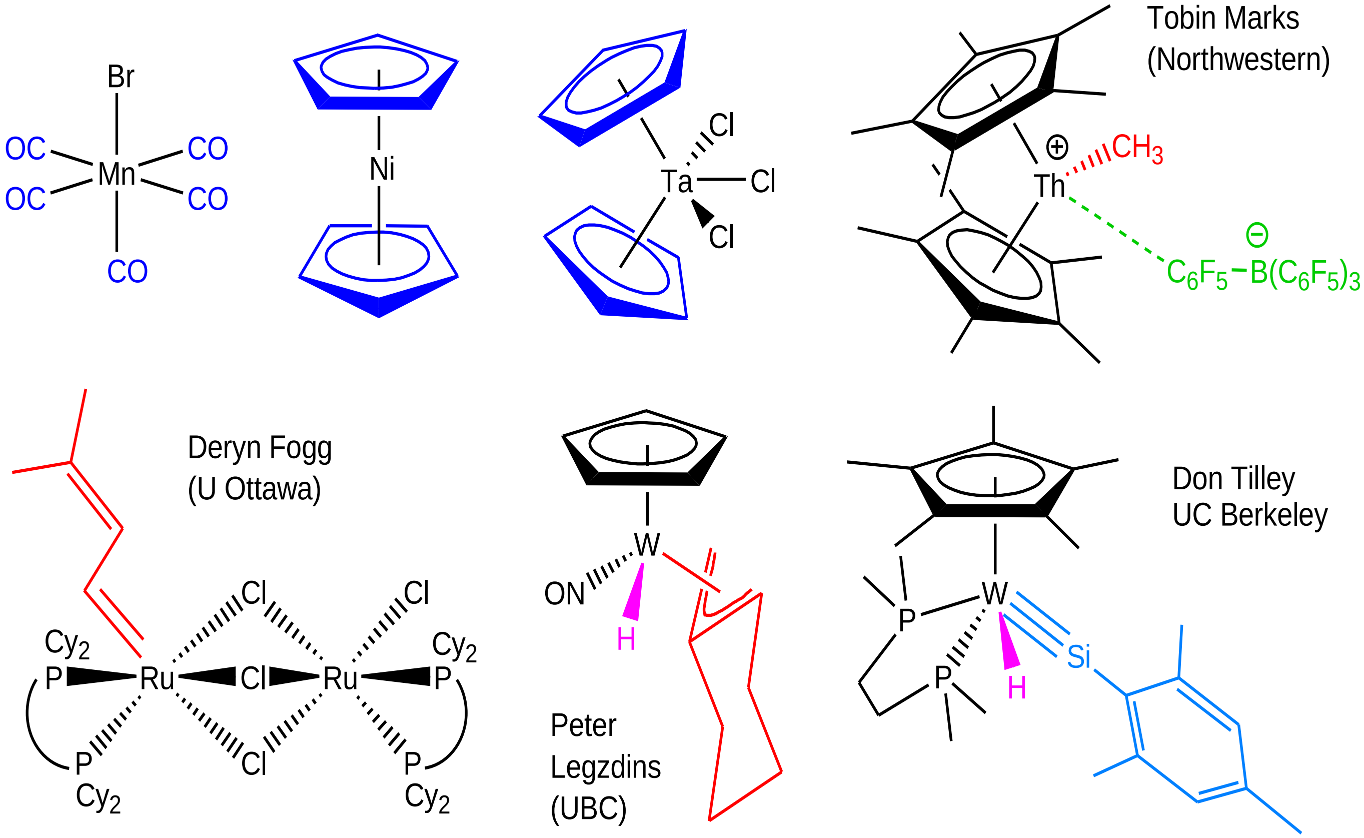
What is Organometallic Chemistry?

- Strict Definition = Compounds containing metal-carbon bonds
- (often extended to include M–Si, M–Ge, M–H etc. due to similarities with M–C)



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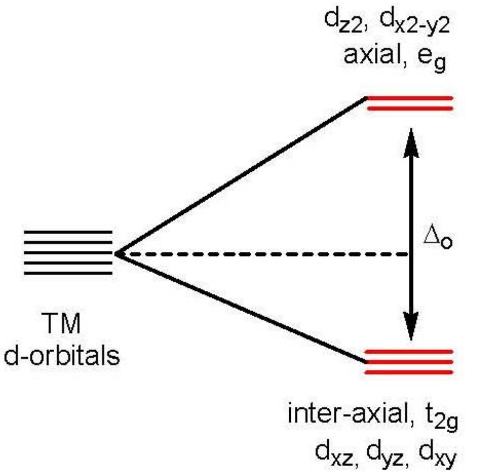
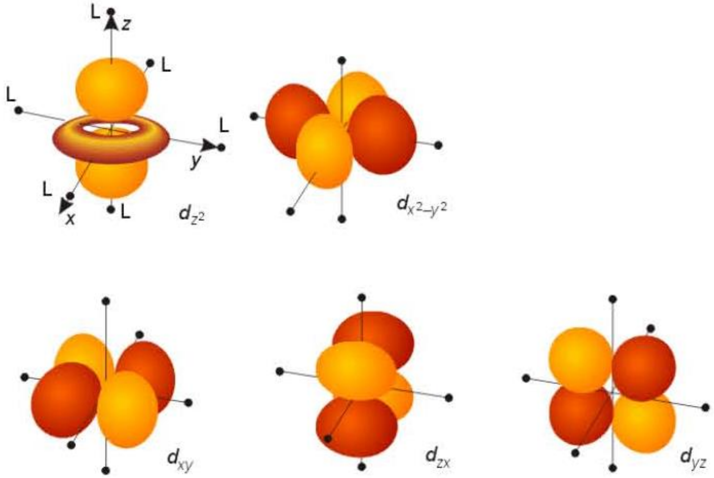
Crystal Field Theory

