

# Inorganic Chemistry

Cheesman

# Contents



Mononuclear Electronic



Mononuclear Magnetic



Crystal Field Theory



Dinuclear



Polynuclear



Extended Structures



Mononuclear Electronic

# Mononuclear Complexes | Electronic

## Free Transition Metal Ion (no ligands, spherical symmetry)

- ▶ s, p, d, f wave functions result from Schrödinger's equation for Hydrogen atom
- ▶ He onwards is complicated due to electron-electron repulsion
- ▶ Use hydrogen orbitals as a basis set

## The electronic configuration ( $d^3$ )

- ▶ How many electrons are in the d-shell that can be arranged in multiple ways in the d-orbitals

## Orbital Angular Momentum

- ▶ Angular momentum properties for single orbital wave functions

	s	p	d	f
l	0	1	2	3
$m_l$	0	+1, 0, -1	+2, +1, 0, -1, -2	Etc...

**Total orbital angular momentum (L)**

**Total spin angular momentum (S)**

- ▶ Derived from arrangement of the spins of the individual electrons
- ▶ Due to the valence electrons
- ▶ Filled subshells don't contribute as they have total angular momenta of  $L=0$  and  $S=0$

**Term Symbols**

- ▶ Energy levels are labelled using term symbols showing values of **L** and **S**
- ▶ Needed to explain spectroscopic and magnetic properties

$$(2S+1)L$$

**Example**

- ▶  $L = 3$  and  $S = 3/2$

$4F$

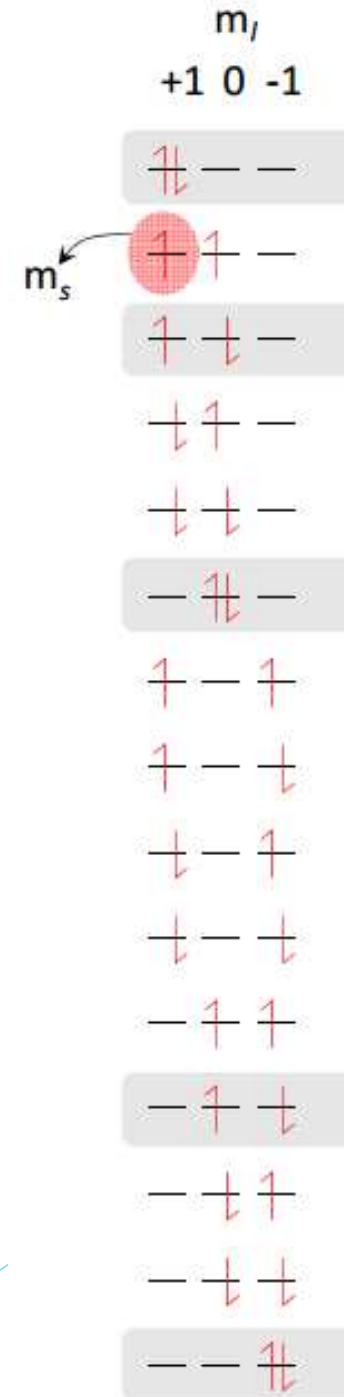
## Identifying the Term Symbols

### Single Electron

- ▶ Takes Spin and Orbital Angular Momentum of single electron
- ▶  $s^1 \rightarrow {}^2S$ ,  $d^1 \rightarrow {}^2D$

### Multiple Electrons

- ▶ Identify all possible arrangements, *microstates*, of electrons using *pauli exclusion principle*
- ▶ Adding the  $m_l$  and  $m_s$  of each state to give total  $M_L$  and  $M_S$
- ▶ Groups of degenerate microstates represent the components of that term
- ▶ Identify the highest value of  $M_L$
- ▶ This must have  $M_S = 0$  and will group with other  $M_L$  values  $M_S = 0$  to give term  ${}^1L$  (grey)
- ▶ The next highest  $M_L$  will have more than one microstate with different spins. These will give  ${}^3(L-1)$  states etc..



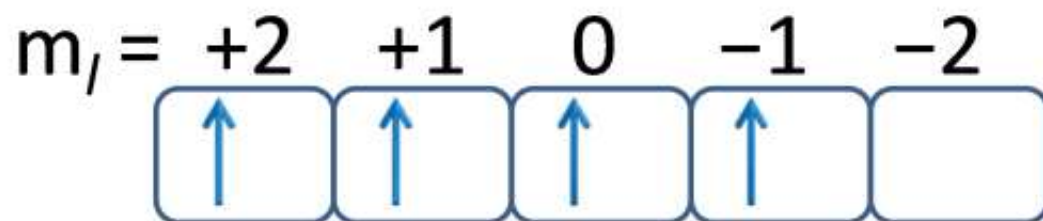
## Identifying the Ground Term

Hund's Rule | The most stable term is predicted by

- ▶ S has the highest value allowed by Pauli,
- ▶ Then, L has the highest possible value

## Quick Method

- ▶ Draw 5 d orbitals, labelled with  $m_l$  values and feed in electrons +2 onwards



- ▶ Add up  $m_l$  values to give  $(+)2 = L=2 = D$
- ▶ Add up spins of 4 electrons:  $4 \times (+)1/2 = S=2 = 2S+1 = 5$
- ▶ Ground term is  $^5D$

# What are the ground terms for

- ▶  $V^{3+}$
  - ▶  $Cr^{3+}$
  - ▶  $Cr^{2+}$
  - ▶  $Ni^{2+}$
- ▶  $3F$
  - ▶  $4F$
  - ▶  $5D$
  - ▶  $3F$

# How many states are within each of these terms

- ▶  $^1G$       ▶ 9
- ▶  $^3F$       ▶ 21
- ▶  $^1D$       ▶ 5
- ▶  $^3P$       ▶ 9
- ▶  $^1S$       ▶ 1

Work out degeneracy of  $L$  ( $2L+1$ )

Work out degeneracy of  $S$  ( $2S + 1$ )

Multiply together to get total number of states



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# Magnetic Properties | Electron

Spin Angular Momentum  $s$

$$|\mathbf{s}| = \sqrt{s(s+1)\hbar}$$

Magnetic Moment

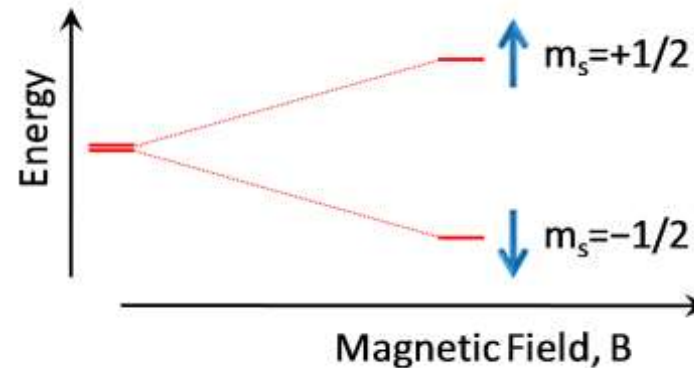
Combination of  $s$  and the charge ( $-e$ ) gives the electron a magnetic moment

$$\mu = -\frac{g_e \mu_B s}{\hbar}$$

The Zeeman Interaction

Magnetic moment of electron has different energies when aligned with or against a magnetic field

$$\Delta E = g_e \mu_B B$$



Magnitude of Zeeman Splitting

For 1 Tesla magnetic field

$$\begin{aligned} \Delta E &= 1.8 \times 10^{-23} \text{ J} \\ &= 1 \text{ cm}^{-1} \text{ (microwave)} \end{aligned}$$

# Magnetic Properties | Electron

## Temperature Dependence

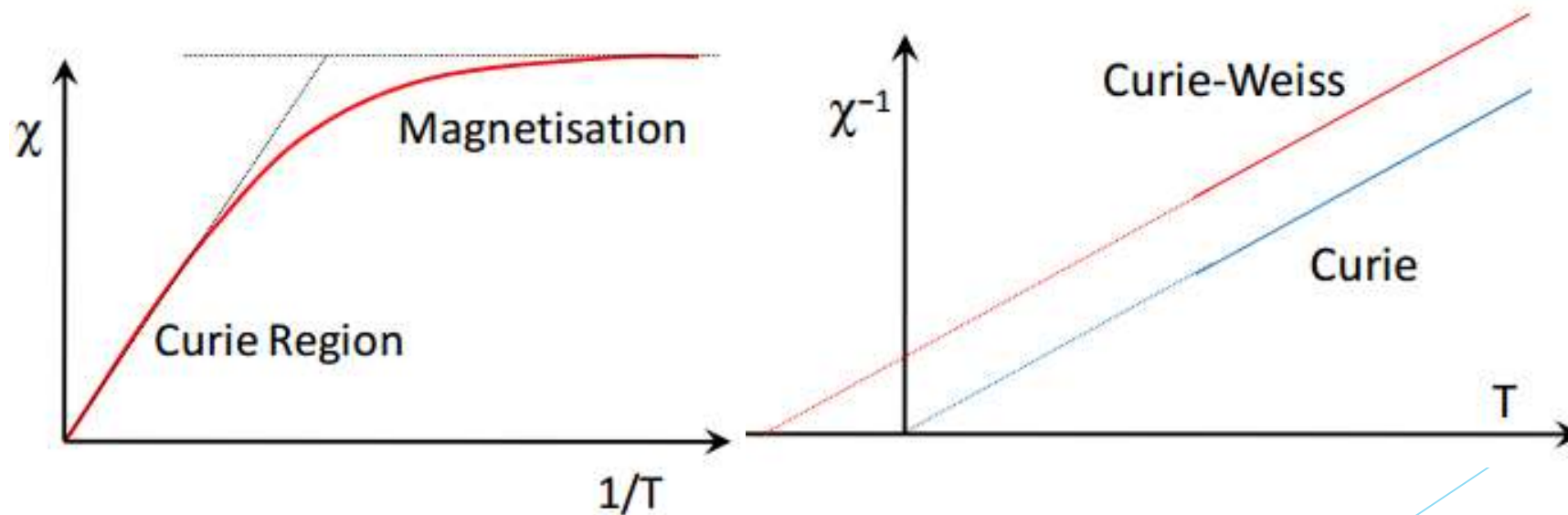
- ▶ Sample containing molecules with one unpaired electron in magnetic field
- ▶ Thermal equilibrium between +1/2 and -1/2 states
- ▶ Magnetic moment is cancelled out
- ▶ Only slight excess in ground state leads to magnetisation  $M$
- ▶ Net bulk magnetisation is derived from measurements of *magnetic susceptibility*  $\chi$
- ▶ Use a faraday balance

By Boltzmann,  $M \propto \frac{1 - e^{-\Delta E/kT}}{1 + e^{-\Delta E/kT}}$  but when  $\Delta E \ll kT$ ,  $M \propto \Delta E/kT$ .

# Magnetic Properties | Electron

## Curie Temperature

- ▶  $M$  or  $X$  are linearly proportional to temperature at high temperature
- ▶ Curie region at low  $1/T$
- ▶ Many PARAMAGNETS obey the Curie Law  $\chi = \frac{C}{T}$
- ▶ Often get better fit using Curie-Weiss  $\chi = \frac{C}{T+\theta}$
- ▶  $\theta$  is the Weiss constant



# Measuring Magnetic Properties

vacuum

paramagnet

diamagnet

Superconductor  
(Meissner)



Mononuclear Magnetic

## Measuring Magnetic Properties

- Boltzmann population differences increase in higher magnetic fields
- This leads to a lower total energy
- A paramagnet is pulled into regions of higher magnetic field intensity

## Traditional Methods

- Faraday balance
- Gouy balance

## Modern Method

- Superconducting Quantum Interface Device (SQUID)

*intensity of magnetisation  
or magnetic moment per unit volume*

*magnetic flux density*

$$B = H + 4\pi I$$

*magnetic field strength*

*susceptibility per volume*

$$\mu = \frac{B}{H} = 1 + 4\pi\kappa$$

*magnetic permeability*

$\kappa \rightarrow \chi \rightarrow \chi_m$  *molar susceptibility*

# Extracting $\mu$ from $\chi$

- ▶ A raw measurement of paramagnetism via  $\chi$  will display a strong temperature dependence
- ▶ We are interested in  $\mu$  the **magnetic moment** of the individual paramagnetic transition ion
- ▶ This will tell us how many unpaired electrons are present
- ▶  $\mu$  is obtained from  $\chi$  by removing the effect of temperature
  
- ▶ At high temperatures the magnetic susceptibility  $\chi$  is proportional to  $1/T$  in the **curie region**
- ▶ Magnetic moment can be obtained from the equation

$$\mu^2 = \left( \frac{3k}{\mu_0 N \mu_B^2} \right) (\chi T) = 6.636 \times 10^5 (\chi T)$$

- ▶ The magnetic moment is usually called the **effective magnetic moment**  $\mu_{eff}$

# Magnetic Moment $\mu$ arises from both S & L

- ▶ Magnetism does not just contain spin of single electron ( $S=1/2$ ) but also L.
- ▶ L results from the freedom of electron to move between orbitals and rotate around the nucleus
- ▶ For free ions, the quantum numbers L and S are known from the term symbol
- ▶ Van Vleck's equation:

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

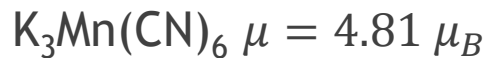
number of d-electrons	L	S	Free-ion ground term	$\mu_{L+S}$	$\mu_S$	$\mu_{obs}$
1	2	1/2	$^2D$	3.00	1.73	1.7-1.8
2	3	1	$^3F$	4.47	2.83	2.8-2.9
3	3	3/2	$^4F$	5.20	3.87	3.7-3.9
4	2	2	$^5D$	5.48	4.90	4.8-5.0
5	0	5/2	$^6S$	5.92	5.92	5.8-6.0
6	2	2	$^5D$	5.48	4.90	5.1-5.7
7	3	3/2	$^4F$	5.20	3.87	4.3-5.2
8	3	1	$^3F$	4.47	2.83	2.9-3.9
9	2	1/2	$^2D$	3.00	1.73	1.7-2.2

# Symmetry-Quenched Magnetic Moments

- ▶ Sometimes the magnetic moments observed are lower than those of the free ion
- ▶ This is because we assume that  $L = 0$  and the Van Vleck's formula reduces to the *spin only formula*

$$\mu = 2\sqrt{S(S + 1)}$$

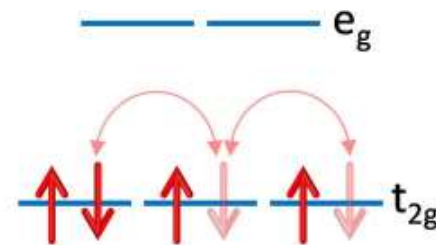
## Example



Source: <https://www.researchgate.net/publication/235501106>

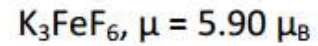
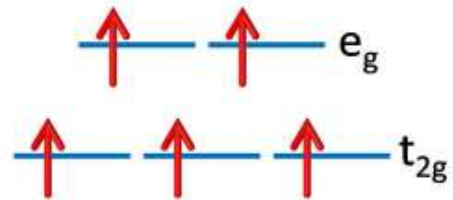
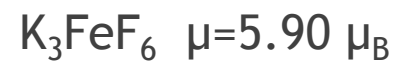
Mn(III) is  $d^4$ . Strong field cyanide ligand puts all electrons in the  $t_{2g}$  orbitals and so there are *two* unpaired electrons. The spin-only magnetic moment for this would be  $2.83 \mu_B$ . The additional magnetic moment arises from a contribution to the total angular momentum

from *orbital* angular momentum. i.e. orbital angular momentum ( $L$ ) adds to the spin angular momentum ( $S$ ). This is present because one of the electrons is delocalised over three orbitals or it can be viewed as moving between the three orbitals. There is no energy restriction on this movement since the three  $t_{2g}$  orbitals are degenerate; there is no spin restriction as the electron "moves" through orbitals containing an electron of the opposite spin.





