB₃ are stable. VCl₅ is not known. V₂O₅ oxidises Cl to Cl₂, giving VCl₃. It is possible to chemically reduce vanadium(V) under forcing conditions to generate lower oxidation state vanadium species.

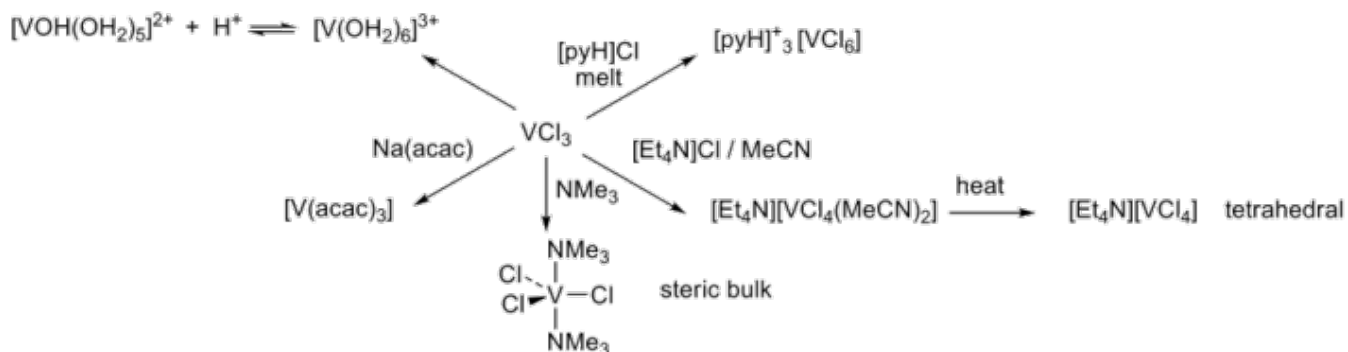


8.2.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Va(IV)

The Va(IV) complex VO(acac)₂ is an important oxidant of alkenes that transforms them to epoxides and is used in organic synthesis. Of the VX₄ compounds, VF₄ is stable, VBr₄ is stable <-20 °C, VI₄ is not known while VCl₄ is a covalent oil that decomposes to VCl₃ + ½ Cl₂.

8.2.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Va (II) and Va(III)

VCl_3 , VBr_3 , VI_3 are semi-covalent layered structures that do not dissolve in organic solvents. $[\text{V}(\text{OH}_2)_6]^{3+}$ can be obtained from VCl_3 (see below). In fact, VCl_3 is a useful precursor to access many different vanadium complexes.



$[\text{V}(\text{OH}_2)_6]^{2+}$ is a strong enough reducing agent to reduce water to hydrogen, but this reaction is slow.

8.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cr

It took Vauquelin several steps to isolate chromium. First he mixed the crocoite solution with potassium carbonate to precipitate out the lead. Then he decomposed the lemon yellow chromate intermediate in acid, and finally removed the compounded oxygen by heating with carbon - leaving behind elemental chromium.

The colour in several gemstones is due to trace chromium. As corundum, beryl, and crysoberyl, these metal oxides are colourless and obscure minerals. But add a dash of chromium, and they become ruby, emerald and alexandrite.

Cr(0) makes steel “stainless”, which is its biggest application. Cr is also combined with other metals to make them hard, shiny and chemically resistant.

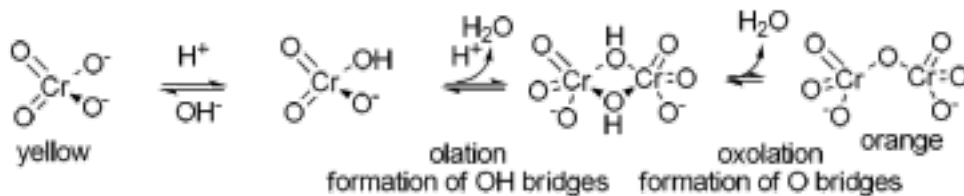
Depending on the oxidation state and the medium, chromium complexes can adopt a wide range of colours (see below).

Oxidation State	In Acidic, Aqueous solution		In Alkali Solution	
	Colour	Ion	Colour	Ion
+2	Blue	Cr^{2+}		
+3	Green	Cr^{3+}	Green	$[\text{Cr}(\text{OH})_4]^{3-}$
+6	Orange	$\text{Cr}_2\text{O}_7^{2-}$	Yellow	CrO_4^{2-}



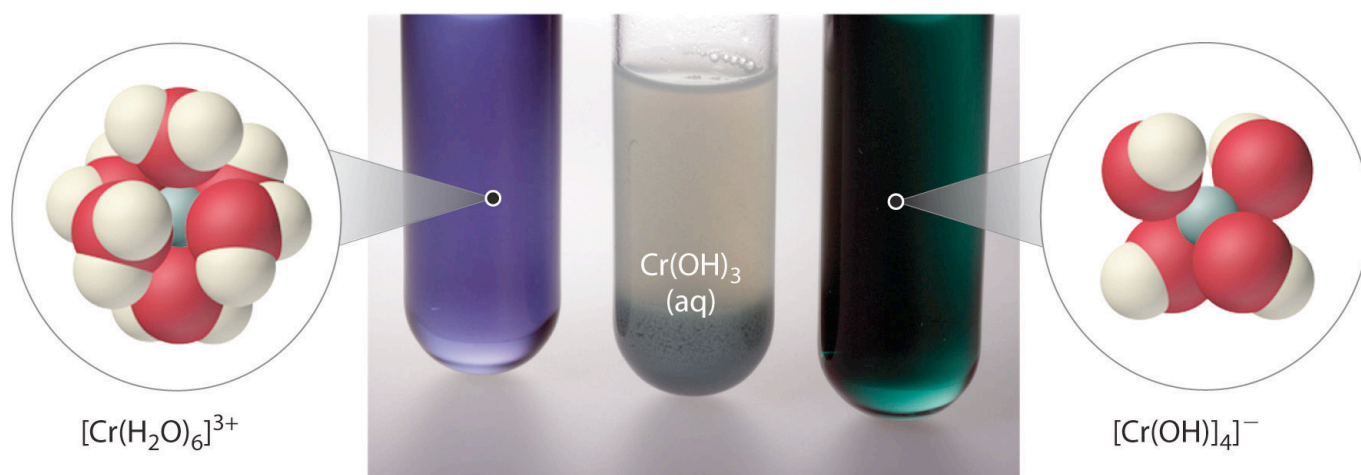
8.3.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cr(VI)