- A useful, but overly simplified theory, for coordination and organometallic chemistry
- Easy method to approximately predict the order of orbital energy levels for a transition metal complex:
    - Ligand lone pair considered to be a point charge (*e.g.* for Cl^-, H^- or CN^-) or the partial negative charge of a dipole (*e.g.* for $:OH_2$, $:NH_3$, $:PF_3$)
    - Ligand is attracted to the transition metal cation since they are point charges → ***purely electatic bonding assumed***
    - Any interactions between ligand and metal electrons are ***repulsive*** → no covalent bonding (σ, π, δ) exists according to this theory!

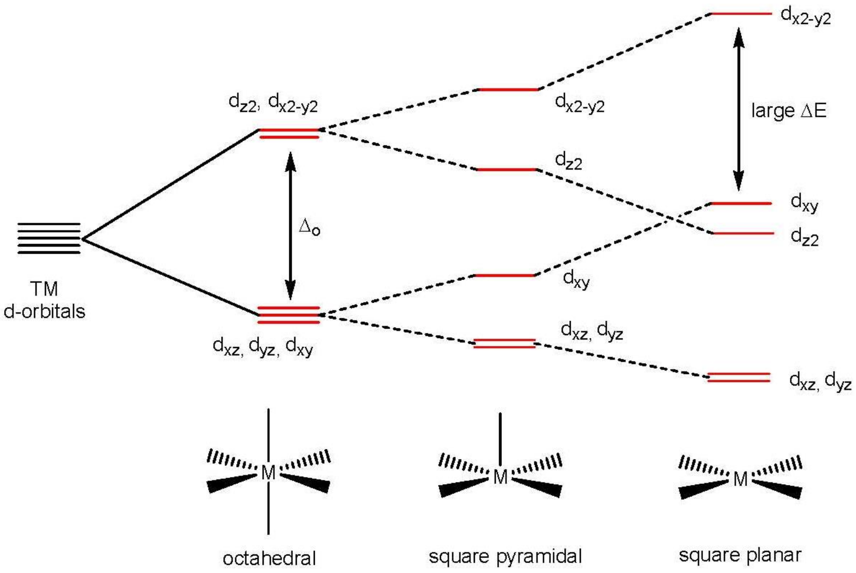




- The axial orbitals (e_g symmetry in an octahedral environment) point directly towards the ligands, so according to crystal field theory, are raised in energy (unfavourable interacton between the ligand and metal electrons.
- The inter-axial ligands (t_{2g} symmetry in an octahedral environment) do not point directly towards the ligands, so are lower in energy than the axial orbitals

Crystal Field Theory

Square pyramidal and square planar geometry from Octahedral:

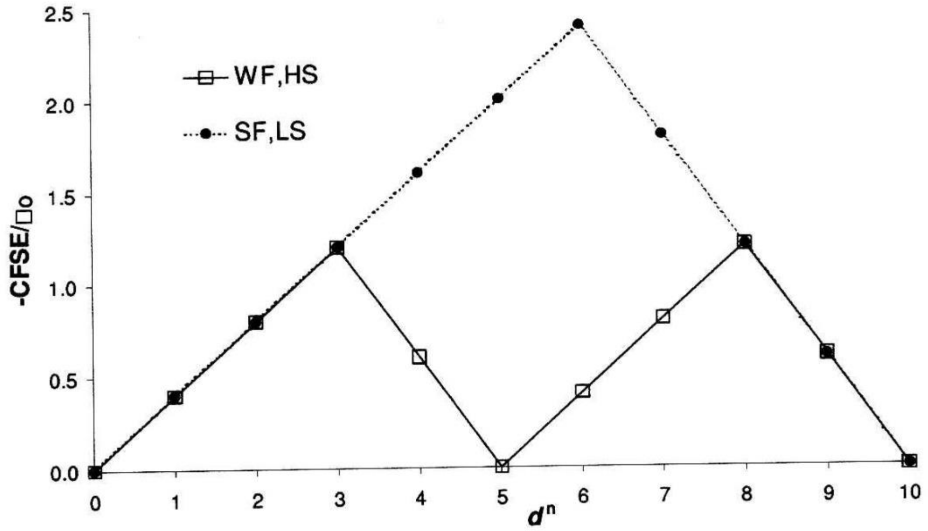


- From the octahedral crystal field splitting diagram, remove one of the ligands along the z-axis
- Since the unfavourable interaction in the z-direction is now partly removed, all orbitals with a z-component (d_{z2}, d_{xz}, d_{yz}) decrease in energy. All others d_{xy} and $d_{x2–y2}$ orbitals. As a result, square planar complexes are almost exclusively d^8 metals (all but extremely antibonding $d_{x2–y2}$ orbital are filled), and so have 16, rather than 18, electrons.
- Crystal field theory is therefore useful for quickly predicting the order of orbital energy levels in transition metal complexes. However, the assumption that all bonding is ionic and no covalent interactions exist is unrealistic. According to this assumption CO (an excellent ligand for electron rich metals) would be a terrible ligand (no negative charge and a small dipole) and ligands would not be expected to bond to metals lacking a formal positive charge (*e.g.* $Pd(PPh_3)_4$, $Fe(CO)_4^{2-}$). It therefore becomes impossible to understand why Δ_o varies according to ligand.