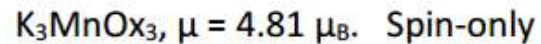
## Example



Fe(III) is  $d^5$ . Weak-field fluoride ligands give small  $\Delta_{oct}$  and electrons occupy all orbitals. Although each unpaired electron has half-filled degenerate orbitals to “move” into, this movement is blocked by the spins - it would violate Pauli principle.

So there is no  $L$  contribution and the spin-only value is observed.

## Example

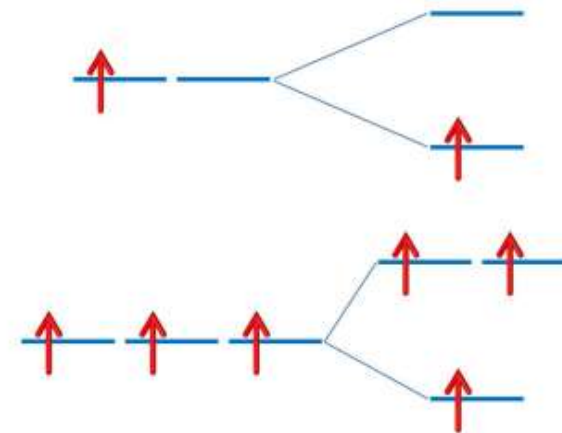


Mn(III) is  $d^4$ . A weak octahedral ligand field should allow “movement” within  $e_g$  orbitals and so a non-zero  $L$  should result.

But spin-only value is observed. Explanation?

Complex is distorted. This lowers the symmetry and raises the degeneracy of orbitals thus restricting electrons to their respective orbitals.

The orbital angular momentum,  $L$ , is said to be *quenched* by the ligand field.



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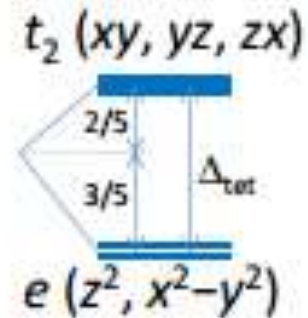
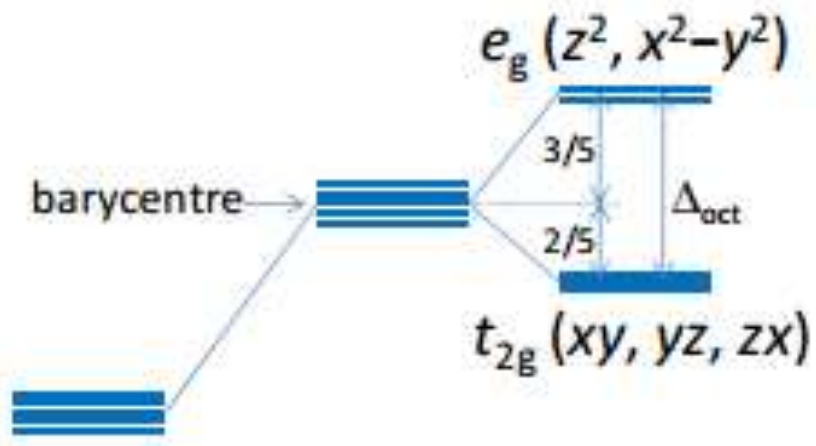
Extended Structures

Crystal Field Theory



# Crystal Field Theory

- ▶ Each ligand is a point electronic charge bound to the metal cation
- ▶ Effect on energy with relative d orbital
- ▶  $ML_6$ 
  1. Surround metal with spherical shell of negative charge (barycentre)
  2. Localise charge to six point charges
  3. The  $d_z^2$  and  $d_{x^2-y^2}$  will raise in energy as they are repelled more along the axis
  4. The  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals drop in energy as they are inbetween the axis



Tetrahedral coordination gives a reversed order of splitting, with  $\Delta_{tet} = (4/9)\Delta_{oct}$ .

# LFSE

For octahedral

$$\text{LFSE} = [(0.4 \times t_{2g} \text{ electrons}) - (0.6 \times e_g \text{ electrons})] \Delta_o + P$$

P = extra pairing energy compared to if it was not in a ligand field (5 degenerate orbitals)

For tetrahedral ( $\Delta_{tet} = \frac{4}{9} \Delta_o$ )

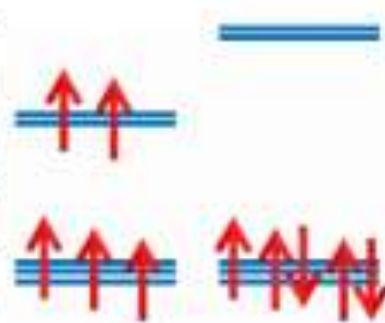
$$\text{LFSE} = [(0.6 \times t_{2g} \text{ electrons}) - (0.4 \times e_g \text{ electrons})] \Delta_{tet} + P$$

Spectroscopic: CFT explains the colour of some transition metal complexes.

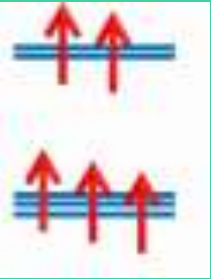

e.g. The 375 nm absorption band that makes  $[\text{Cr}(\text{CN})_6]^{3-}$  yellow in colour.



Magnetic: different spin states for specific oxidation states of a metal ion. e.g.  $d^5$  Large  $\Delta_{oct} >$  electron repulsion (pairing energy) gives low-spin  $S=1/2$  state. A smaller  $\Delta_{oct} <$  electron repulsion results in the high-spin  $S=5/2$  state.



# Spectrochemical Series

 High Spin Weak Field Small $\Delta_o$	$\sigma/\pi - donor$	$\sigma - donor$	$\sigma - donor$ $\pi - acceptor$	 Low Spin Strong Field Large $\Delta_o$
	High Spin	High Spin	Low Spin	
	Halogens Sulphur  $I^- < Br^- < S^{2-} <$ $\underline{SCN}^- < Cl^- <$ $NO_3^- < F^-$	Oxygen  $< HO^- < C_2O_4^{2-}$ $< H_2O^-$	Nitrogen Carbonyls Carbonyls Amines Phosphines  $< \underline{NCS} < CH_3CN <$ $NH_3 < en < bipy$ $< phen < NO_2^- <$ $PPh_3 < CN^- < CO$	

$\Delta_o$

Increases with oxidation state  
 Higher charge  $\rightarrow$  smaller ion  $\rightarrow$  shorter M-L

Increases going down a group  
 Expanded 4d and 5d = better M-L bonding

# Molecular Orbital Theory

## Molecular Orbital Theory

### Orbital Overlap

*A bond can only be formed when two atomic orbitals of two atoms overlap*

Orbitals must be of similar energy

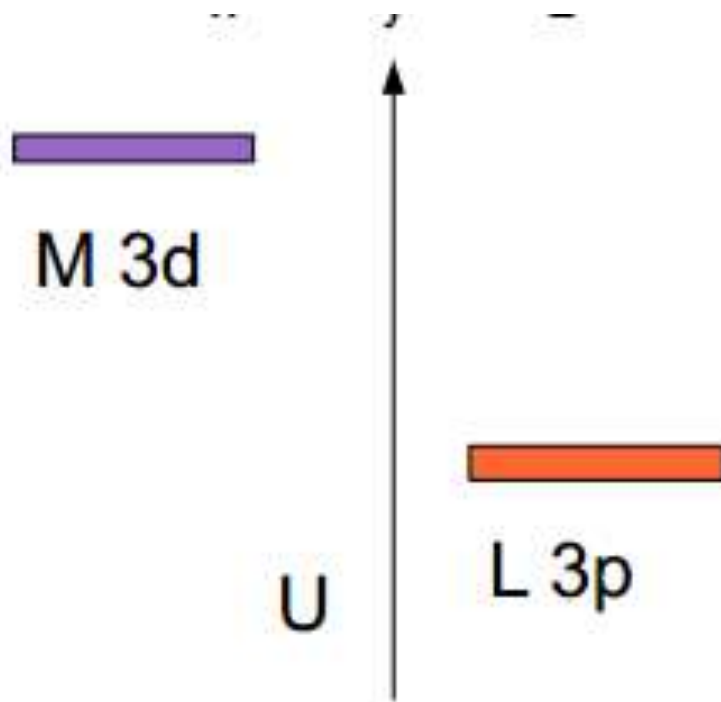
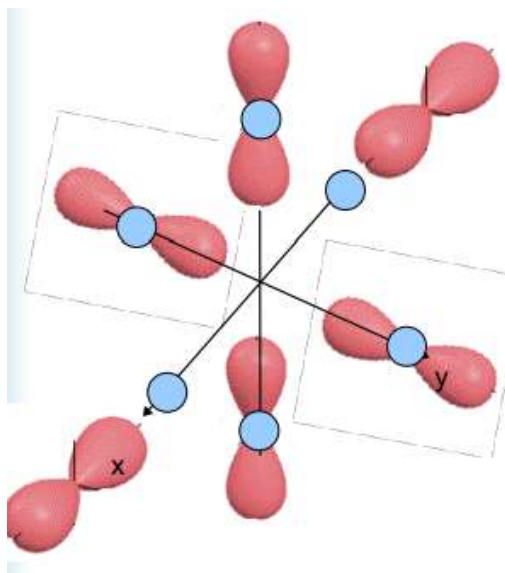
To simplify the theory in our context, **the 4s and 4p orbitals on the metal atom are ignored.**

Recall the different types of donor/acceptor behaviour

# Sigma Donor

Ligands point along axis

Example,  $Cl^-$



# Sigma Donor

For the  $\text{Cl}^-$  ion:

Electrons are in a p-orbital

Can be donated to form a sigma bond by overlapping with  $e_g$  orbitals

*Metal based  $e_g$  raised in energy*

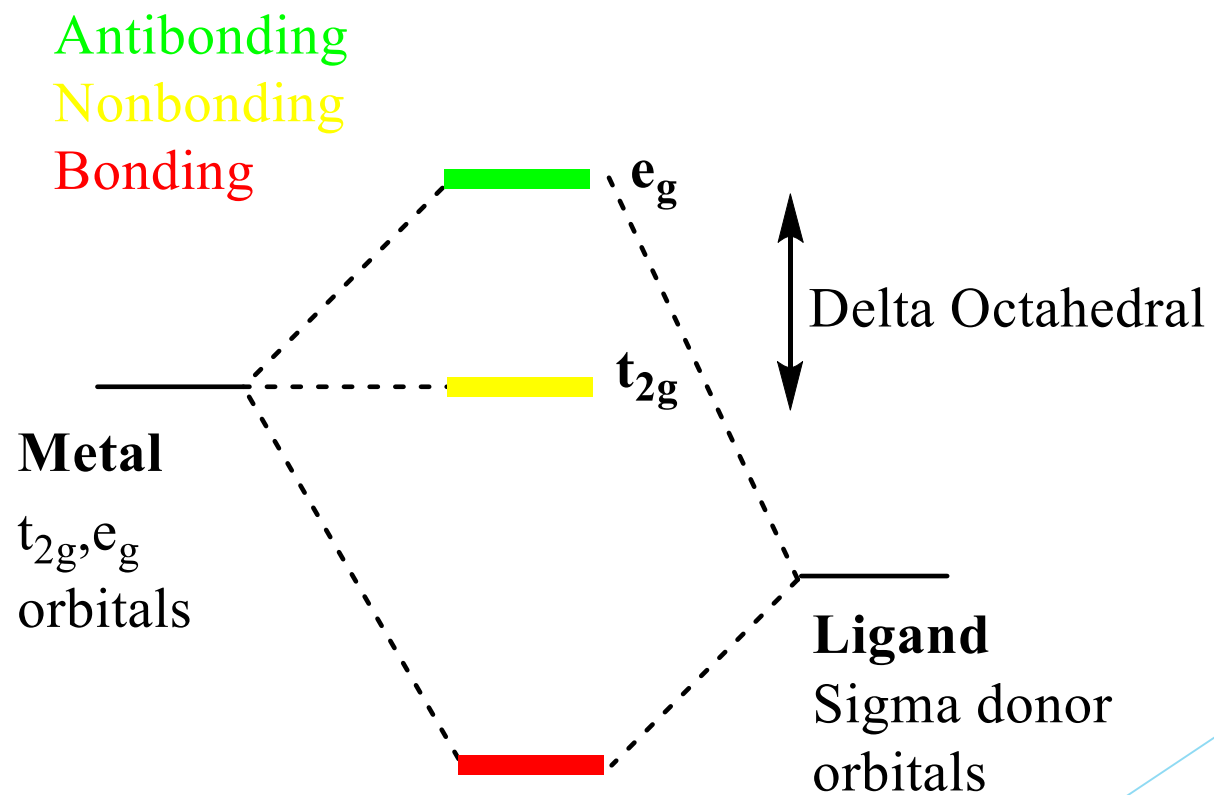
No net overlap with  $t_{2g}$

*Hence energy of  $t_{2g}$  unchanged*



# Sigma Donor

## Molecular Orbital Diagram



# Effect of Sigma Donation

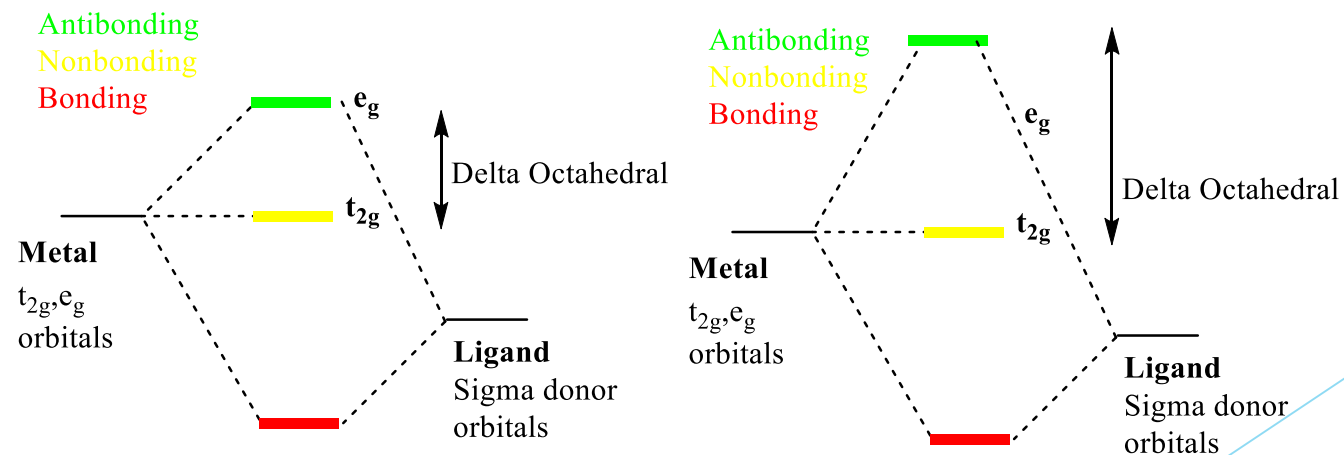
What happens as strength of sigma donation increases?