Cr^{VI} is $3d^0$. Cr^{VI} complexes are very strong oxidizing agents that can oxidize alcohols to carboxylic acids (Jones reagent – $\text{CrO}_3 + \text{H}_2\text{SO}_4$). $[\text{Cr}_2\text{O}_7]^{2-}$ can oxidize NH_4^+ to NO_2 and H_2O with most of the O coming from the metal as it is reduced to Cr^{3+} . For many years CrO_4 was used as a pigment in yellow paint that was used to paint school buses, amongst other things, despite the fact that Cr^{VI} is extremely toxic. Chromate is converted to dichromate through a condensation reaction known as olation (shown below).



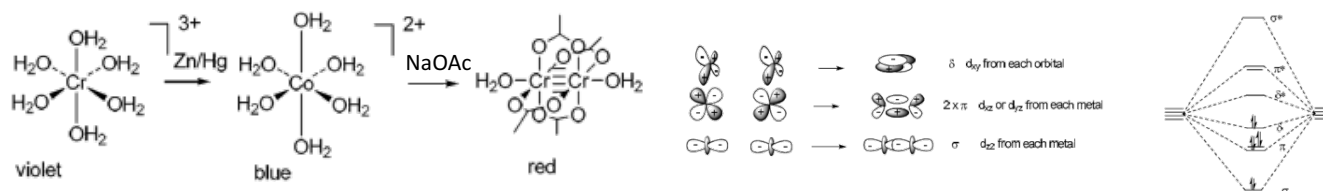
8.3.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cr(III)

Cr^{III} is $3d^3$. It is usually found as green $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$. This dissolves in water to give dark green solution, which is $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$. The solution becomes purple as the chloride ligands are substituted for aqua ligands. These aqua ligands can be deprotonated, resulting in a green solution that is $[\text{Cr}(\text{OH})_4]^-$.



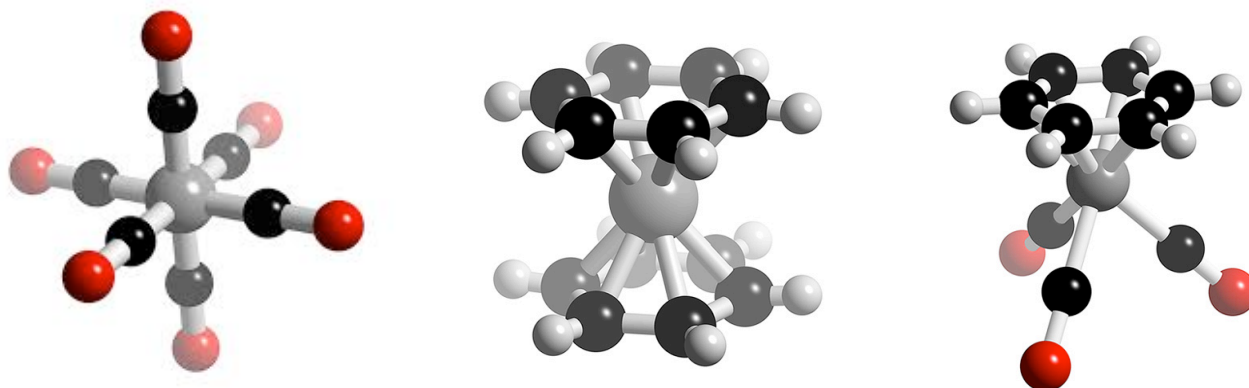
8.3.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cr(II)

Cr^{II} complexes are far less common but can be made by reduction of Cr^{VI} or Cr^{III} . $[\text{Cr}(\text{OH}_2)_6]^{2+}$ is high spin $3d^4$ and so experiences Jahn Teller distortion and very easily oxidized. Upon treatment of two equivalents of $[\text{Cr}(\text{OH}_2)_6]^{2+}$ with NaOAc a diamagnetic red solid forms with an unusual quadruple bond formed between the two chromium atoms as a result of δ -bonding of two d_{xy} orbitals.



8.3.4 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cr(0)

$\text{Cr}(\text{O})$ is $3d^6$. $\text{Cr}(\text{O})$ complexes that are stabilized with good π -acceptor ligands and obey $18e^-$ rule can form. Examples include: $[\text{Cr}(\text{CO})_6]$, $[\text{Cr}(\text{C}_6\text{H}_6)_2]$ and the piano stool complex $[\text{Cr}(\text{C}_6\text{H}_6)\text{CO}_3]$.



η^6 bonding!

8.4 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Mn

The first recognition of manganese's existence as a distinct element was in 1740 when the German chemist, Johann Heinrich Pott, stated that pyrolusite (manganese dioxide) contained a new earth metal.

Until then pyrolusite was believed to have been a compound of iron. Pott prepared potassium manganate by fusing caustic potash (potassium hydroxide) with pyrolusite in air. The color changes he observed in the product were green/blue/red/green, establishing that pyrolusite did not contain iron. Metallic manganese was isolated in 1770 by PhD student Ignatius Gottfried Kaim.

One of the most important reactions in biology, photosynthesis, is completely dependent on Mn. It is an essential component in the reaction center of photosystem II, where water molecules are converted to oxygen. Without Mn, there would be no photosynthesis as we know it and there would be no oxygen in the atmosphere.

Mn complexes exhibit the widest range of oxidation states amongst 3d elements – from Mn^{VII} – Mn^{III} , with the most common being +7, +4 and +2. The most common use of Mn is in steel making.