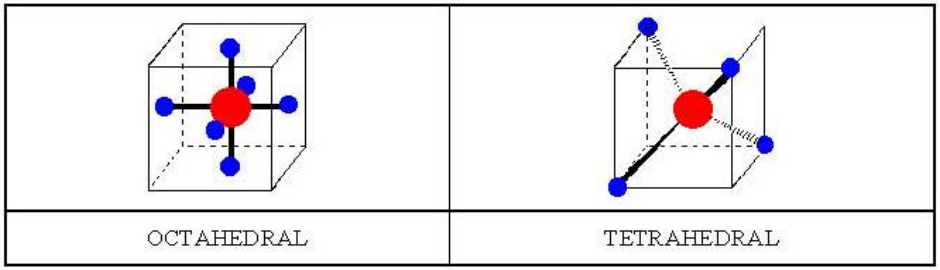
Crystal Field Theory

Crystal Field Stabilization Energy (CFSE):

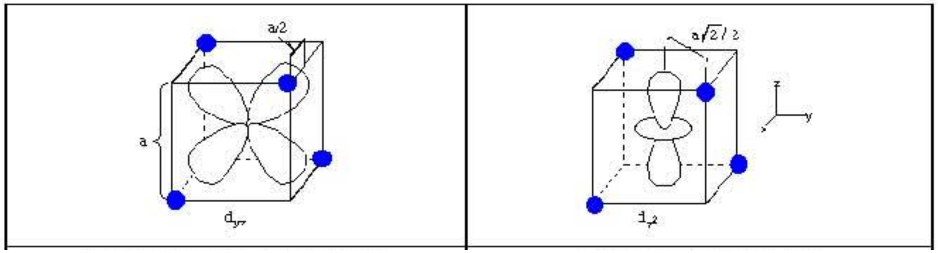
Configuration	High Spin		Low Spin
d^0		$t_{2g}^{0}e_{g}^{0} = 0.0\,\Delta_o$	
d^1		$t_{2g}^{1}e_{g}^{0} = -0.4\,\Delta_o$	
d^2		$t_{2g}^{2}e_{g}^{0} = -0.8\,\Delta_o$	
d^3		$t_{2g}^{3}e_{g}^{0} = -1.2\,\Delta_o$	
d^4	$t_{2g}^{3}e_{g}^{1} = -0.6\,\Delta_o$		$t_{2g}^{4}e_{g}^{0} = -1.6\,\Delta_o + P$
d^5	$t_{2g}^{3}e_{g}^{2} = 0.0\,\Delta_o$		$t_{2g}^{5}e_{g}^{0} = -2.0\,\Delta_o + 2P$
d^6	$t_{2g}^{4}e_{g}^{2} = -0.4\,\Delta_o + P$		$t_{2g}^{6}e_{g}^{0} = -2.4\,\Delta_o + 3P$
d^7	$t_{2g}^{5}e_{g}^{2} = -0.8\,\Delta_o + 2P$		$t_{2g}^{6}e_{g}^{1} = -1.8\,\Delta_o + 3P$
d^8		$t_{2g}^{6}e_{g}^{2} = -1.2\,\Delta_o + 3P$	
d^9		$t_{2g}^{6}e_{g}^{3} = -0.6\,\Delta_o + 4P$	
d^{10}		$t_{2g}^{6}e_{g}^{4} = 0.0\,\Delta_o + 5P$	

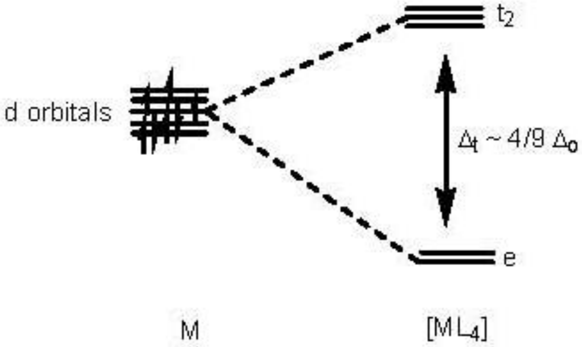


Crystal Field Theory



Tetrahedral:



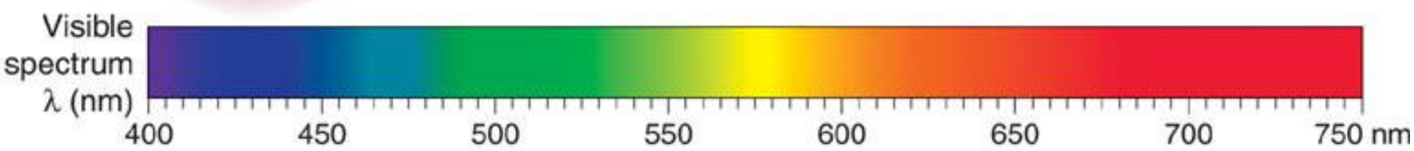


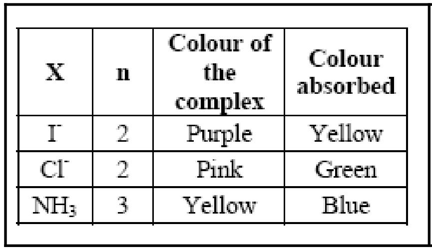
- Inter-axial ligands point more directly at the 4 ligands → more of an unfavourable interaction between the ligand and metal electrons → **higher in energy**
- Axial orbitals point less directly at the 4 ligands → less of an unfavourable interaction between the ligand and metal electrons → **lower in energy**
- Δ_t is much smaller than Δ_o, partly because none of the metal orbitals point directly at the ligands, so overlap is less efficient.