Energy of interaction increases

Splitting between the bonding and anti-bonding orbitals gets larger

$e_g$  moves higher in energy

Ligand field splitting ( $\Delta_o$ ) increases



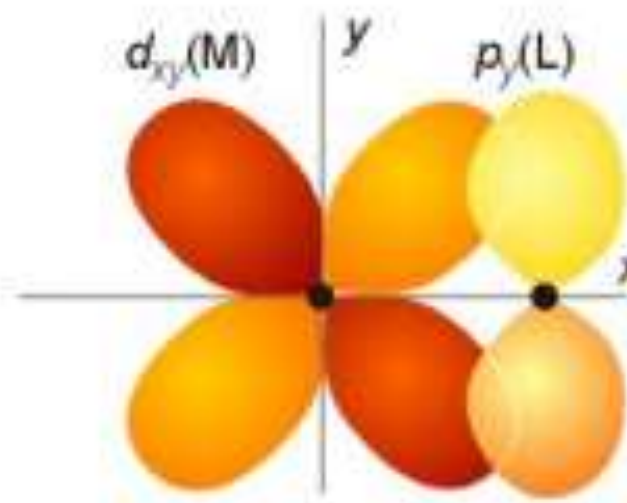
# Pi donor

Certain p-orbitals can interact with  $t_{2g}$  to give pi bonds

Overlap is possible

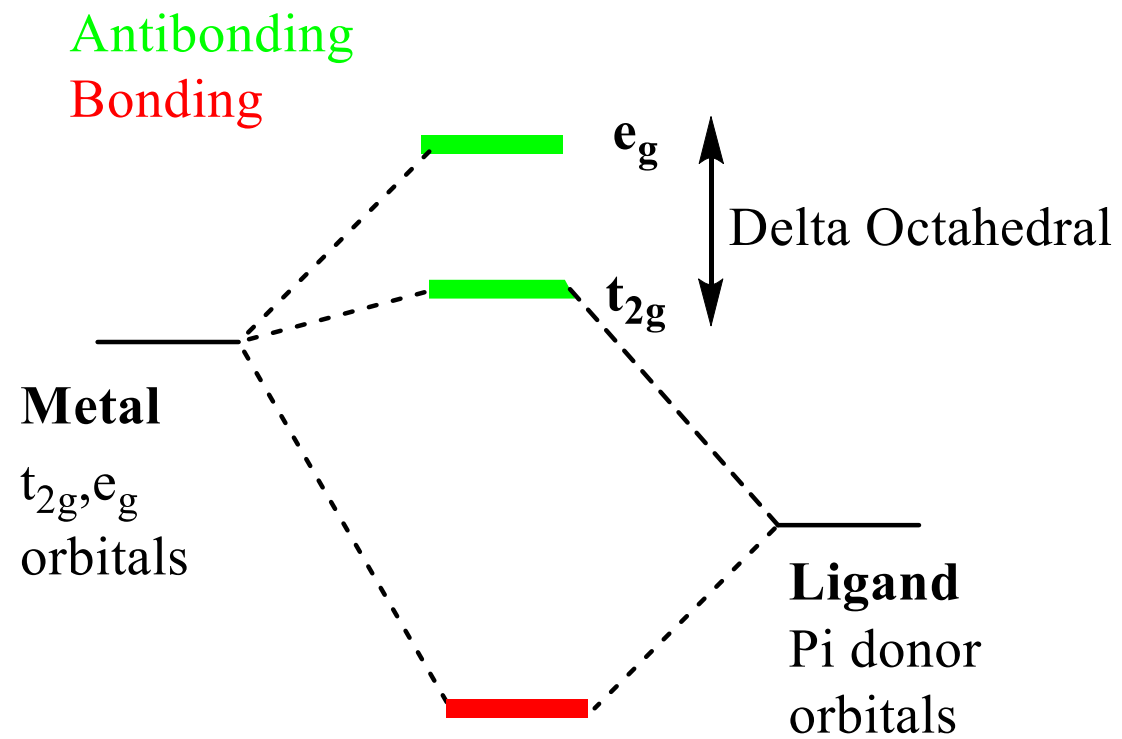
*Example  $Cl^-$*

No net overlap with  $e_g$  sets



# Pi donor

## Molecular Orbital Diagram



# Effect of Pi Donation

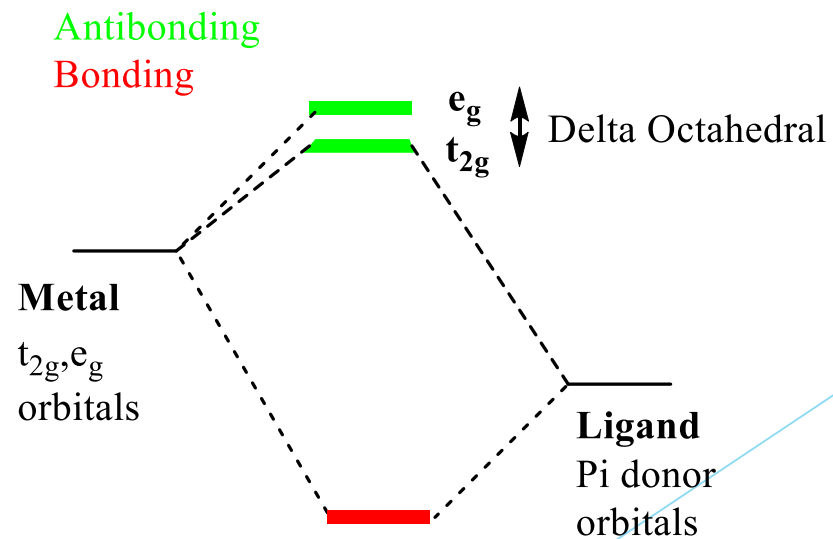
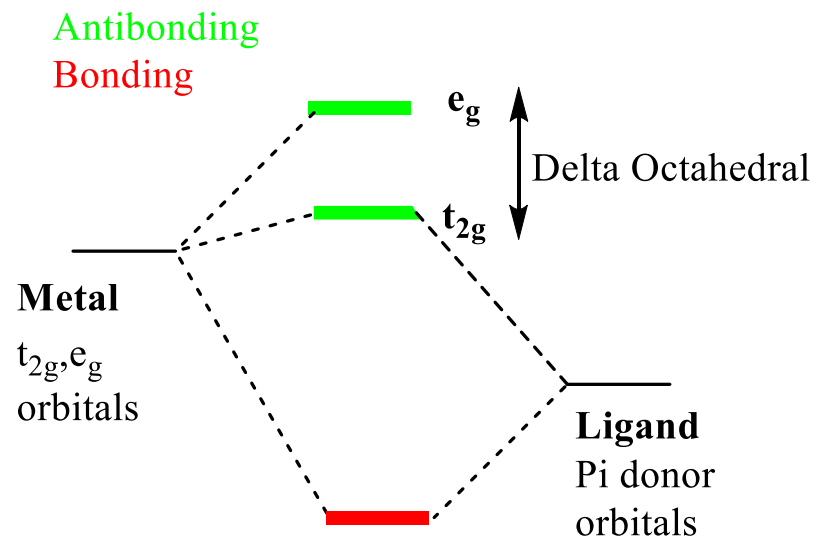
What happens when Pi Donor interactions increases?

Energy of inter-actions increases

Splitting between bonding and anti-bonding orbitals increases

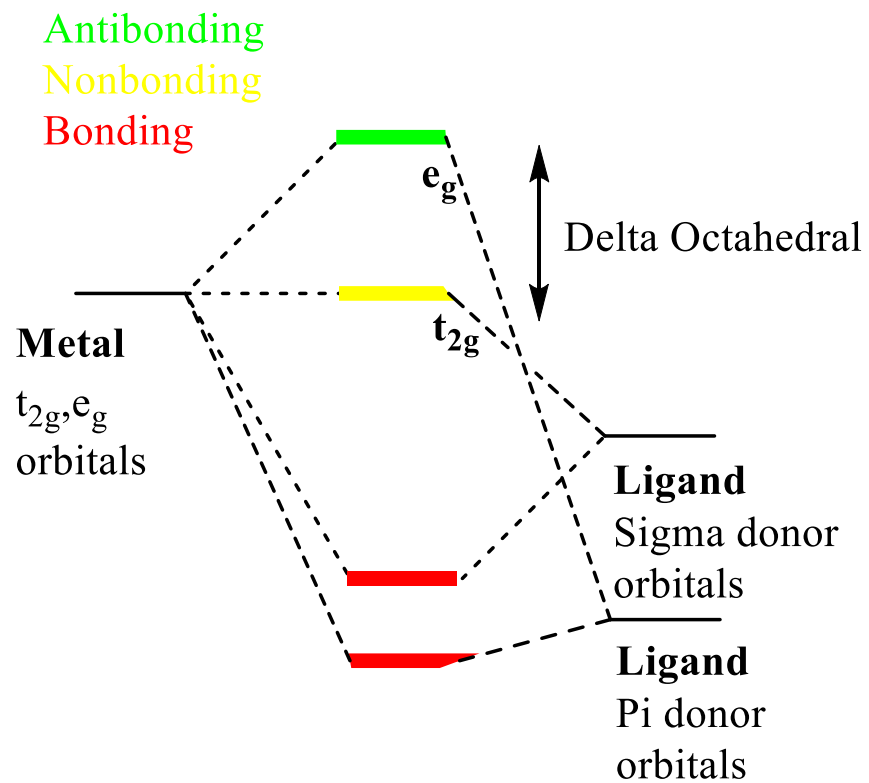
$t_{2g}$  moves higher in energy

Ligand field splitting ( $\Delta_o$ ) decreases



# Complete Molecular Orbital Diagram

Combination of sigma and pi donor interactions

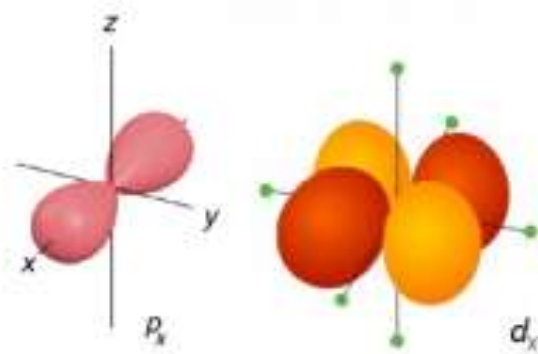
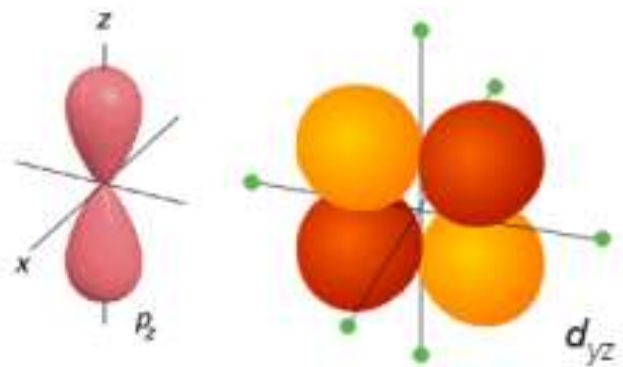


# Pi acceptor

Metal orbitals involved are the same as pi donor

Symmetry of atomic orbital overlap determines sigma or pi interaction

Only interacts with  $t_{2g}$



# Pi acceptor

## Requirements

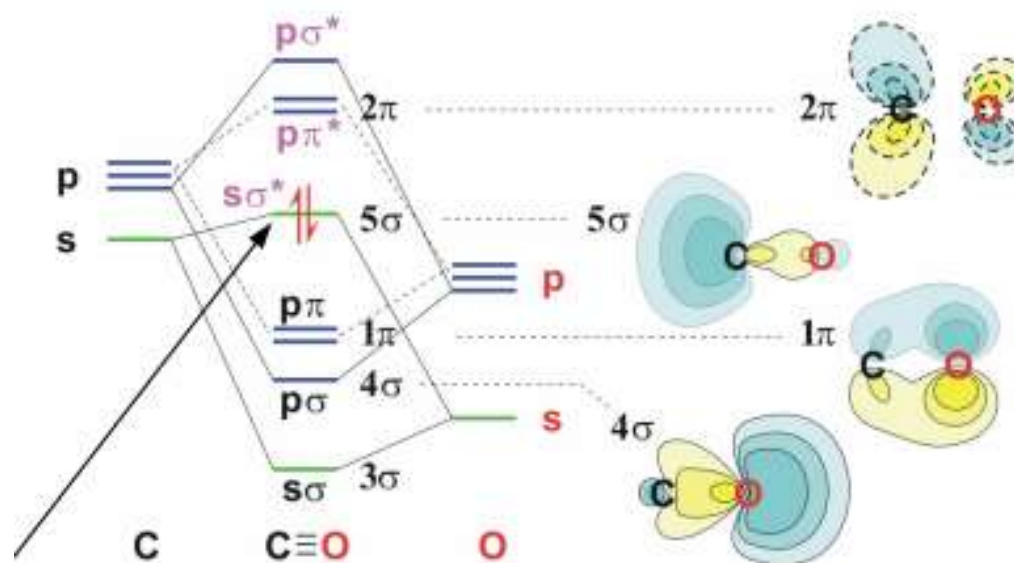
Ligand must have an empty or partially filled orbital of pi symmetry