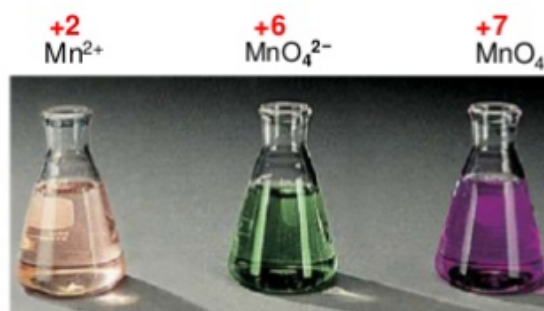
8.4.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Mn(VII) AND Mn(VI)

MnO_4^- , despite being d^0 , has a deep purple colour because of an LMCT transition. It is a very strong oxidizing agent. MnO_4^{2-} is d^1 and is a green colour, which now originates from a d-d transition.

MnO_4^- slowly decomposes in acid solution so fresh solutions must be made up for titrations
 $4\text{MnO}_4^- + 4\text{H}^+ \rightarrow 3\text{O}_2 + 2\text{H}_2\text{O} + \text{MnO}_2$

MnO_4^{2-} disproportionates in acid following:
 $3\text{Mn}^{\text{VI}}\text{O}_4^{2-} + 4\text{H}^+ \rightarrow 2\text{Mn}^{\text{VII}}\text{O}_4^- + \text{Mn}^{\text{IV}}\text{O}_2 + 2\text{H}_2\text{O}$

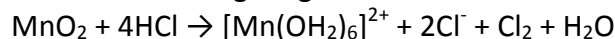
MnO_4^- also reacts with strong alkali
 $4\text{MnO}_4^- + 4\text{OH}^- \rightarrow 4\text{MnO}_4^{2-} + \text{H}_2 + \text{O}_2$



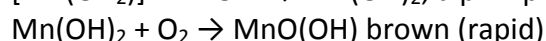
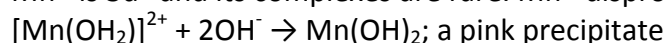
8.4.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Mn(V) AND Mn(IV)

Mn^V is 3d² and metal complexes involving Mn^V are rare. Mn^V is stable in fused NaOH. MnO₄³⁻ is blue.

Mn^{IV} is 3d³. Perhaps the most common Mn^{IV} compound is MnO₂, which is the most common oxide of Mn and is an oxidizing reagent

**8.4.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Mn(III) AND Mn(II)**

Mn^{III} is 3d⁴ and its complexes are rare. Mn^{III} disproportionates to MnO₂ + Mn^{II}. It can form in air:

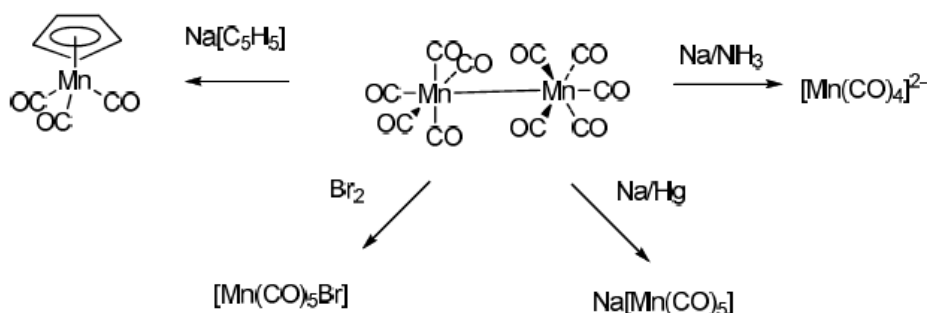


Mn^{II} is 3d⁵. Its complexes derive extra stability from a half-filled shell. It is a pale pink colour as the transitions are both spin- and symmetry forbidden.

No difference in CFSE for O_h vs T_d so Mn^{II} can adopt both octahedral and tetrahedral geometries. *e.g.*,
 $[\text{Mn}(\text{DMSO})_6]^{2+}$ $[\text{MnCl}_4]^{2-}$

8.4.4 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: LOW OS Mn

Since Mn has an odd number of electrons, Mn(CO)_n cannot form as an 18e⁻ complex. The only stable carbonyl complex of Mn is [Mn₂(CO)₁₀], shown below.

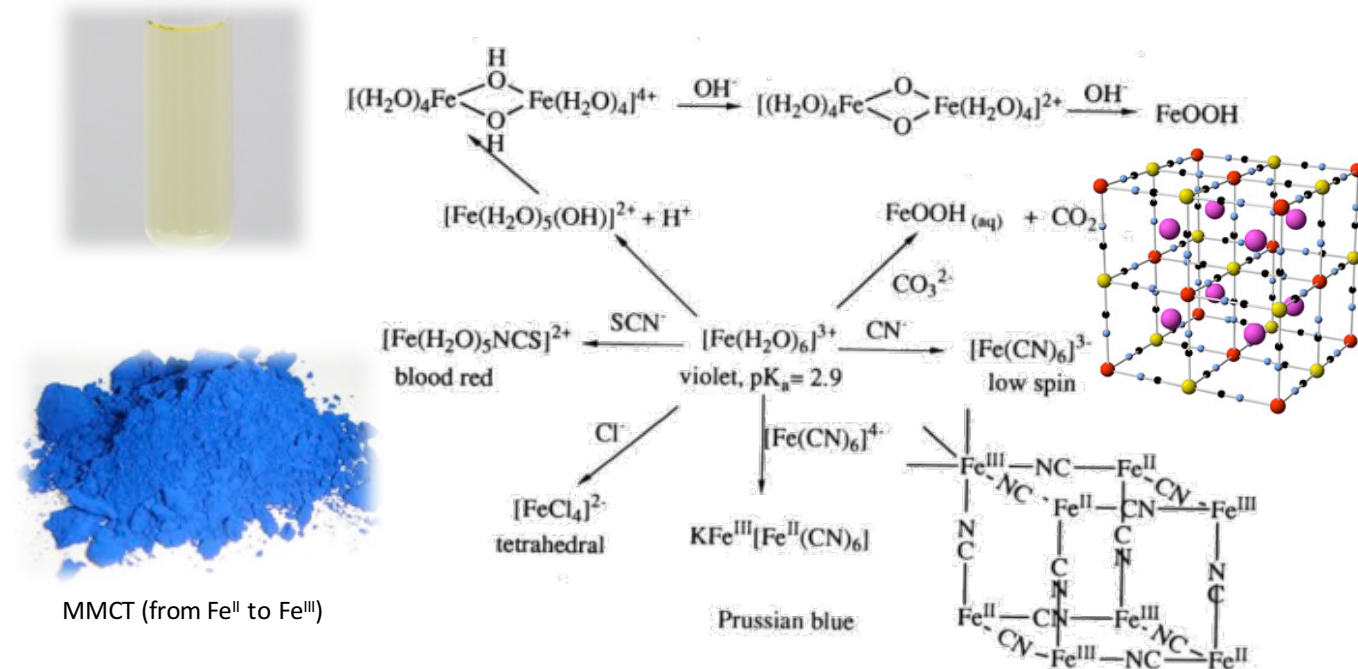
**8.5 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Fe**