Crystal Field Theory

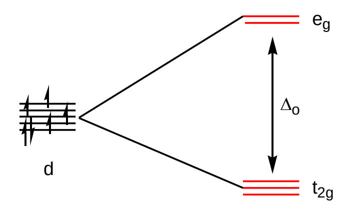
Why is the series of ligands or metals named a *spectrochemical* series ?

- Variations in the size of Δ_o can often be seen visually, for example in $[Co^{III}X(NH_3)_5]^{n+}$ (a d^6 complex).





X	n	Colour of the complex	Colour absorbed
I^-	2	Purple	Yellow
Cl^-	2	Pink	Green
NH_3	3	Yellow	Blue



- The colour of the complexes above results from promotion of an electron from a t_{2g} orbital to an e_g orbital. The energy of light absorbed therefore corresponds to the size of Δ_o. [Note: This type of simple treatment can only be applied in certain cases (*e.g.* d^1 or d^9 complexes and octahedral 3d complexes with a HS d^4 or HS d^6 configuration)].
- For complexes with a single absorption in the visible region of the spectrum, the colour of light absorbed can be determined from the colour wheel (the colour of the light absorbed is found opposite the colour of the complex).
- Since the order of energy is blue > green > yellow, then the NH_3 complex can be seen to have a larger Δ_o than the Cl^- complex, which has a larger Δ_o than the I^- complex.
- From the colours of such complexes it has been possible to build up a series of ligands which is arranged in order of increasing Δ_o. *Since the effect of the ligands on the size of Δ_o is a visible change, the resulting series of ligands is called the spectrochemical series*.

The Spectrochemical Series of Ligands

Experimentally determined values of Δ_o in $[ML_6]$ complexes:

	Ion	**Ligand**				
		Cl^-	**H_2O**	**NH_3**	**en**	**CN^-**
d^3	Cr^{3+}	13.7	17.4	21.5	21.9	26.6
d^5	Mn^{2+}	7.5	8.5		10.1	30
	Fe^{3+}	11.0	14.3			(35)
d^6	Fe^{2+}		10.4			(32.8)
	Co^{3+}		(20.7)	(22.9)	(23.2)	(34.8)
	Rh^{3+}	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
d^8	Ni^{2+}	7.5	8.5	10.8	11.5	

(units = 1000 cm^{-1}, values in brackets are for low spin complexes)

- For octahedral transition metal complexes, Δ_o varies depending on the nature of the ligands:

weak field ligands (small Δ_o)

strong field ligands (large Δ_o)

$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < F^- < OH^- < OH_2 < MeCN < NH_3 < PR_3 < CN^- < CO < NO^+$

good π-donors | OK π-donors | σ-donors | good π-acceptors

- Using Ligand Field Theory instead of Crystal Field Theory, we will see that ligands can be σ-donors, π-donors or π-acceptors, and that the ability of a given ligand to act as a π-donor or π-acceptor has a large effect on the magnitude of Δ_o. As a result, the order of ligands in the spectrochemical series closely follows their behaviour as π-donors, σ-donors or π-acceptors.

The Spectrochemical Series of Metals

- Δ_o depends not only on the nature of the ligands, but also on the metal and its oxidation state.

The spectrochemical series for metal ions (approximate) is shown below:

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

- This series is not quite as regular as the spectrochemical series of ligands, but there are obvious trends:

(1) For a given metal and ligand set, Δ_o increases with increasing oxidation state ($Co^{2+} < Co^{3+}$ etc.).

Explanation: Metal ions in a higher oxidation state have greater polarizing power. As a result, bonding becomes more covalent and less ionic.

(2) For a given oxidation state and ligand set, Δ_o increases down a group ($Co^{3+} << Rh^{3+} < Ir^{3+}$).

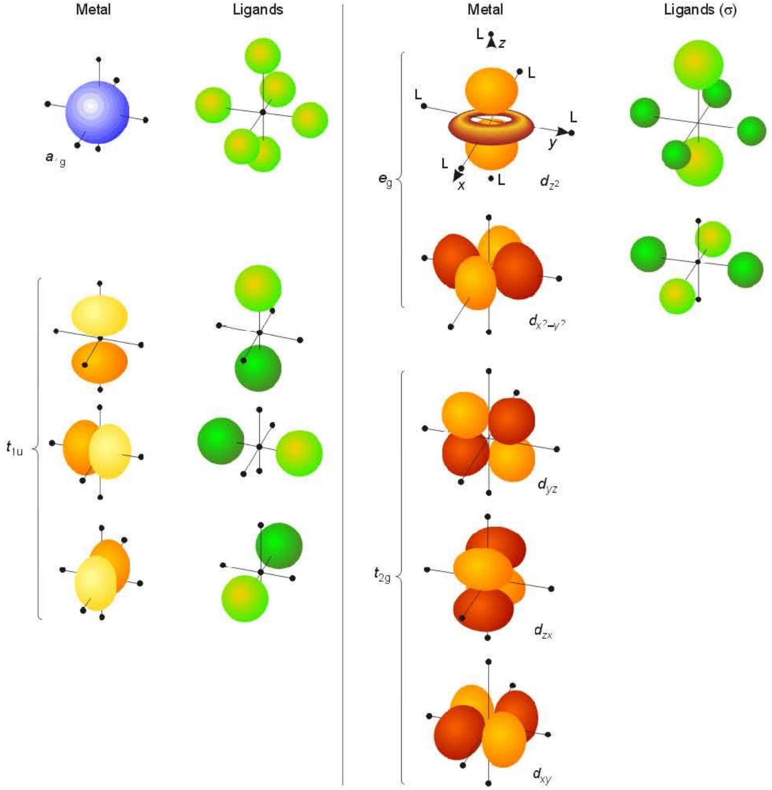
Explanation: M–L bonding is more effective for larger 4d and 5d orbitals relative to the 3d orbitals. Also, higher effective nuclear charge on the metal.