*Accepting electron density*

*Typically anti-bonding orbitals*

Results in Back Donation

*Examples, CO and CN<sup>-</sup>*

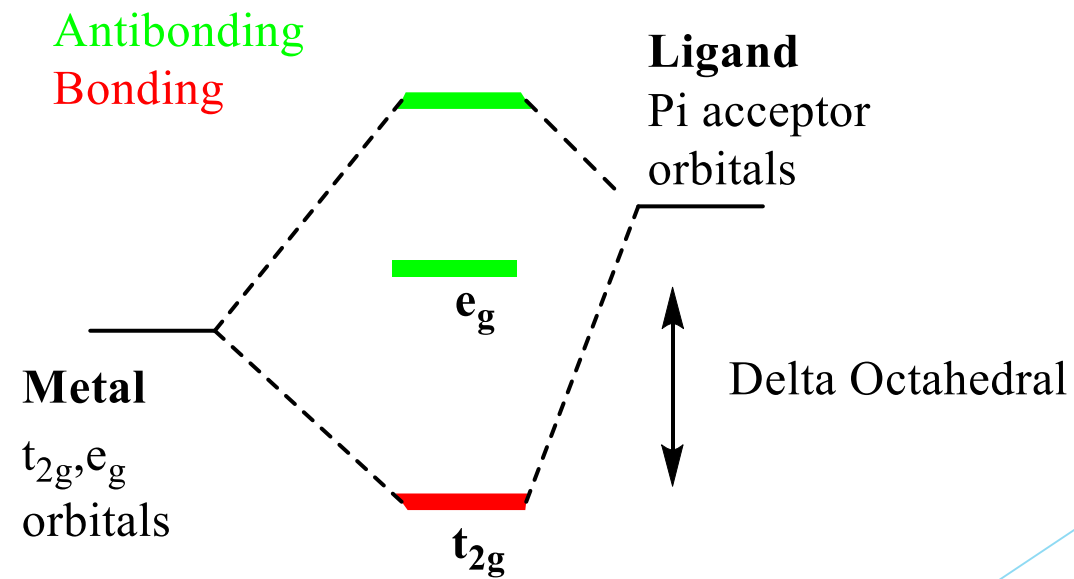




# Pi acceptor

## Molecular Orbital Diagram

Pi acceptors increases  $\Delta_o$

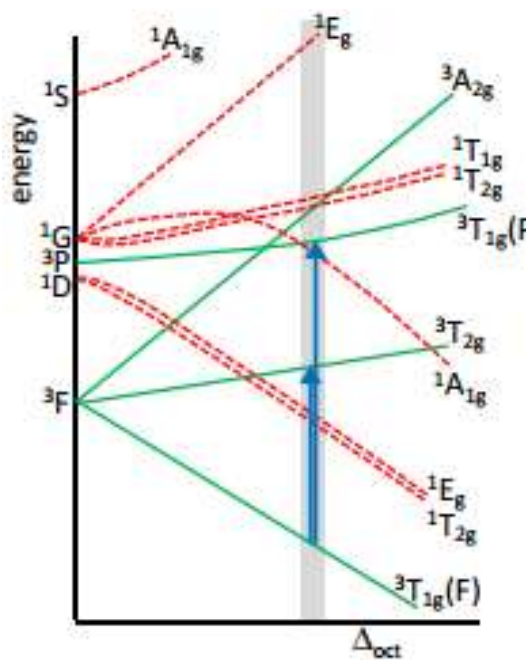


# Electronic Spectra

- ▶ Place terms on a diagram to work out transitions
- ▶ As octahedral ligand field is imposed, terms split and move further apart as ligand strength increases
- ▶ Distances between lines is proportional to energy not intensity

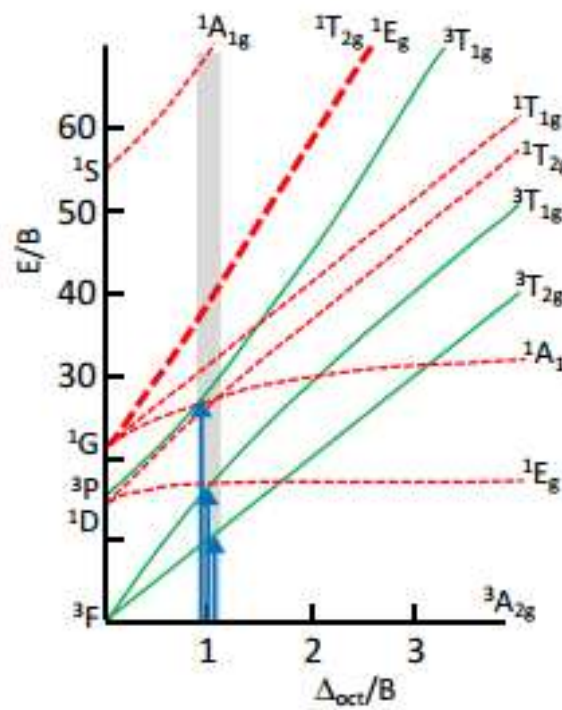
## Orgel Diagram

- ▶ Lowest line is ground state
- ▶ Same spin multiplicity as ground state are allowed



## Tanabe-Sugano Diagram

- ▶ Related to a Racah parameter
- ▶ Ground state runs along the x-axis



# Selection Rules

- ▶ More 'allowed' transitions have greater **intensities** not energies!
- ▶  $\Delta L = \pm 1$
- ▶  $\Delta S = 0$
- ▶ For d-d transitions all should be weak due to **L** rule but d orbitals not purely d for non hydrogen atom due to mixing of orbitals with p.
- ▶ Laporte rule ( $g \leftrightarrow g$  and  $u \leftrightarrow u$  forbidden) But  $u \leftrightarrow g$  Allowed
- ▶ Therefore  $t_{2g} \leftrightarrow e_g$  Forbidden (octahedral)
- ▶  $t_2 \leftrightarrow e$  allowed (tetrahedral)

## Numbers

Transition Type	Typical epsilon ( $M^{-1} \text{ cm}^{-1}$ )
$\text{Pi} - \text{Pi}^*$	10,000 - 100,000
CT	10,000 - 100,000
Spin allowed, Laporte Allowed	500
Spin allowed, Laporte Forbidden	10
Spin Forbidden, Laporte Forbidden	0.1

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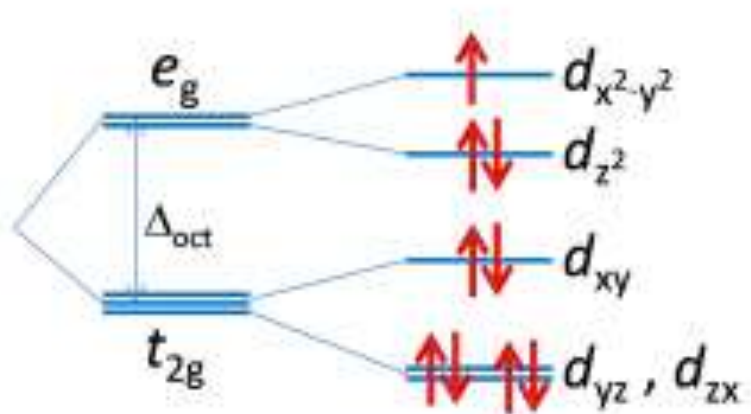
# Cages and Clusters

- ▶ **Cages ( M - L - M )**      Super exchange via ligands and magnetism  
Copper acetate nonohydrate
- ▶ **Cluster ( M - M )**      Multiple bonds and  $\delta$  molecular orbitals  
Chromium acetate nonohydrate

## Cages

### Copper acetate nonohydrate

- ▶ Cu-Cu 2.64 Å (longer than 2.56 Å in metallic copper)



# Cages

## Copper acetate nonohydrate

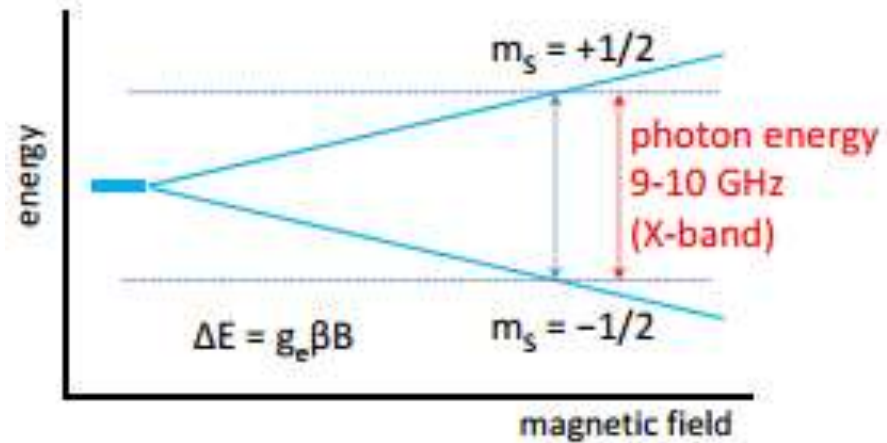
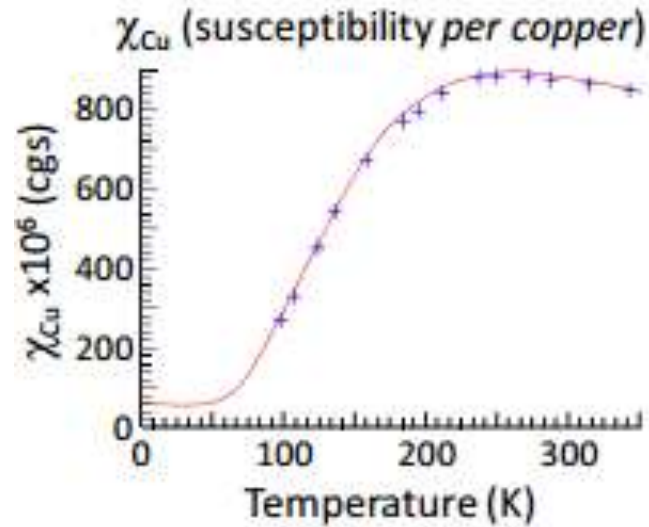
Unpaired electron in singly degenerate orbital

Magnetic susceptibility  $\chi$  drops at low temperatures

Becomes diamagnetic  $< 77$  K

Room temperature EPR signal

EPR disappears  $< 77$  K



# Coupling of spins

## Coupling of spins

$S_1 + S_2$  to give maximum spin

$S_1 - S_2$  to give minimum spin

Every other spin state =  
subtracting 1 from maximum  
until you reach minimum

$J$  is positive for *ferromagnetic coupling*

$J$  is negative for  
*antiferromagnetic coupling*

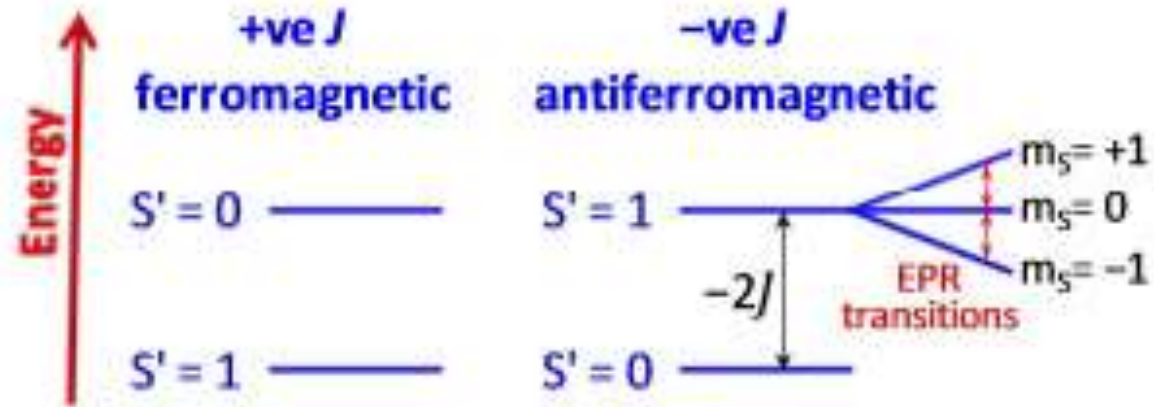
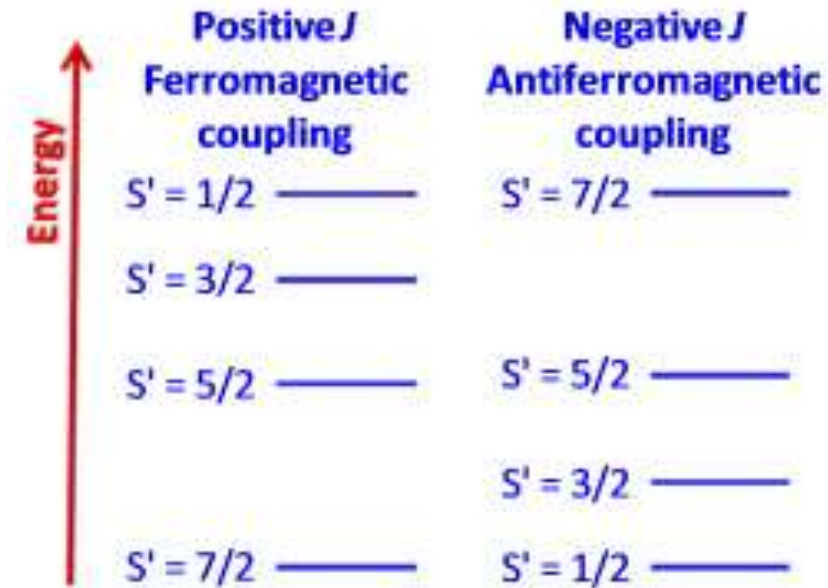
## Copper acetate