Fe is plentiful on Earth and originates from fusion in high-mass stars, where the production of nickel-56 (which decays to the most common isotope of iron) is the last nuclear fusion reaction that is exothermic. Fe is the 4th most abundant element on Earth and is cheap (though used to be 8x more than gold!). It has been used for more than 6000 years. It has a wide number of accessible oxidation states from Fe²⁺ to Fe⁶⁺.

8.5.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Fe(VI) AND Fe(III)

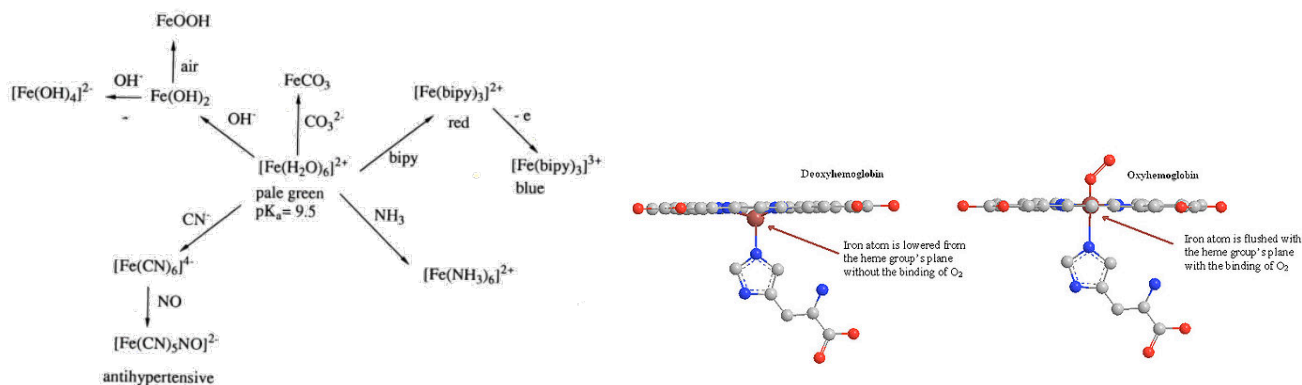
Fe^{VI} is 3d². [Fe^{VI}O₄]²⁻ + heat – gives [Fe^VO₄]³⁻ + O₂, showing the strongly oxidizing nature of Fe^{VI}

Fe^{III} is $3d^5$. Complexes of Fe^{III} are high spin. Weak absorption as $\Delta I = 0$ – $[\text{Fe}(\text{OH}_2)_6]^{3+}$ is pale violet. Some of the chemistry of Fe^{III} is shown below.



8.5.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: $\text{Fe}(\text{II})$

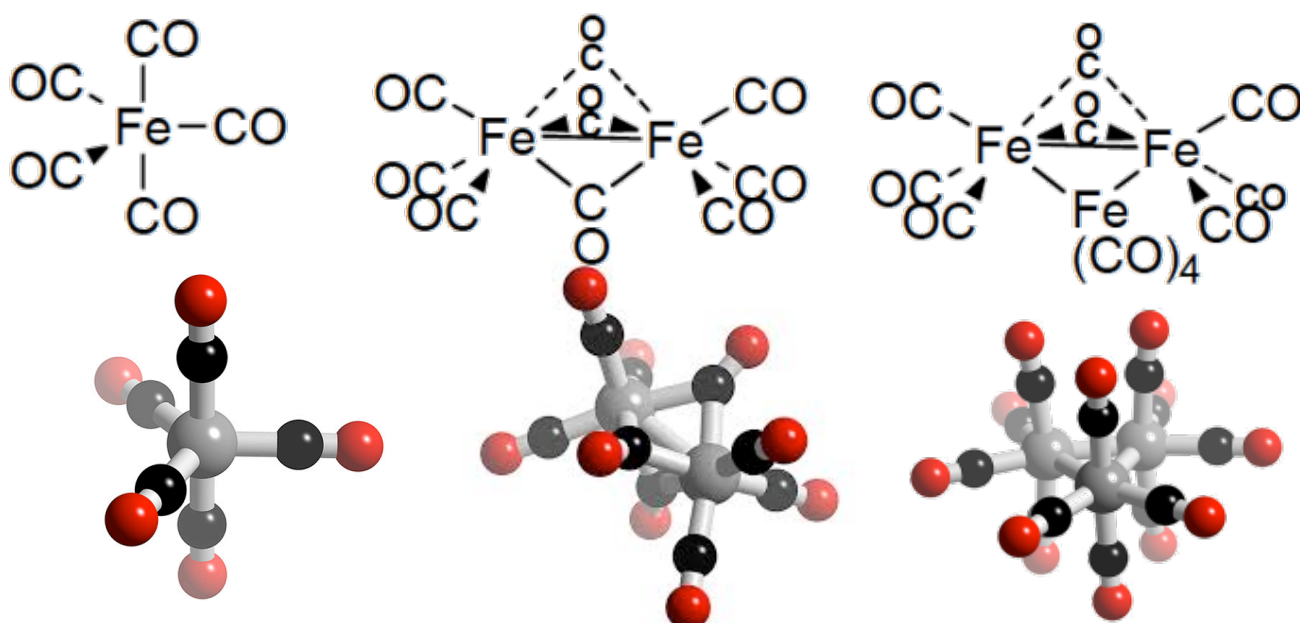
Fe^{II} is $3d^6$. Much substitution chemistry is possible. Strong field ligands stabilize Fe^{II} . Some of the chemistry of Fe^{II} is outlined below. Probably the most important Fe^{II} compound is hemoglobin. When deoxygenated in the blood the Fe_{II} is high spin but upon O_2 complexation the Fe is oxidized to Fe^{III} and becomes low spin.