(3) For a given oxidation state and ligand set, Δ_o varies irregularly across the transition metals (groups 3 to 12).

Explanation: Depends on a variety of factors!

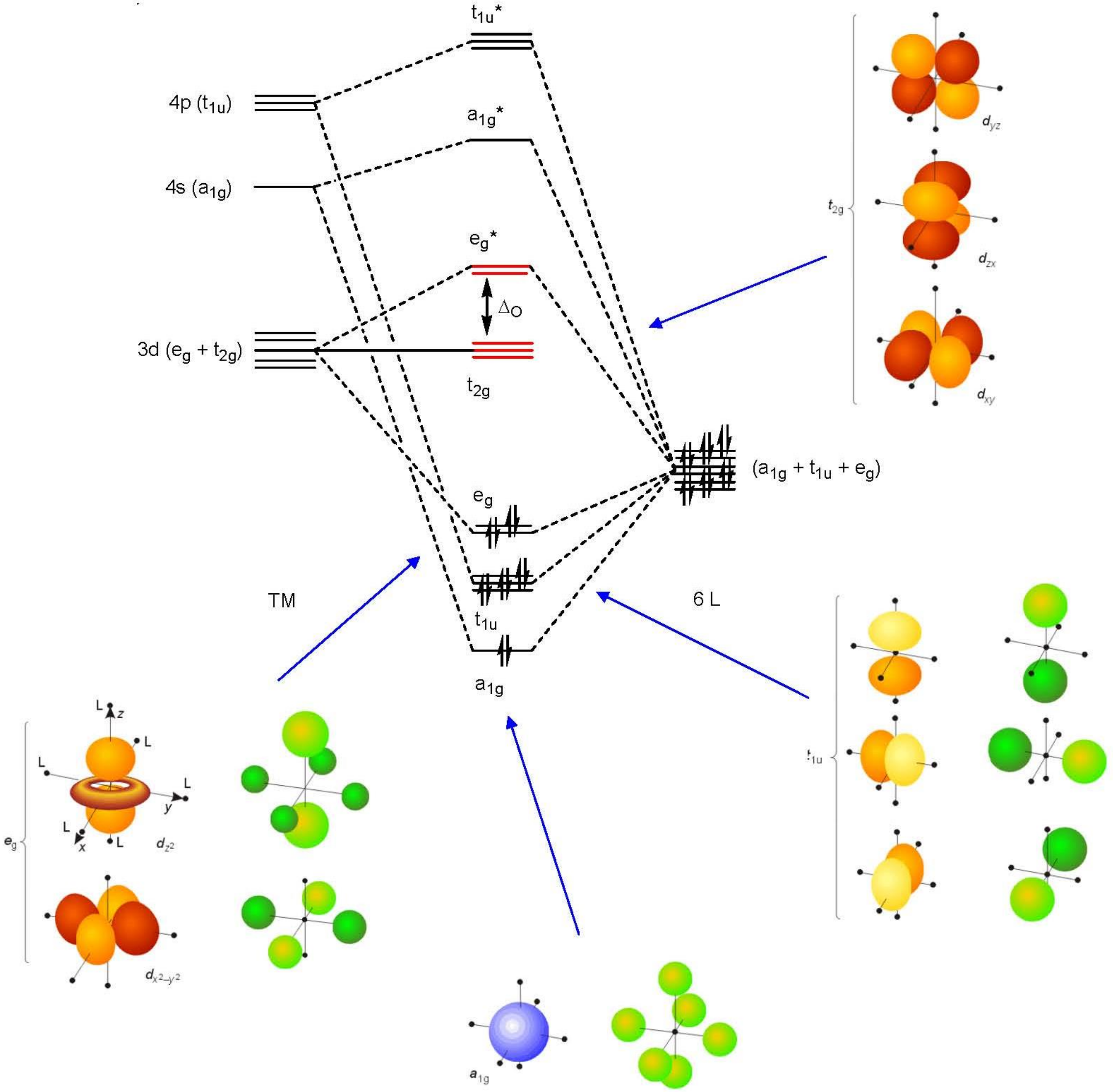
Ligand Field Theory

Symmetry adapted combinations of ligand σ-orbitals in an octahedral complex:



- In an octahedral environment the metal orbitals (3d, 4s, 4p for a 1st row TM) divide by symmetry into 4 sets: s = a_{1g}, p = $_{t1u}$, axial d = e_g, inter-axial d = t_{2g}
- The orbitals of the six ligands can be combined to give six symmetry-adapted linear combinations which are of the correct symmetry to interact with the s, 3 p and 2 axial d-orbitals, but not the inter-axial d-orbitals
- The 3 inter-axial d-orbitals are non-bonding, while the rest (6 metal orbitals and 6 ligand orbitals) combine to form 6 bonding and 6 antibonding molecular orbitals

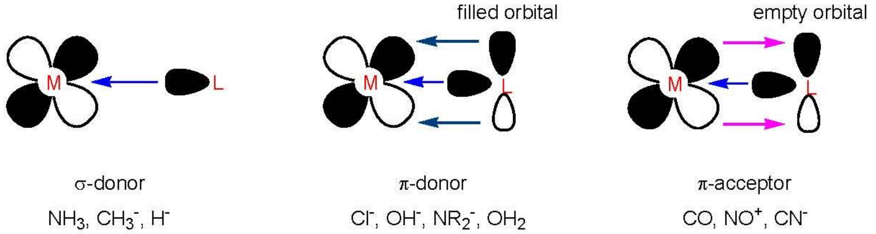
Ligand Field Theory



- The 6 bonding orbitals are filled with 12 electrons from the 6 ligands
- Orbitals shown in red (t_{2g} and e_g*) are the frontier molecular orbitals where d-electrons reside

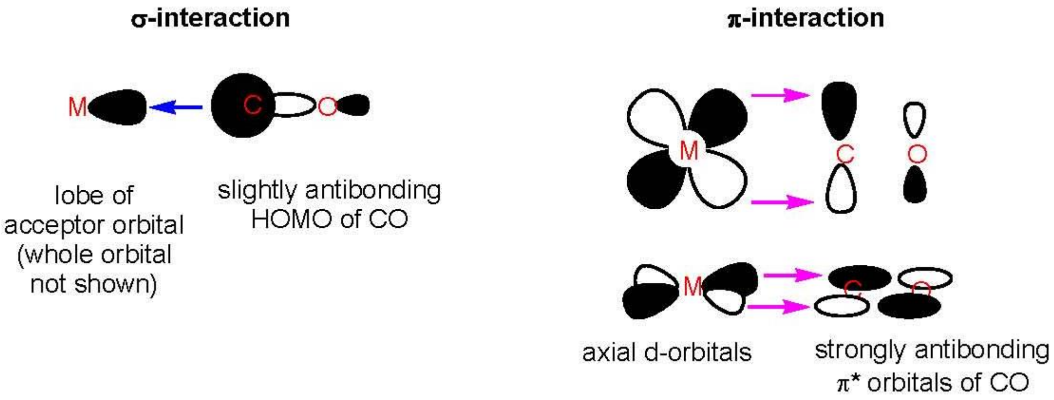
Ligand Field Theory: π-Acceptor Ligands

π-acceptor ligands:



- For π-acceptor ligands, the bonding is *synergic*: σ-donation to the metal strengthens π-backbonding to the ligand, and π-donation from the metal to the ligand strengthens the σ-donor component of bonding.
- This is because σ-donation leads to increased electron density on the metal, which allows for increased p-backdonation. Conversely, π-backdonation reduces the amount of electron density on the metal, which allows more σ-donation from the ligand to the metal.

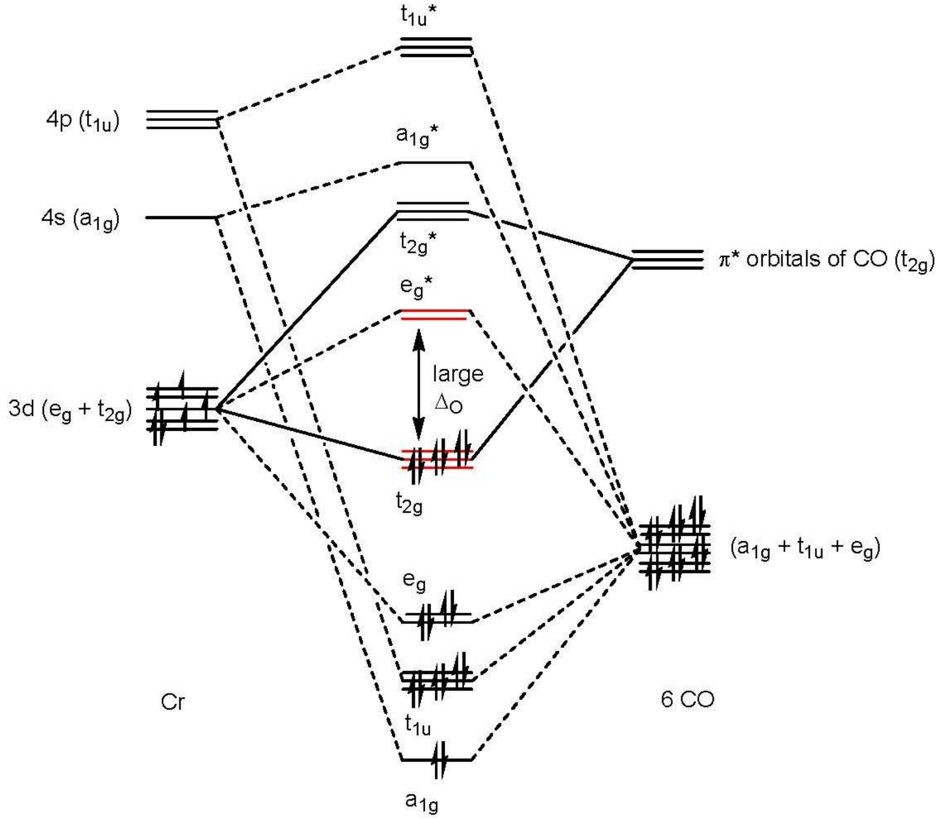
$Cr(CO)_6$: Octahedral complex with good π-acceptor ligands