For copper acetate

$$S_1 = \frac{1}{2}$$

$$S_2 = \frac{1}{2}$$

$$\rightarrow S' = 1 \text{ or } 0$$



Drop temperature, bottom level is filled more than top  
Hence Cu acetate is antiferromagnetic due to RT EPR spectrum

# Cages

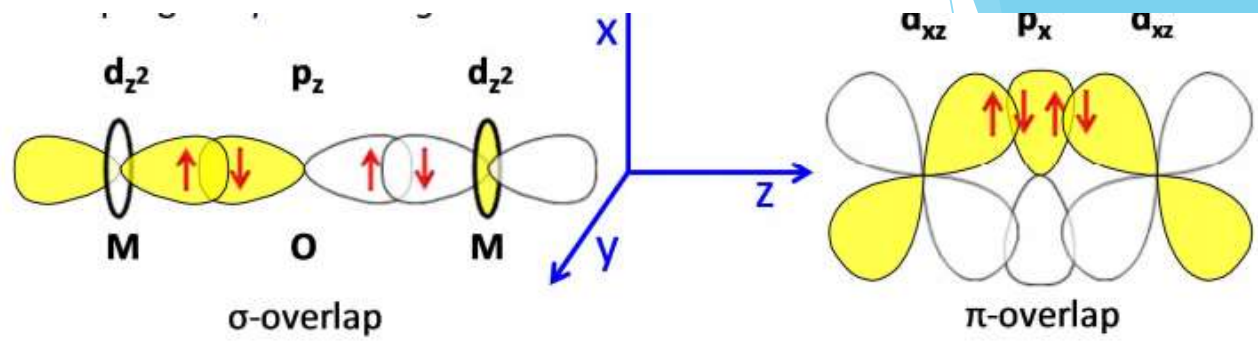
## Magnetic Exchange

Nature of M - M interaction is through the ligand

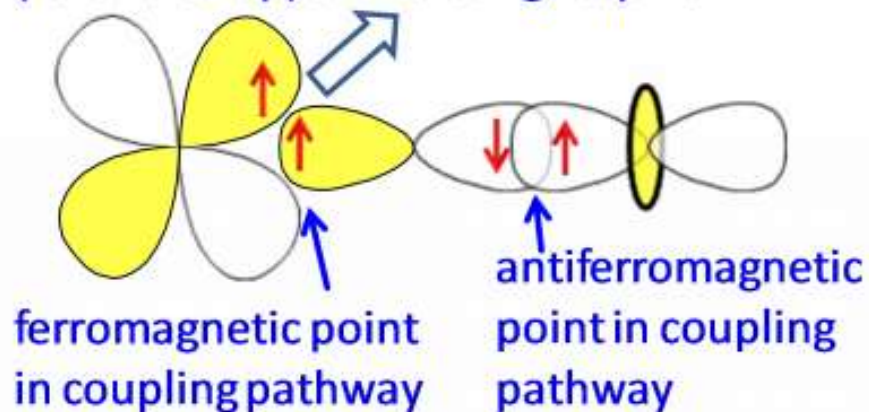
Ligand mediated coupling is *super exchange*

Spin polarisation across the three atoms favours pairing of spins, leads to antiferromagnetic coupling (with exceptions)

Ferromagnetic coupling requires orthogonality in coupling pathway. High symmetry required and is rare



exchange interaction between orthogonal (zero-overlap) orbitals aligns spins





# Clusters

## Chromium acetate nonohydrate

Evidence for M - M

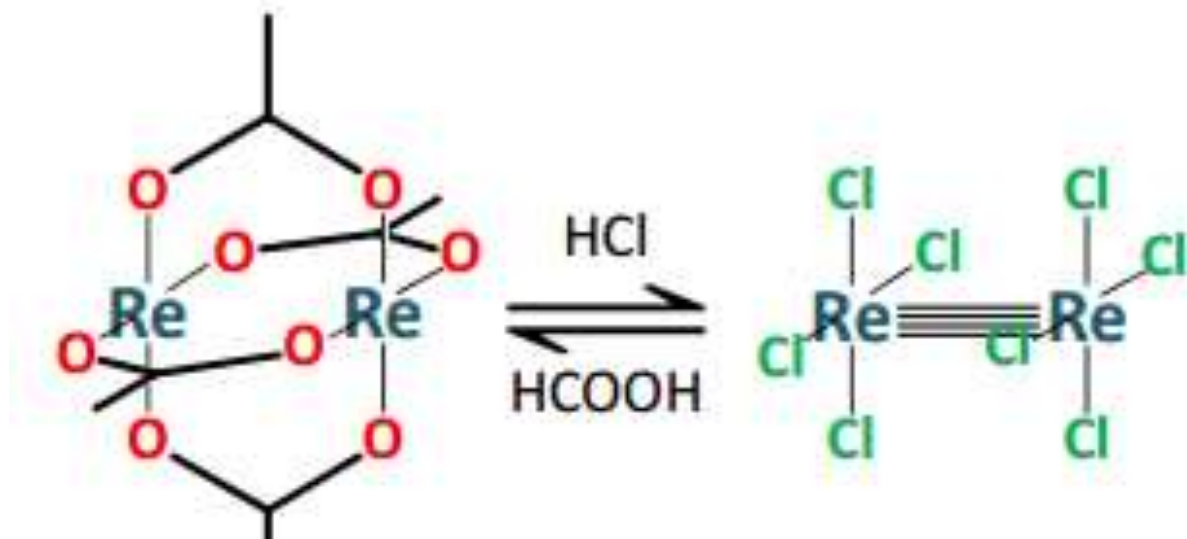
Cr - Cr = 2.36 Å (shorter than that found in metal 2.58 Å)

## Evidence for M - M

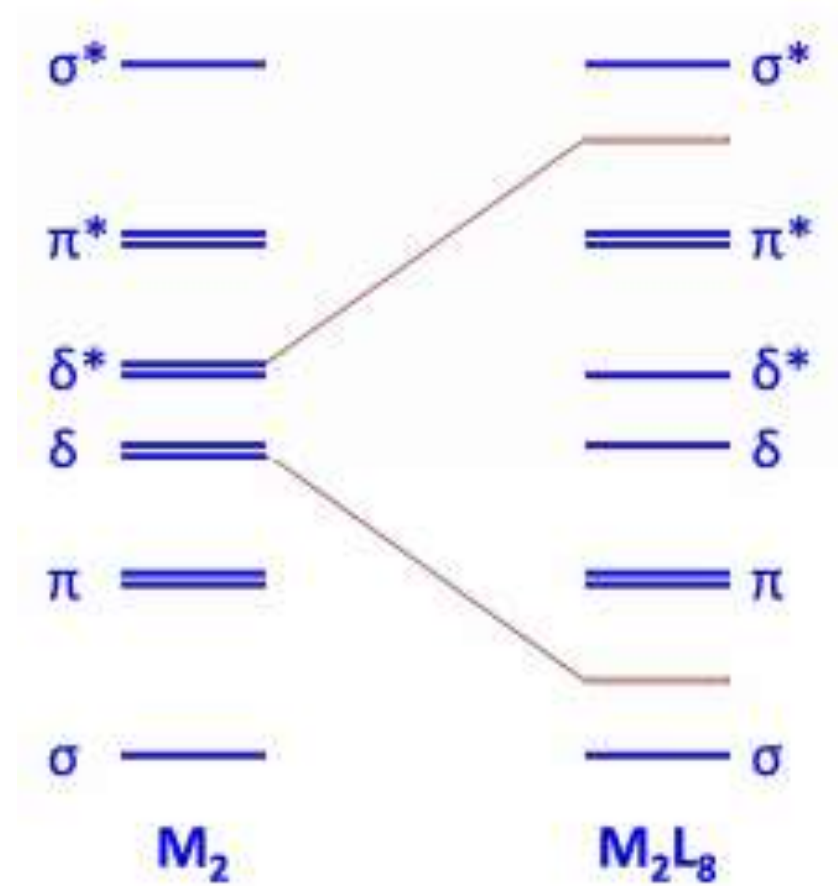
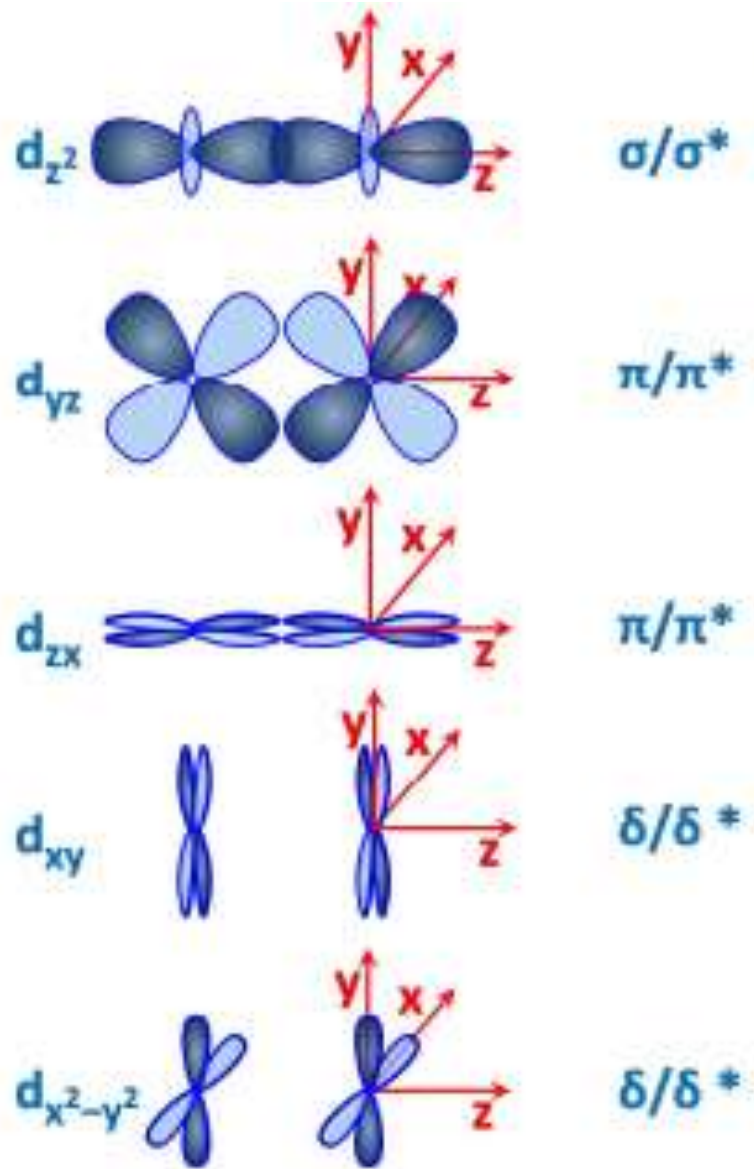
Eclipsed structures and possible formation of quadruple bonds

Short bond lengths (bond length increases with higher bond order)

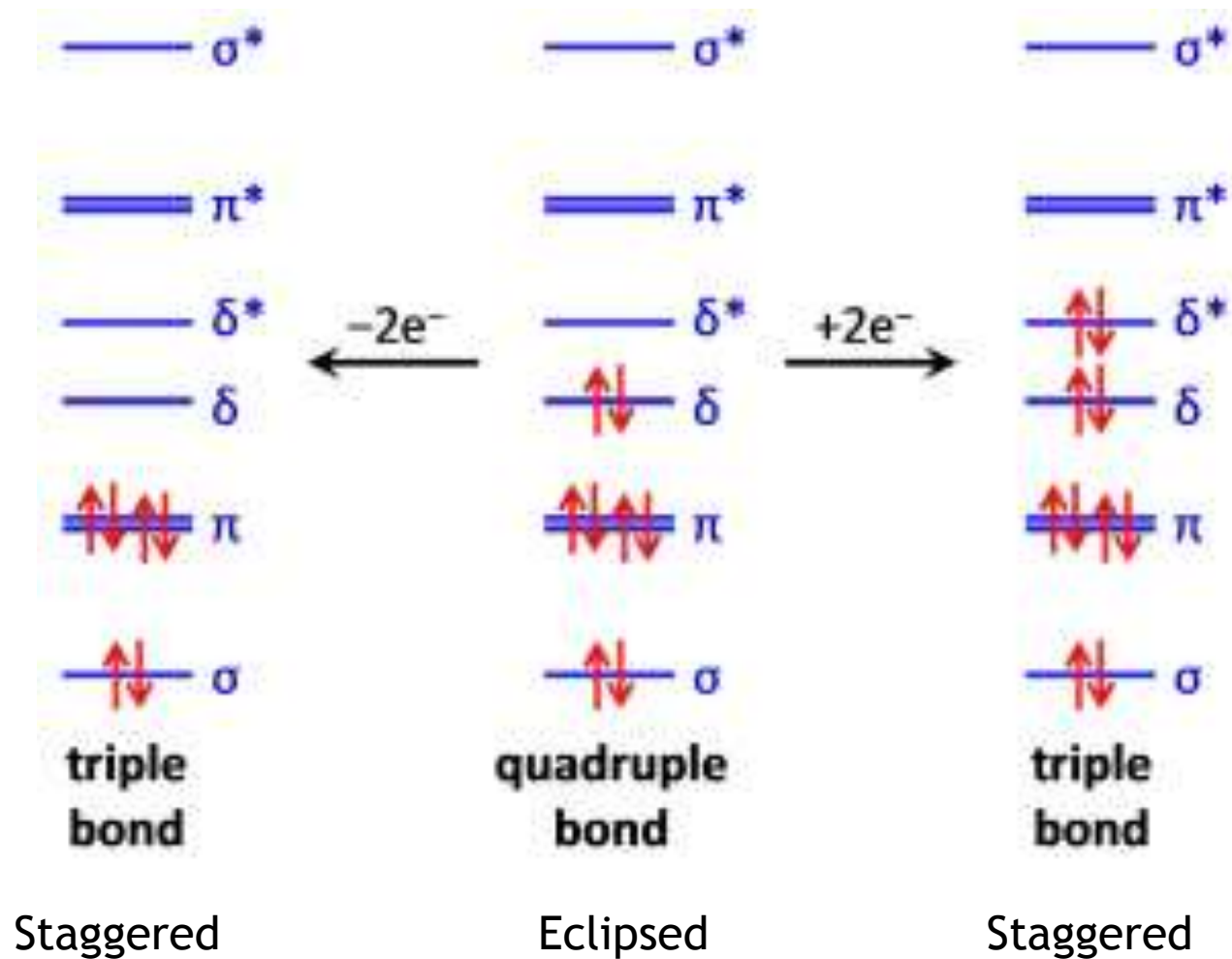
Short bond lengths have higher vibrational frequencies