Another common complex of Fe^{II} is ferrocene, which is used as a standard in electrochemistry measurements.

8.5.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: $\text{Fe}(\text{0})$

Several $\text{Fe}(\text{0})$ carbonyl complexes exist and are shown below.



8.6 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Co

Since ancient times cobalt compounds have been used to produce blue glass and ceramics. The element was first isolated by Swedish chemist George Brandt in 1735. He showed it was the presence of Co that caused the blue color in glass, not bismuth as previously thought. In about 1741 he wrote, "As there are six kinds of metals, so I have also shown with reliable experiments... that there are also six kinds of half-metals: a new half-metal, namely cobalt regulus in addition to mercury, bismuth, zinc, and the reguluses of antimony and arsenic." The word cobalt is derived from the German 'kobold', meaning goblin or elf.

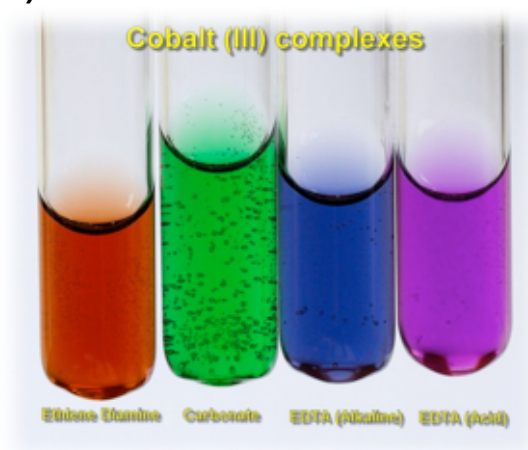
Cobalt has been known and used by people for its beautiful colouring and pigment properties as far back as 2500 BCE. Egyptian cobalt blue paints and Prussian cobalt oxide necklaces have been dated back to this time while cobalt glass has been found in a Greek vase dated at 100 BCE. Cobalt was also used to colour glass in the Chinese Tang dynasty from 618 CE. In fact all the way up until the beginning of the 20th century people have only really exploited cobalt for its beautiful colour.

Cobalt is very important biologically as it is found in vitamin B12. Deficiencies in vitamin B12 can lead to anaemia. China and Canada are the biggest producers of Co. It has many uses but is most commonly used in superalloys and in batteries.

8.6.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Co(III)

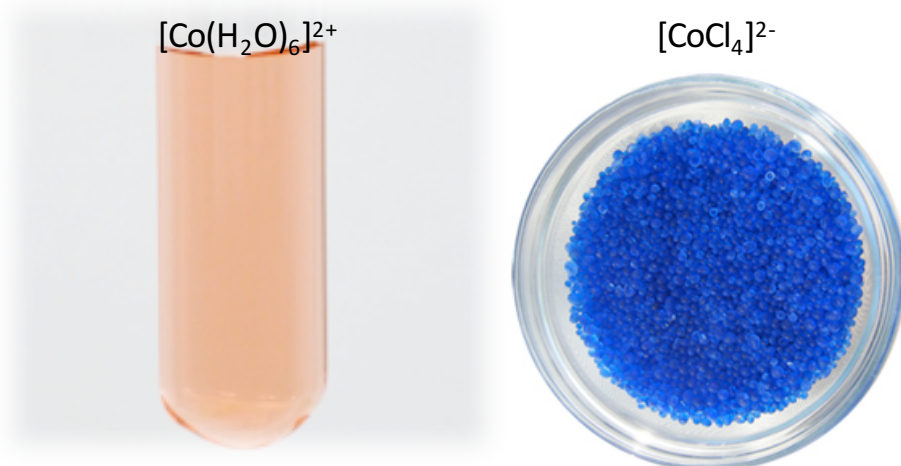
Co^{III} and Co^{II} are the only really important oxidation states (OS range from Co^{-3} - Co^4). Co^{III} is $3d^6$. $[\text{Co}(\text{OH}_2)_6]^{3+}$ is a rare example of a low spin aqua complex in the 1st row. It oxidizes water slowly to O_2

Co^{III} low spin complexes are generally inert due to high CFSE. It is possible to access a wide range of colours depending on the choice of ligand in Co^{III} complexes.

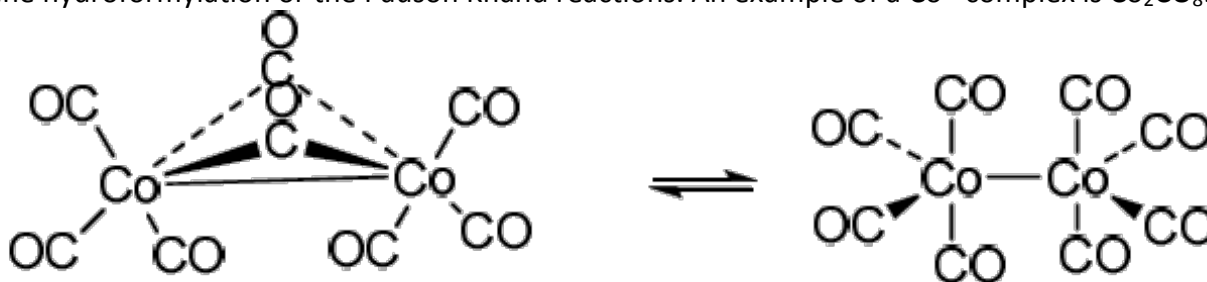


8.6.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Co(II)

Co^{II} is $3d^7$. Tetrahedral complexes are quite common, especially $[\text{CoX}_2]^{2-}$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) as there is not such a big difference in CFSE between O_h and T_d . Colour differences in both intensity and energy can be dramatic (see below).