- Note: The 12 empty π* orbitals of the 6 CO ligands can be combined to form 12 linear combination of orbitals (3 T_{1u}, 3 T_{2g}, 3 T_{1g} and 3 T_{2u}). Only the 3 linear combinations with T_{2g} symmetry are of the correct symmetry to interact with the t_{2g} orbitlas (d_{xy}, d_{xz} and d_{yz}) on the metal.

Ligand Field Theory: π-Acceptor Ligands

[$Cr(CO)_6$]:



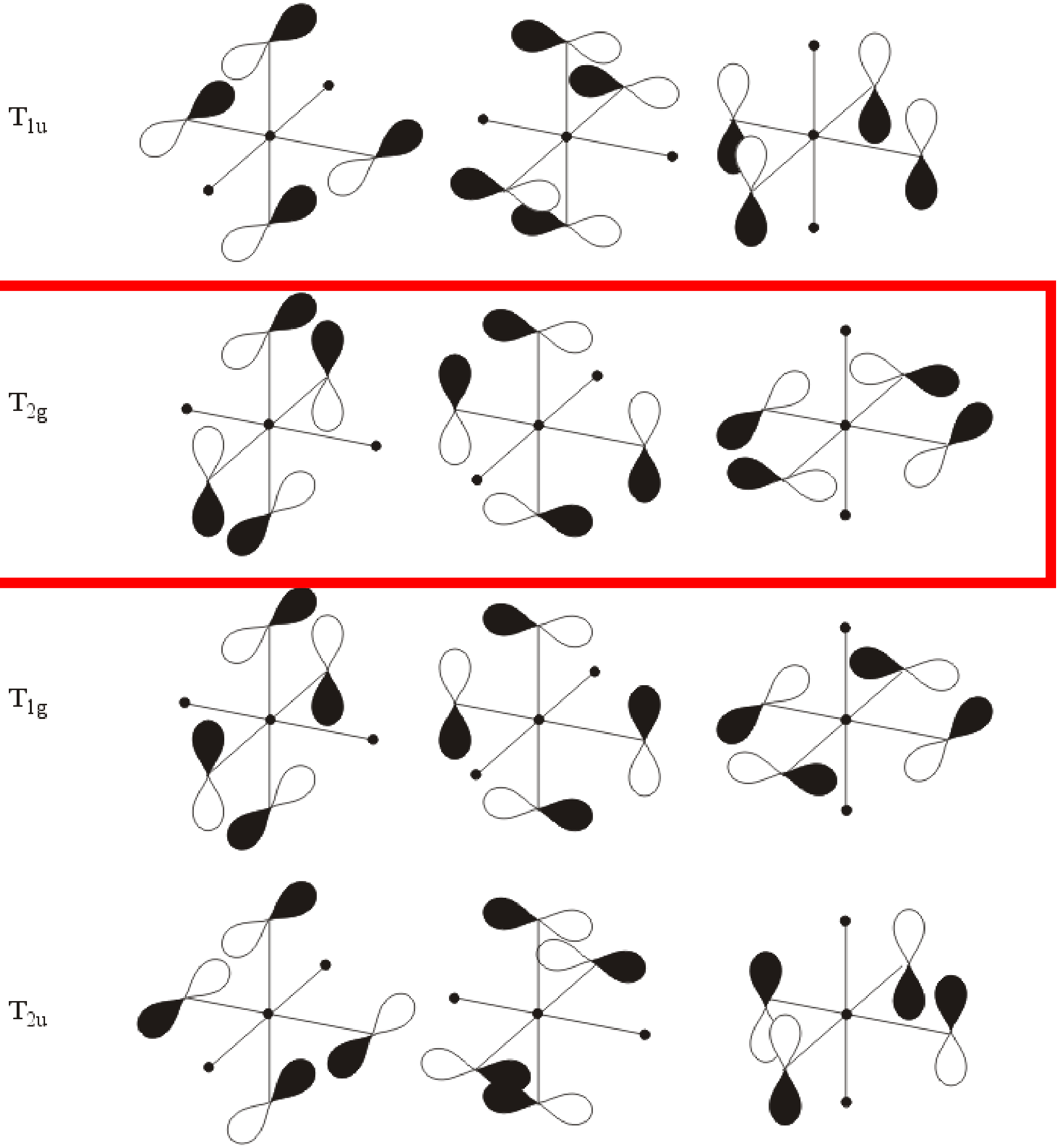
- π-backdonation to CO from the t_{2g} orbitals (which are non-bonding in the absence of π-interactions between the metal and ligands).
- The 3 t_{2g} orbitals and 3 high lying π* orbitals of the CO ligands form 3 bonding molecular orbitals and 3 antibonding molecular orbitals.
- Since the CO π* orbitals are empty, the d-electrons occupy the bonding molecular orbitals
- The results is:
  1) a very large Δ_o, so the e_g orbitals are likely to remain empty.
  2) The t_{2g} orbitals are strongly bonding (large preference to be filled with 6 electrons) → complexes with strong π-acceptor ligands are most likely to obey the 18-electron rule