# Overlap of d orbitals in $M_2$ fragment



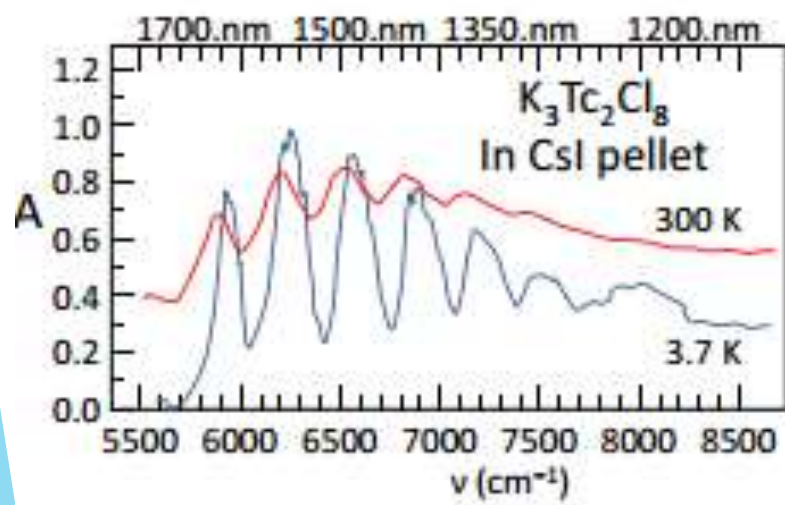
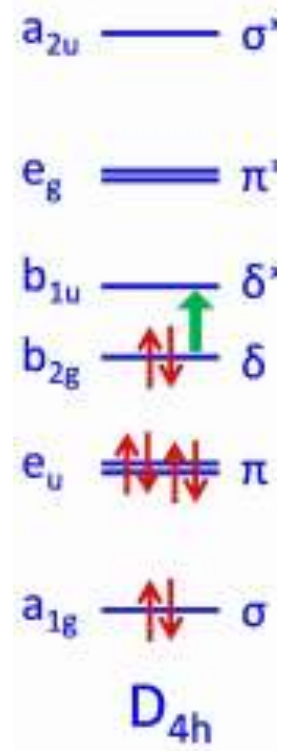
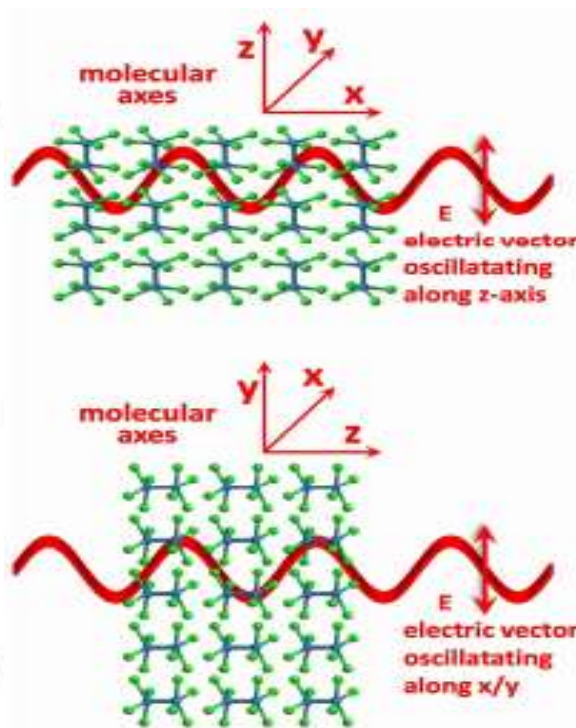
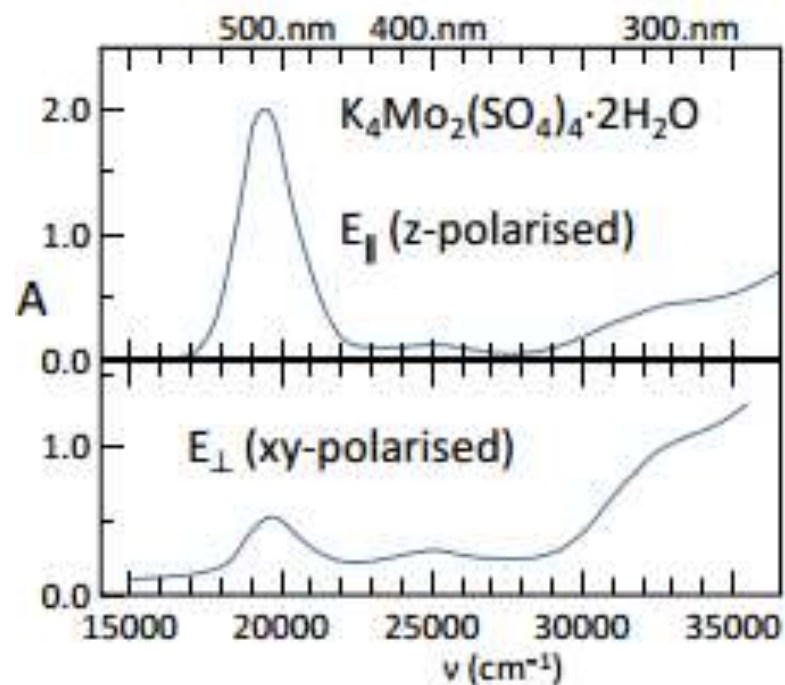
# Overlap of d orbitals in $M_2$ fragment



3.5 also Eclipsed

d/d\* orbitals can only exist when the molecule has elipsed alignment. The formation of the d/d\* orbitals rests the complex better than it being staggered due to steric strain

# Evidence of d-bond



Several transitions can be observed for the [Tc<sub>2</sub>Cl<sub>8</sub>]<sup>3-</sup> ion:

- LMCT 31400 cm<sup>-1</sup> (318 nm)
- δ\* → π\* 20000 cm<sup>-1</sup> (500 nm)
- π → δ\* 13600 cm<sup>-1</sup> (735 nm)
- δ → δ\* 5900 cm<sup>-1</sup> (1695 nm)

(Cotton *et al.* (1977) JACS **99** 5642)

The δ → δ\* electronic change is associated with significant extension of the M–M bond (~1 Å) leading to the observation of up to 10 vibrational overtones. These can be analysed (Birge-Sponer extrapolation) to obtain estimates of bond dissociation energies:

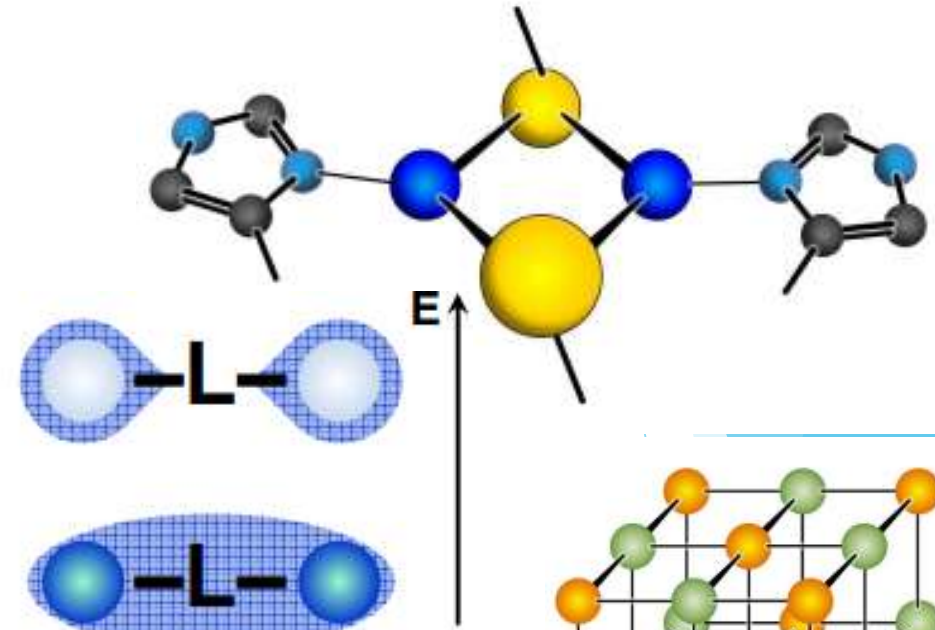
<b>kJ.mol<sup>-1</sup></b>	
K <sub>4</sub> [Mo <sub>2</sub> Cl <sub>8</sub> ]	722 ± 84
[n-Bu <sub>4</sub> N] <sub>2</sub> [Re <sub>2</sub> Cl <sub>8</sub> ]	638 ± 80
Rb <sub>4</sub> [Mo <sub>2</sub> Cl <sub>8</sub> ]	798 ± 105
[n-Bu <sub>4</sub> N] <sub>2</sub> [Re <sub>2</sub> Br <sub>8</sub> ]	584 ± 105
Cs <sub>4</sub> [Mo <sub>2</sub> Cl <sub>8</sub> ]	533 ± 63

# Valence Delocalised

- ▶ When you reduce this  $\text{Cu}_A$  species by one electron, the electron. It is shared...

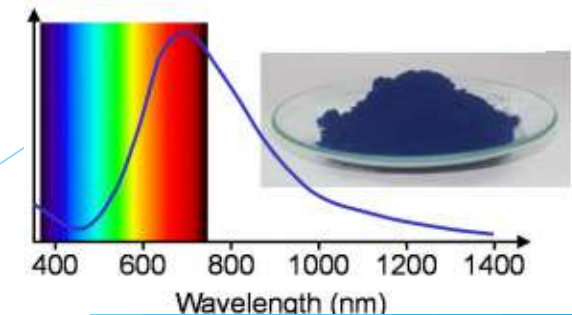
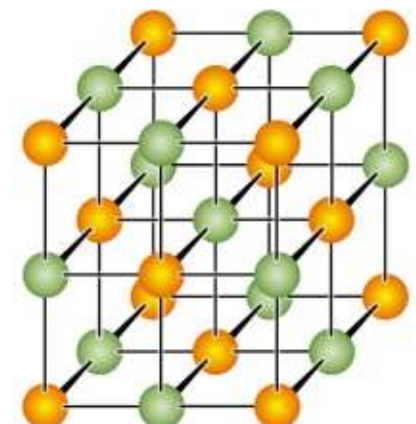


- ▶ The MO is delocalised across both copper ions.
- ▶ Transitions can occur from this MO to higher antibonding Mos and this transition can be intense ( $\text{Cu}_A$  is blue/purple)



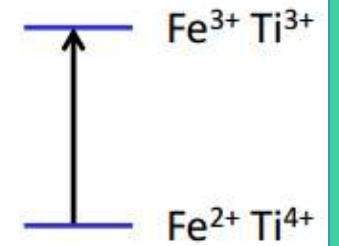
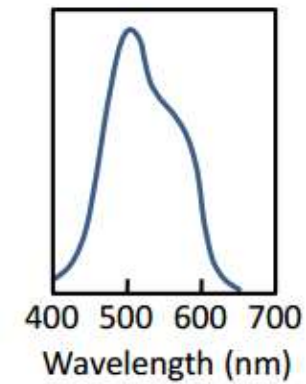
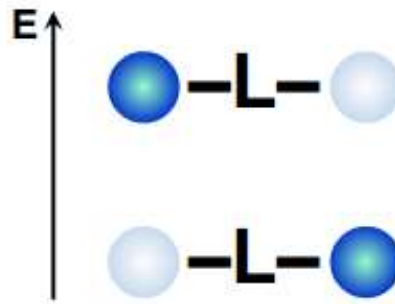
# Valence Trapped

- ▶ Prussian Blue  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$
- ▶ Inter Valence Charge Transfer Band
- ▶ Distinct ligand environments lock oxidation states in place
- ▶ Reduction of  $\text{Fe}^{\text{III}}$  to  $\text{Fe}^{\text{II}}$  is colourless
- ▶ pi system of cyanide crucial for charge transfer process
- ▶ Similar IVCT bands from low level iron in brown glass and brown sandstone



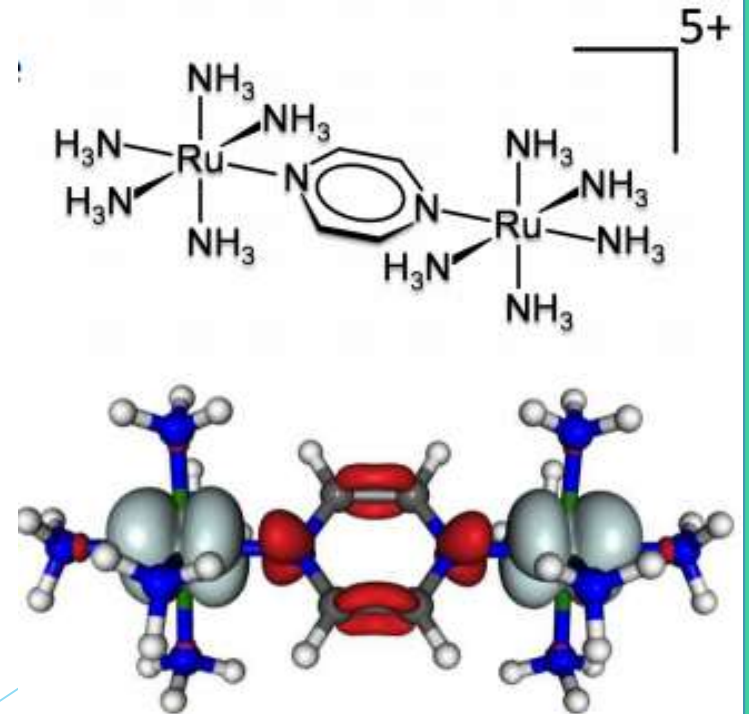
# Valence Trapped (More Examples)

- ▶ Corundum (Crystalline  $\text{Al}_2\text{O}_3$ )
- ▶ Little titanium = colourless
- ▶ Little iron = very pale yellow
- ▶ Both Ti and Fe = Intense blue sapphire
- ▶ IVCT band of  $\text{Fe}^{2+} \rightarrow \text{Ti}^{4+}$  transition
- ▶ Oxidation states briefly altered while the molecule is in the excited state



## Intermediate Behaviour

- ▶ Creutz-Taube ion
- ▶ Any degree of valence trapping e.g.  $\text{Ru}^{2.4+}$   $\text{Ru}^{2.6+}$  leads to slightly different bond lengths
- ▶ Franck-Condon: electron jump instantaneous
- ▶ Then ligand environment relaxes
- ▶ Transition is IVCT like but bond lengths are optimised shortly after oxidation