**8.6.3 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Co(0)**

Co^0 is $3d^9$. Rare examples and formed with strong field π -acid ligands. These can be used as catalysts for alkene hydroformylation or the Pauson Khand reactions. An example of a Co^0 complex is Co_2CO_8 .

**8.7 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ni**

Nickel is the second most abundant metal after iron and is present as a result of metallic meteorites and so has been in use since ancient times. Artifacts made from metallic meteorites have been found dating from as early as 5000 BCE. It was not until the 1750s that Ni was discovered to be an element.

In the 1600s, a dark red ore, often with a green coating, had been a source of irritation for copper miners in Saxony, Germany. They believed the dark red substance was an ore of copper, but they had been unable to extract any copper from it. In frustration, they had named it 'kupfernickel', which could be translated as 'goblin's copper' because clearly, from the miners' point of view, there were goblins at work, preventing them extracting the copper.

The discoverer of Ni was Cronstedt, who was a pupil of George Brandt, the man who had discovered cobalt, which sits immediately to the left of nickel in the periodic table.

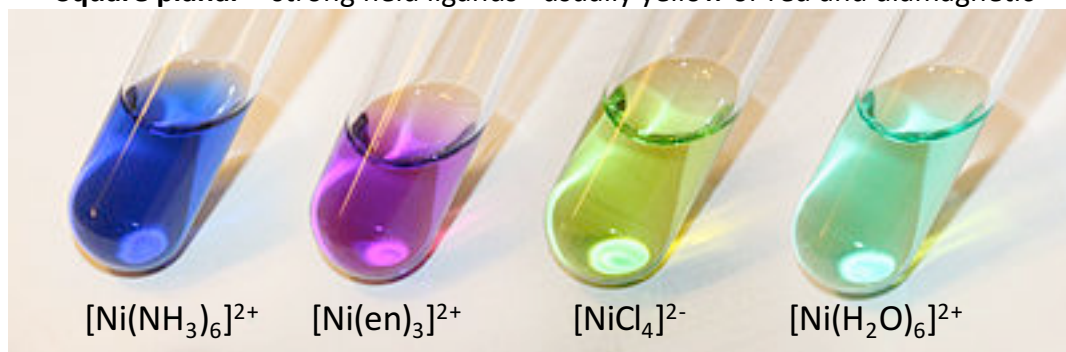
The names of both elements have their origins in the frustrations of miners caused by metal-arsenic ores: nickel arsenide and cobalt arsenide. Cobalt's name is derived from the German 'kobold' meaning 'goblin' – a close relative of the creature from which nickel's name was derived.

Ni deposits are found across the globe with Russia, the Philippines, Indonesia, Canada and Australia being major producers of Ni. Ni is corrosion resistant and used in stainless steel, which accounts for about 65% of its use. Importantly, Ni is paramagnetic and is used to construct some of the most powerful permanent magnets.

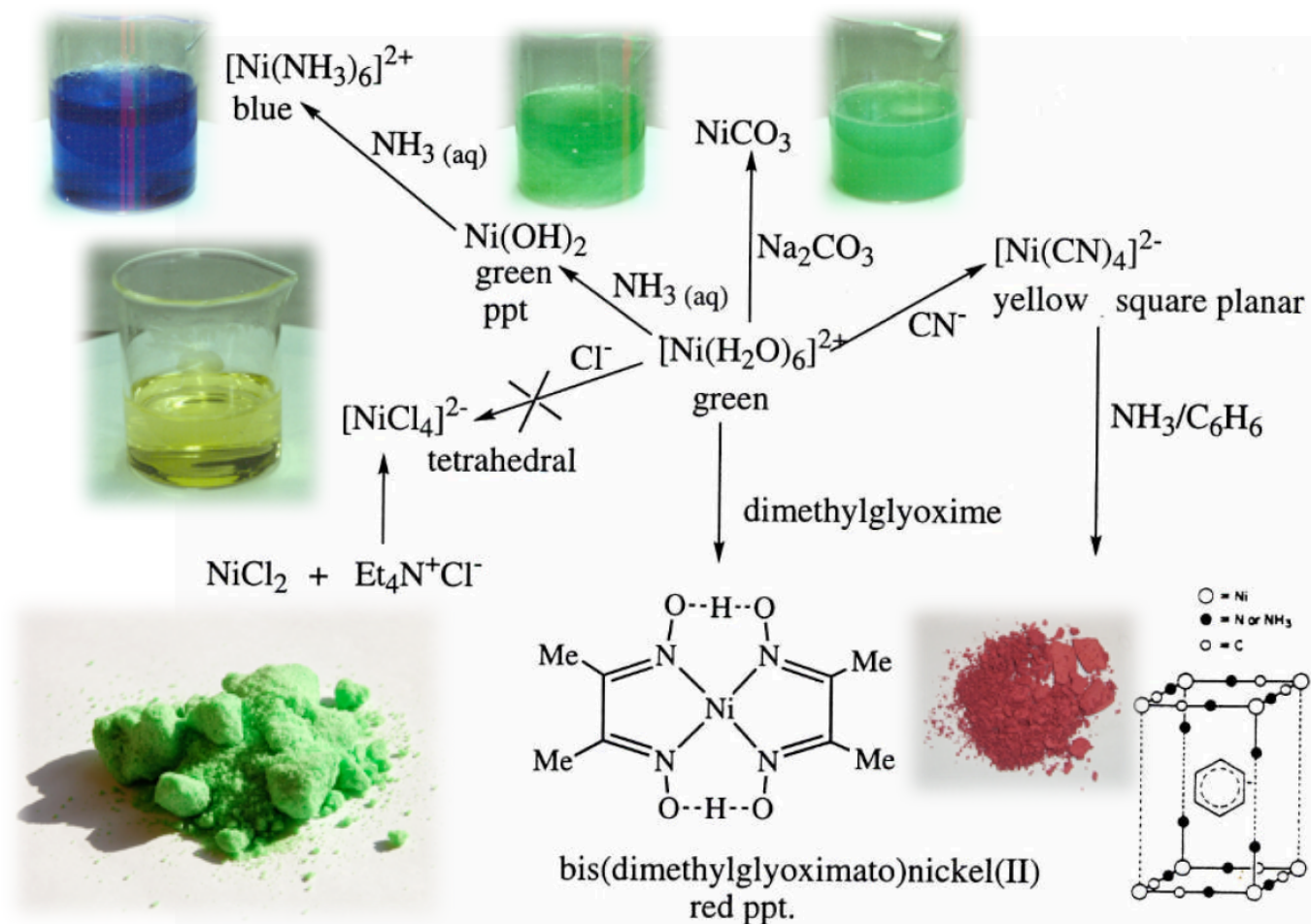
8.7.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ni(II)