Ligand Field Theory: π-Acceptor Ligands

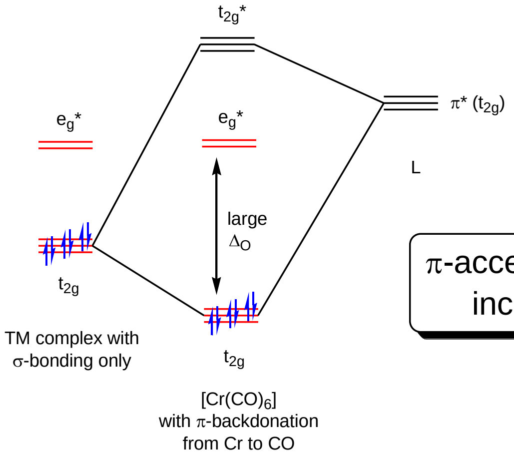
Symmetry adapted linear combinations of π* orbitals in ML_6 complexes:

- Why are there only three ligand π-acceptor orbitals shown in the MO diagram for $[Cr(CO)_6]$ when there are 6 ligands, each with two empty π* orbitals?

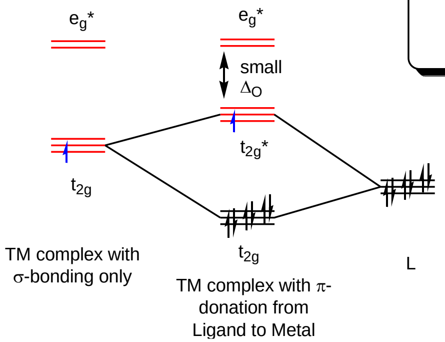
- The 12 π* orbitals of the ligands can be combined to form 12 symmetry adapted linear combinations of atomic orbitals (3 T_{1u}, 3 T_{2g}, 3 T_{1g} and 3 T_{2u}). Only the three T_{2g} linear combinations are of the correct symmetry to interact with the t_{2g} orbitals (d_{xy}, d_{xz}, d_{yz}) on the metal.



Ligand Field Theory: π-Donor Ligands



π-acceptor ligands increase Δ_O

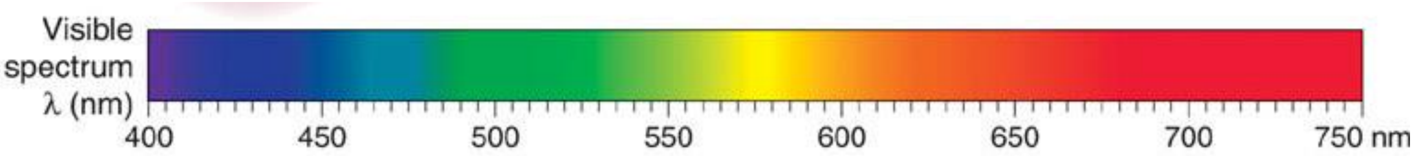


π-donor ligands decrease Δ_O

- π-donation from the ligands to the t_{2g} orbitals → the 3 t_{2g} metal orbitals and 3 low lying, filled ligand orbitals of π-symmetry form 3 bonding MOs and 3 antibonding MOs.
- Since the interacting ligand orbitals are full, these electrons occupy the bonding t_{2g} and the d-electrons occupy the antibonding MO.
- The result is:
  1) a small Δ_o
  2) the t_{2g} orbitals are weakly antibonding

Ligand Field Theory

- Using molecular orbital (ligand field) theory, instead of crystal field theory, ligands can be classified as σ-donors, π-donors and π-acceptors, explaining why ligands strongly affect the size of Δ_o in octahedral complexes
- This can be observed visually in $[Co^{III}X(NH_3)_5]^{n+}$ (a d^6, 18 electron complex).



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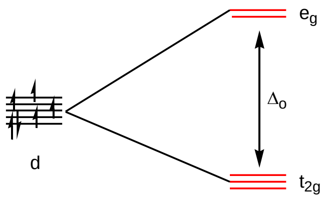

- The colour of the complexes above results from promotion of an electron from a t_{2g} orbital to an e_g orbital. The energy of light absorbed therefore corresponds to the size of Δ_o. [Note: This type of simple treatment can only be applied in certain cases (*e.g.* d^1 or d^9 complexes and octahedral 3d complexes with a HS d^4 or HS d^6 configuration)].
- For complexes with a single absorption in the visible region of the spectrum, the colour of light absorbed can be determined from the colour wheel (the colour of the light absorbed is found opposite the colour of the complex).
- Since the order of energy is blue > green > yellow, then the NH_3 complex can be seen to have a larger Δ_o than the Cl^- complex, which has a larger Δ_o than the I^- complex.

Ligand Field Theory

weak field ligands (small Δ_o) strong field ligands (large Δ_o)

$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < F^- < OH^- < OH_2 < MeCN < NH_3 < PR_3 < CN^- < CO < NO^+$

good π-donors | OK π-donors | σ-donors | good π-acceptors

- However, these π-effects are not the entire story. Organometallic ligands, such as CH_3^- or H^- are located high in the spectrochemical series (H^- is similar to CO).
- Both H^- and CH_3^- (in the absence of α-agostic interactions) are purely σ-donor ligands, so their ability to act as strong field ligands is a result of their extremely high σ-donors ability