# Strength of Electronic Interactions

Class	$\alpha$	Band	Interaction	
I	$\sim 0$	none or at very high energy	none	Oxidation states trapped. No easy interconversion. Encouraged by very different ligand fields. $[(H_3N)_5Ru^{3+} \cdot Pyz \cdot Ru^{2+}Cl(bipy)_2]^{4+}$
II	$0 - 1/\sqrt{2}$	IVCT (VIS/nIR)	intermediate	Oxidation states of sites distinct but can interconvert. Typically occurs when sites similar but not equivalent. $[(bipy)_2ClRu \cdot Pyz \cdot RuCl(bipy)_2]^{3+}$ (distorted with O.S.)
III	$> 1/\sqrt{2}$	Yes! But not pure IVCT e.g. CT, $\sigma \rightarrow \sigma^*$ (VIS/nIR)	very strong	Individual sites not distinguishable. Orbital delocalisation. Better considered as united site. For same ions, oxidation states are essentially equivalent and the two metals best described as having same half integer oxidation state. Probably Creutz-Taube $[(H_3N)_5Ru^{2.5+} \cdot Pyz \cdot Ru^{2.5+}(H_3N)_5]^{5+}$

# Contents



Mononuclear Electronic



Mononuclear Magnetic



Crystal Field Theory



Dinuclear



Polynuclear



Extended Structures

Polynuclear





# Trinuclear - Same properties as dimers

- ▶ Cages M - L - M
- ▶ Copper acetate behaviour  $\rightarrow [\text{Cr}_3\text{O}(\text{O}_2\text{CC}_6\text{H}_5)_6(\text{py})_3]\text{ClO}_4$

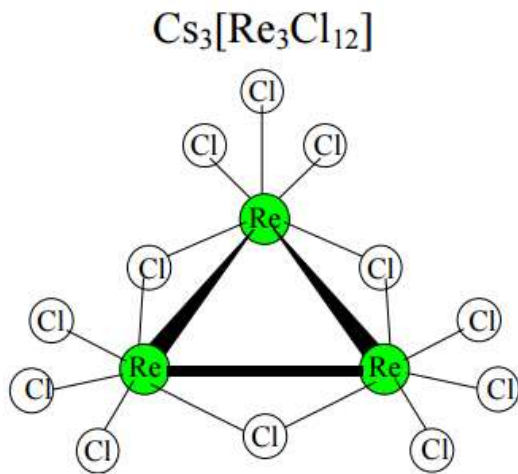
Even though each interaction is antiferromagnetic due to superexchange, the moments on each three centres can not be cancelled

## SPIN FRUSTRATION

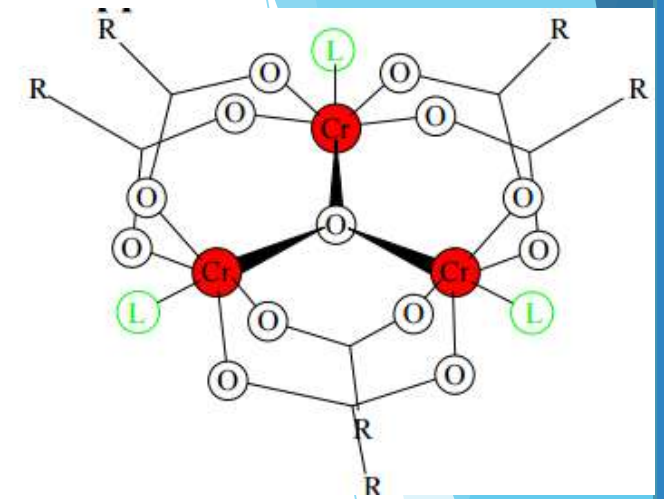
Spin states couple in the same way

Couple  $S_1$  with  $S_2$

Couple each state with  $S_3$

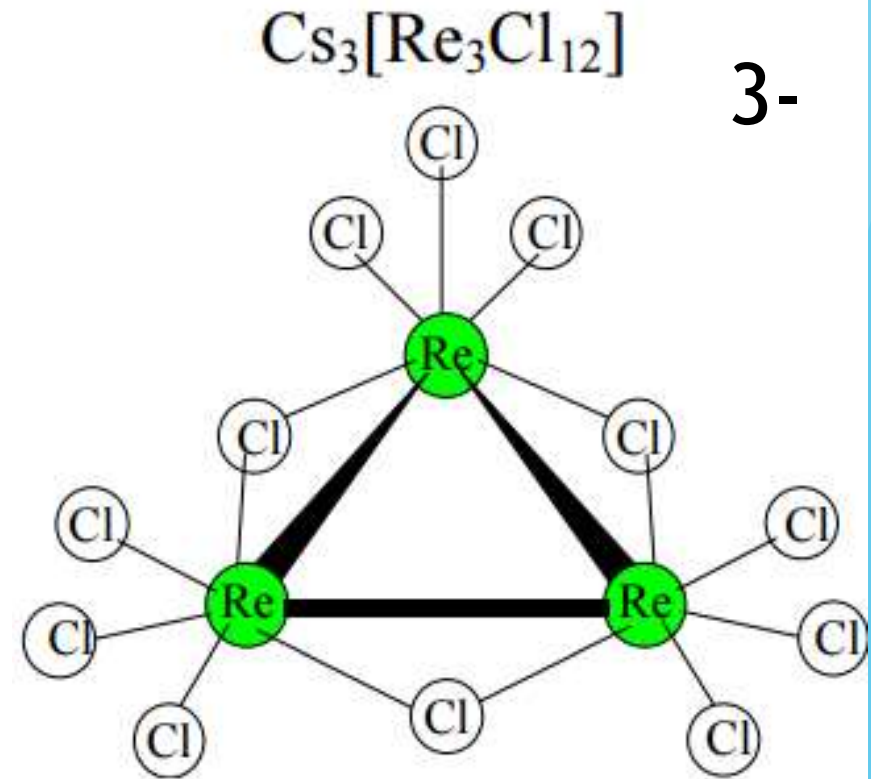


- ▶ Clusters M - M
- ▶ Chromium acetate behaviour  $\rightarrow \text{Cs}_3[\text{Re}_3\text{Cl}_{12}]$
- ▶ Has Re-Re double bonds
- ▶ Lower Halides
- ▶ Early block transition metals in low oxidation states
- ▶ No M-M bonds ever seen for  $> \text{(VI)}$  due to d-orbital contraction
- ▶ High order M-M bonds encountered
- ▶ Steric effects compete with electronic
- ▶  $< 18$  electron complexes often seen



# 18 electron counting

<b>Re (group 7)</b>	
Re	7
3 x terminal Cl <sup>-</sup>	3
share of 2 x bridging Cl <sup>-</sup>	3
2 x double bonds	4
net charge	1
<b>Total</b>	<b>18</b>



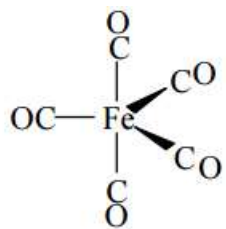
# 18 electron counting on dimers

$[\text{Re}_2\text{Cl}_8]^{2-}$		$[\text{Mo}_2\text{Cl}_8]^{4-}$		$[\text{W}_2\text{Cl}_9]^{3-}$	
Re	7	Mo (group 6)	6	W (group 6)	6
4 x terminal $\text{Cl}^-$	4	4 x terminal $\text{Cl}^-$	4	3 x terminal $\text{Cl}^-$	3
quadruple bond	4	quadruple bond	4	3 x bridging Cl	4 ½
net charge	1	net charge	2	triple bond	3
				Charge	1 ½
Total	16	Total	16	Total	18

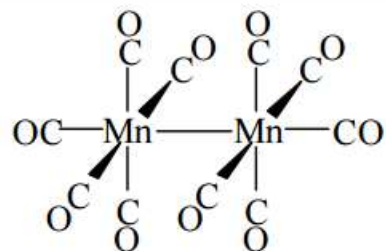
18 electron rule not as uniformly obeyed for d block as you go down group  
d - d bonds are general feature of early d-block elements in low oxidation states

These tend to follow 18 electron rule, especially carbonyls

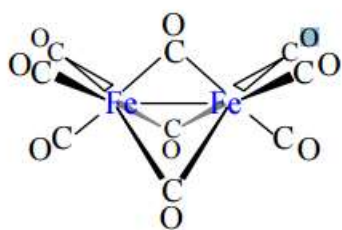
# Carbonyl Clusters



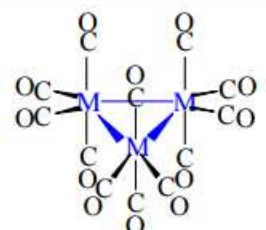
**[Fe(CO)<sub>5</sub>]**  
 Fe: (3d<sup>6</sup>4s<sup>2</sup>)  
 5 x CO



**[Mn<sub>2</sub>(CO)<sub>10</sub>]**  
 Mn: (3d<sup>5</sup>4s<sup>2</sup>)  
 5 x CO  
 Single bond



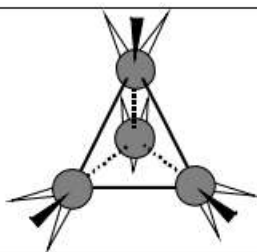
**Fe<sub>2</sub>(CO)<sub>9</sub>**  
 Fe<sup>0</sup>: d<sup>8</sup>  
 3 x terminal CO  
 1½ x bridging CO  
 1 single bond



M = Ru or Os

**M<sub>3</sub>(CO)<sub>12</sub>**  
 M<sup>0</sup>: d<sup>8</sup>  
 4 x CO  
 2 single bonds

For Co and Rh,  
 symmetry is lowered  
 by some CO moving  
 to edge bridging  
 positions.



**Ir<sub>4</sub>(CO)<sub>12</sub>**  
 Ir<sup>0</sup>: d<sup>9</sup>  
 3 x term. CO  
 3 single bonds

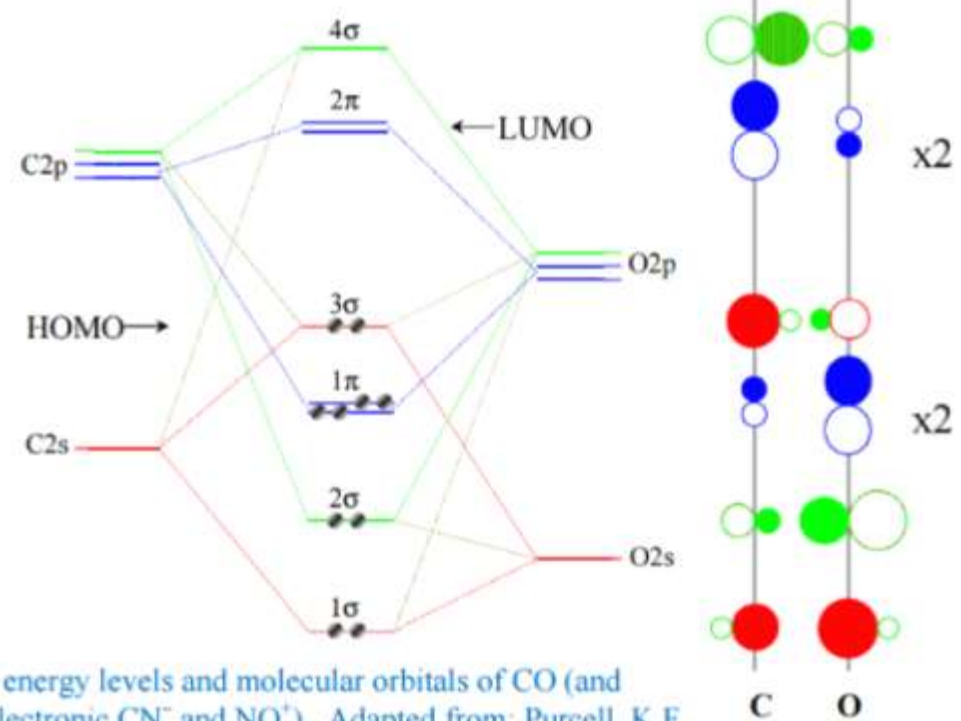
**18-electron rule?**  
 Usually <18 (steric)      Usually 18      16

Metal clusters with p-donor ligands					Metal clusters with p-acceptor ligands			
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au

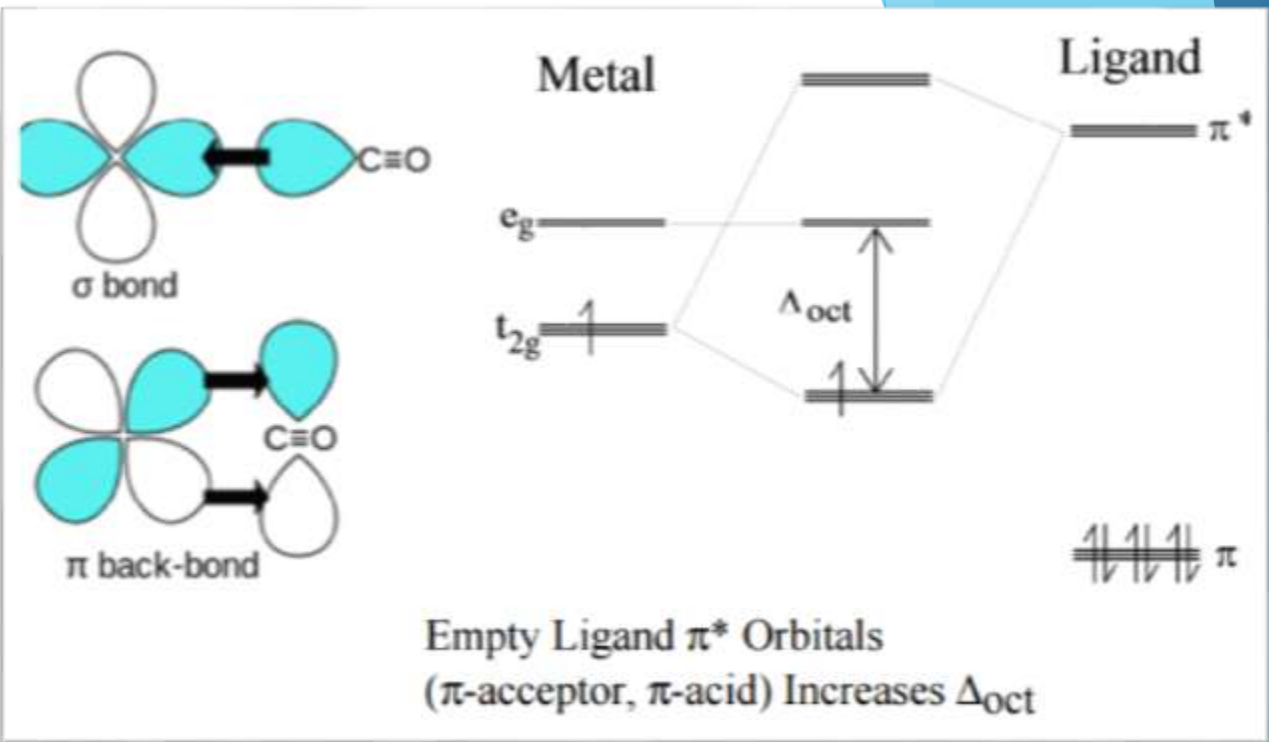
Polynuclear

# Carbon Monoxide

Carbon Monoxide, CO  $1\sigma^2 2\sigma^2 1\pi^4 3\sigma^2$

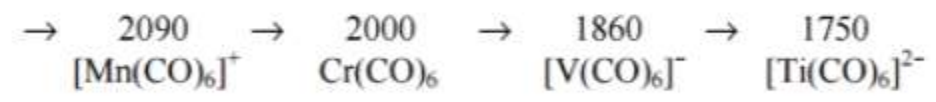


The energy levels and molecular orbitals of CO (and isoelectronic  $CN^-$  and  $NO^+$ ). Adapted from: Purcell, K.F. and Kutz, J.C. "Inorganic Chemistry".