Ni^{II} is 3d⁸ and is the main oxidation state of Ni. Ni^{II} can adopt several different geometries, depending on the nature of the ligand.

- **Octahedral:** small weak field ligands, including water - usually pale green or blue
2 unpaired electrons - $\mu_{\text{eff}} = 2.83$ BM
- **Tetrahedral:** large ligands especially negatively charged - dark blue or green
2 unpaired electrons - $\mu_{\text{eff}} = 3.05\text{-}4.00$ BM
- **Square planar** – strong field ligands - usually yellow or red and diamagnetic



Ni^{II} can do a wealth of chemistry (outlined below).



8.7.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Ni(0)

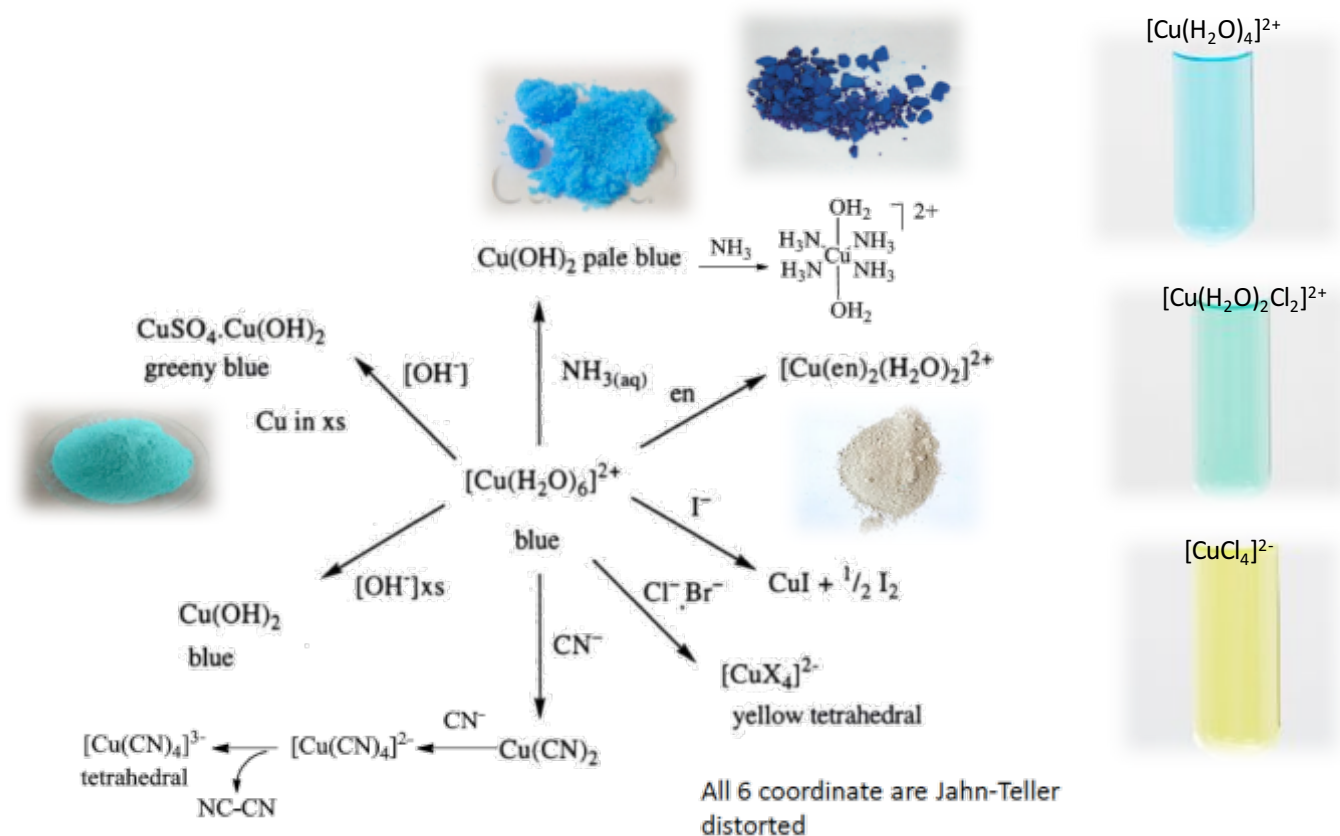
Ni^0 is $3d^{10}$. An important Ni^0 complex is $[\text{Ni}(\text{CO})_4]$, which is tetrahedral. This complex is an intermediate in the Mond process for the purification of Ni metal and is very toxic.

8.8 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cu

Cu has been used by humans for at least 11 000 years. Cu is second only to Ag in electrical conductance. Cu is very corrosion resistant as well. Cu is a very soft metal and so must be incorporated into alloys like brass (with Zn) or bronze (with Sn). Chile is by far the biggest producer of Cu in the world. Cu is mostly used in construction and then in wiring.

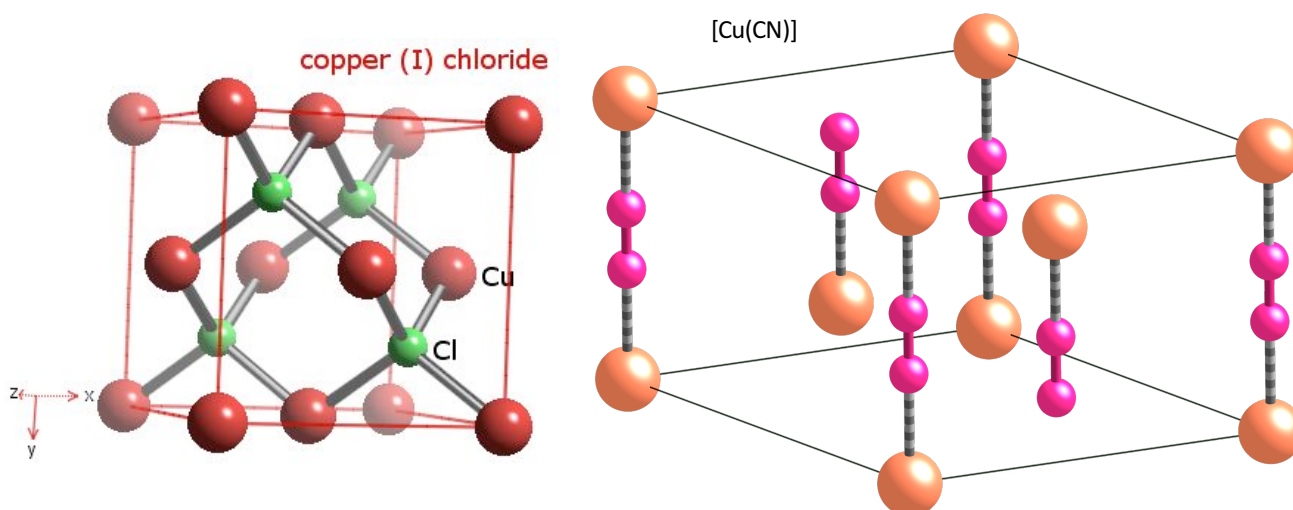
8.8.1 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cu(II)

Cu^{II} is $3d^9$ and therefore Jahn Teller distortion occurs. Depending on the geometry and the nature of the ligand, the colour of $\text{Cu}(\text{II})$ complexes can be somewhat tuned. $[\text{CuCl}_4]^{2-}$ and $[\text{CuBr}_4]^{2-}$ both exist. CuI_2 does not exist as Cu^{II} can oxidise iodide to iodine.



8.8.2 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: Cu(I)

Cu^I is $3d^{10}$. Complexes are often linear and usually colourless though $\text{Cu}(\text{I})$ complexes with organic ligands such as bpy or even Cl^- are frequently tetrahedral.



8.9 DESCRIPTIVE CHEMISTRY OF 3D-METAL COMPLEXES: SUMMARY

Through this survey it is evident that there is a wide range of properties of 3d metal complexes, particularly in terms of their colour. A summary table of the colour of metal salts in water is provided below.

OS	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
3	purple	green	Green	Brown (MnOOH)	pale violet or brown	brown		
2		lilac	royal blue	Colourless (v pale pink)	pale green	pink	Green Red/ yellow	blue
Other	colourless (Ti ^{IV})	Pale yellow [V ^{VO} O ₂] ⁺ royal blue [V ^{IVO} O] ²⁺	yellow [Cr ^{VI} O ₄] ²⁻ orange [Cr ^{VI} O ₇] ²⁻	purple [Mn ^{VII} O ₄] ⁻ Green [Mn ^{VI} O ₄] ²⁻ Blue [Mn ^{VO} O ₄] ³⁻ Brown MnO ₂				Colourless (Cu ^I)

For other oxidation states and geometries see notes on individual elements

9. REVISION AID FOR 3D-TRANSITION METAL COMPLEXES

For a given complex work out the d-electron configuration – **ALL** outer electrons are in the d shell. Below are some key points to consider based on the d-electron count of the complex

- **d⁰** – If coloured then from LMCT
- **d¹** – UV Vis explained by simple model. Unsymmetrically filled t_{2g} set. Therefore, orbital contribution
- **d²** – UV Vis explained by simple model. Orbital contribution
- **d³** – Inert (high CFSE). O_h very much favoured over T_d (CFSE) relatively large metal center and so very few tetrahedral compounds
- **d⁴** – High spin. Jahn Teller distortion easily oxidized to d³ or reduced to d⁵
d⁴ – Low spin. Orbital contribution – relatively inert
- **d⁵** – High spin. Totally half-filled shell – very stable. Very pale colour. CFSE = 0 for O_h and T_d Tetrahedral complexes are common
d⁵ – Low spin. Fairly inert (high CFSE) readily reduced to LS d⁶. Orbital contribution Very unusual electronic configuration. Needs strong field ligands or 2nd or 3rd row metals
- **d⁶** – High spin. Easily oxidized to HS d⁵. Orbital contribution. Rather unusual electronic configuration. Needs weak field ligands such as F⁻
d⁶ – Low spin. Very stable (totally filled sub-shell) and inert (very high CFSE).
- **d⁷** – High spin. CFSE_{oct} >> CFSE_{tet}, small ion. Orbital contribution. T_d complexes very common.
d⁷ – Low spin. Jahn Teller distortion. Easily oxidized to LS d⁶
- **d⁸** – CFSE_{oct} >> CFSE_{tet}. Usually O_h but with large ligands T_d dominates. Square planar for strong field ligands and for 2nd and 3rd row metal complexes
- **d⁹** – Jahn Teller distortion. Square planar for strong field ligands and for 2nd and 3rd row metal complexes. Very unusual electronic configuration
- **d¹⁰** – Often linear or tetrahedral. Usually colourless