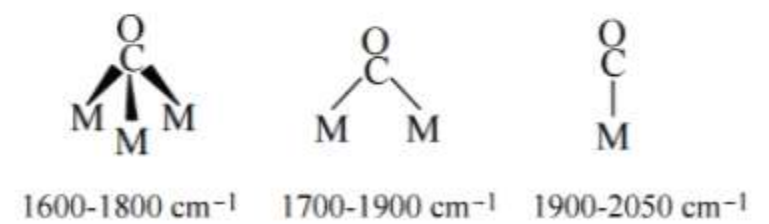


Empty Ligand  $\pi^*$  Orbitals  
( $\pi$ -acceptor,  $\pi$ -acid) Increases  $\Delta_{oct}$

Consequently  $\nu_{CO}$  of gaseous CO at  $2143\text{ cm}^{-1}$  is shifted progressively downwards as increasing negative charge delocalised into the  $\pi^*$  orbitals weakens the CO bond:



CO can bind terminally or by bridging 2 or 3 metal atoms.  
More metals  $\Rightarrow$  more  $e^-$  density  $\Rightarrow$  weaker CO bond:



Neutral ligand with small dipole  
Weak 2 electron sigma donor  
An extremely good pi acceptor

# Nitric Oxide NO

Normally NO written as  $\text{NO}^+$  as a 3 electron donor

Anti bonding pi electron transferred to metal giving a  $\text{NO}^+$  (nitrosonium ion) ligand

This is a two electron sigma donor analogous to CO

It is approximately linear ( $160 - 180^\circ$ )

The odd electron is removed from anti bonding orbital, the stretching frequency is usually similar or greater than NO itself

Due to charge  $\text{NO}^+$  is much better pi acceptor ligand showing better levels of back bonding

Pi acceptor ligand strengths

$\text{CN}^- < \text{NN} < \text{CO} < \text{NO}^+$  (isoelectronic)

Some complexes better describe it as NO or even  $\text{NO}^-$  (nitroxyl)

This is bent ( $120 - 135^\circ$ )

Do not need linear for pi overlap

No analogous behaviour to CO

# Nitric Oxide NO

	N-O (Å)	$\nu_{\text{NO}}$ (cm <sup>-1</sup> )	
<b>NO<sup>+</sup></b>	<b>1.06</b>	<b>2200-2400</b>	<b>in nitrosonium salts e.g. NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> (bond order 3)</b>

“Linear NO<sup>+</sup>” in metal complexes:

$$\nu_{\text{NO}} 1630-1940 \text{ cm}^{-1}$$

$$\angle \text{M-N-O } 160-180^\circ$$

		1935	[Fe(CN) <sub>5</sub> NO] <sup>2-</sup> nitroprusside ion diamagnetic short N-O 1.13 Å NO <sup>+</sup> complex of Fe <sup>2+</sup> (178 °)
		1925	<i>met</i> -Hemoglobin + NO
<b>NO</b>	<b>1.15</b>	<b>1876</b>	<b>gaseous form (bond order 2.5)</b>
		1867	[Fe(NO)(mnt) <sub>2</sub> ] <sup>-</sup> (180 °)
		1852	[Co(diars)(NO)] <sup>2+</sup> (179 °)
		1745	[Fe(H <sub>2</sub> O) <sub>5</sub> NO] <sup>2+</sup> (brown ring test for nitrate) $\mu_{\text{eff}} = 3.9 \text{ B.M.} = 3 \text{ upe } d^7 \text{ Fe}^1 \text{ NO}^+$
		1700-1900	Co(NO) <sub>3</sub> , Fe(NO) <sub>2</sub> (CO) <sub>2</sub> , (NO)(CO) <sub>5</sub>
		1645	[Fe(NO)(mnt) <sub>2</sub> ] <sup>2-</sup> (165 °)

“Bent NO” in metal complexes:

$$\nu_{\text{NO}} 1520-1720 \text{ cm}^{-1}$$

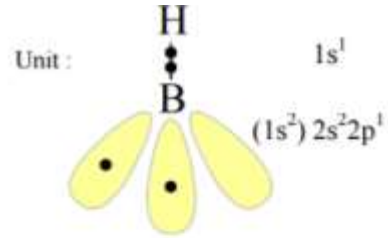
$$\angle \text{M-N-O } 120-135^\circ$$

“NO”			
		1720	[Ir(CO)I(NO)(PPh <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub> .C <sub>6</sub> H <sub>6</sub> (124 °)
		1626	[Co(NO)(S <sub>2</sub> CNMe <sub>2</sub> ) <sub>2</sub> ] (~ 135 °)
		1610	[Co(NH <sub>3</sub> ) <sub>5</sub> NO] <sup>2+</sup> (119 °)
		1525	[Ir(CH <sub>3</sub> )I(NO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (120 °)
“NO”		1150-1170	Rare. Only in complexes so description again approximate.

As with CO, the frequency  $\nu_{\text{NO}}$  also drops with bridging to > 1 metal.

# Large Clusters - Wades Rules

As cluster size increase, 18 electron rule fails

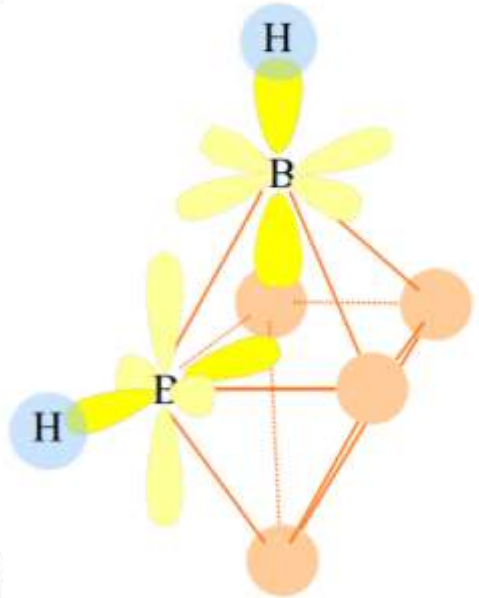
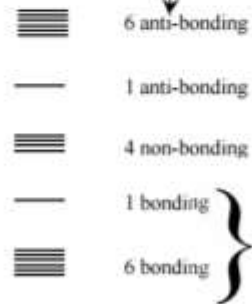


Hybridise on B  $\rightarrow sp + sp + p_x + p_y$  and place at vertices of  $O_h$ .

One of  $sp$  orbitals bonds apical H. Second  $sp$  orbital projects into centre of  $O_h$  for molecular orbital formation.

"Tangential"  $p_x$  and  $p_y$  lie over edges and form framework molecular orbitals.

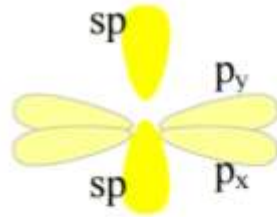
6 x  $sp$   
 6 x  $p_x$   
 6 x  $p_y$



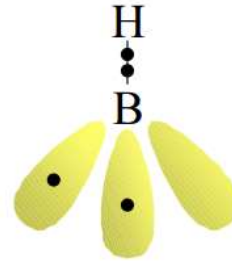
On the basis of this model, **14 electrons** are needed to stabilise the octahedron. After bonding to apical H, each B-H unit has 2 remaining valence  $e^- = 12$  electrons. Plus charge of  $[B_6H_6]^{2-}$  ion = total of **14 electrons**.

*In general, (n+1) PAIRS of framework bonding electrons stabilise a structure based on a regular deltahedron of order n.*

Consider the  $[B_nH_n]^{2-}$  ion series. (regular growth of polyhedral forms from  $n = 6 \rightarrow 12$ ).



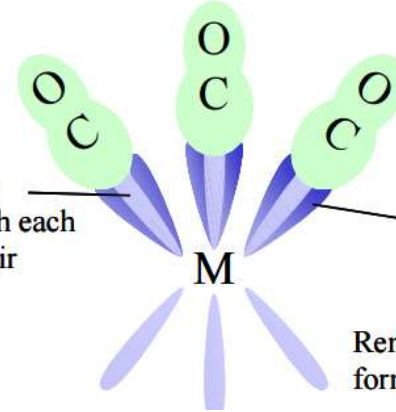
A similar approach provides some degree of understanding of the structures of larger transition metal complexes which do not follow the 18-electron rule. It is argued that an  $M(CO)_3$  group can be treated in a similar manner to the B-H unit.



Each metal has NINE valence orbitals. SIX hybrid orbitals form  $\sigma/\pi$  double bonds to each CO. The bonding electron framework forms using 3 orbitals from each metal.

1 orbital in  $\sigma$ -bond with each CO lone pair

1 orbital in  $\pi$ -bond with each CO



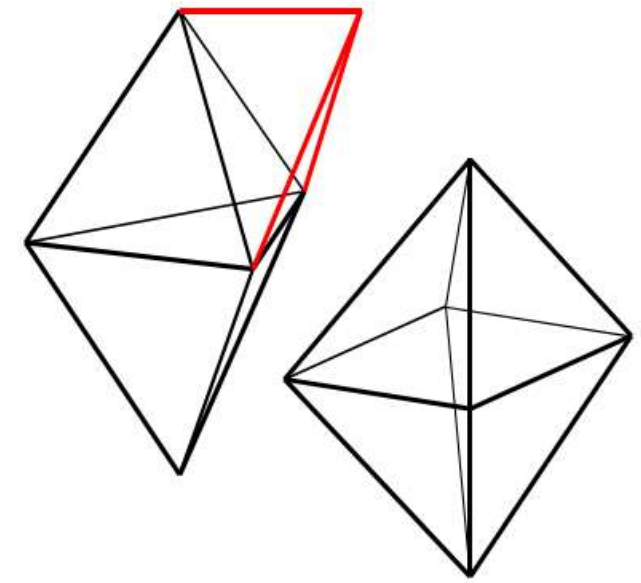
Remaining 3 orbitals form bonding framework.

$Rh_6(CO)_{16}$  by Wade?



# Large Clusters - Wades Rules

As cluster size increase, 18 electron rule fails



6 x Rh 54

16 x CO 32

TOTAL ELECTRONS 86

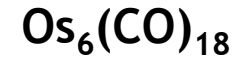
Use 6 orbitals per metal  
for M-CO bonds - 72

Electrons left for  
bonding framework 14

Electron Pairs (n+1) with n = 6

**Octahedron**

But octahedral edges aren't bonds  
Did not actually have 3 CO per metal



6 x Os 48

16 x CO 36

TOTAL ELECTRONS 84

Use 6 orbitals per metal  
for M-CO bonds - 72

Electrons left for  
bonding framework 12

Electron Pairs (n+1) with n = 5

**Capped Trigonal Bipyramid**

These rules compare it to the points of an octahedron

# Contents



Mononuclear Electronic



Mononuclear Magnetic



Crystal Field Theory



Dinuclear



Polynuclear



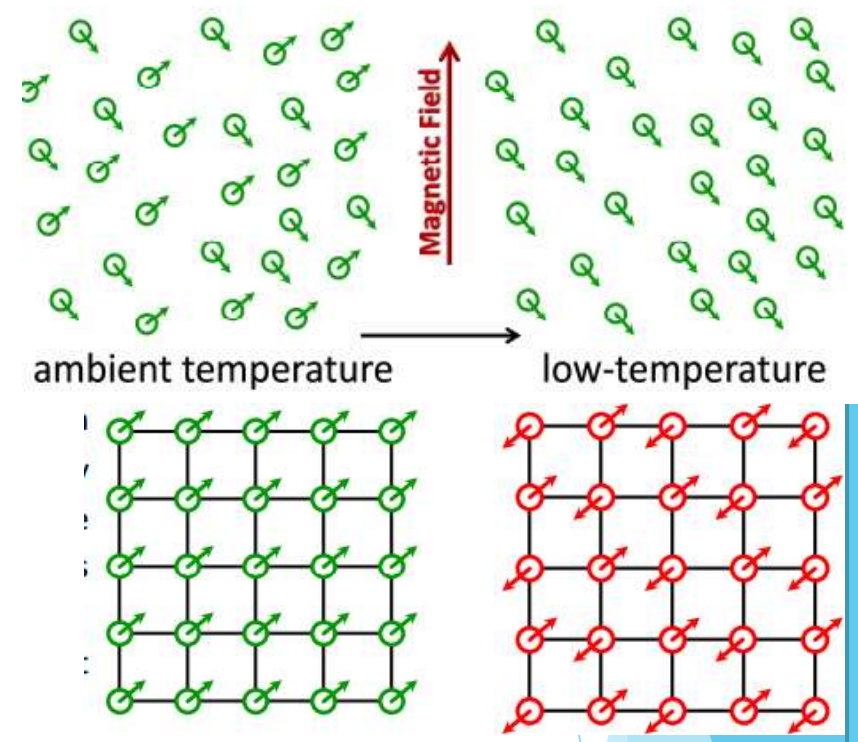
Extended Structures

Extended Structures



# Paramagnets

- ▶ Drop in temperature increases magnetisation due to population of states etc etc etc
- ▶ Curie temperature and that shit (go back to slide 12)
- ▶ NO INTERACTION ON SPIN BETWEEN DIFFERENT MOLECULES

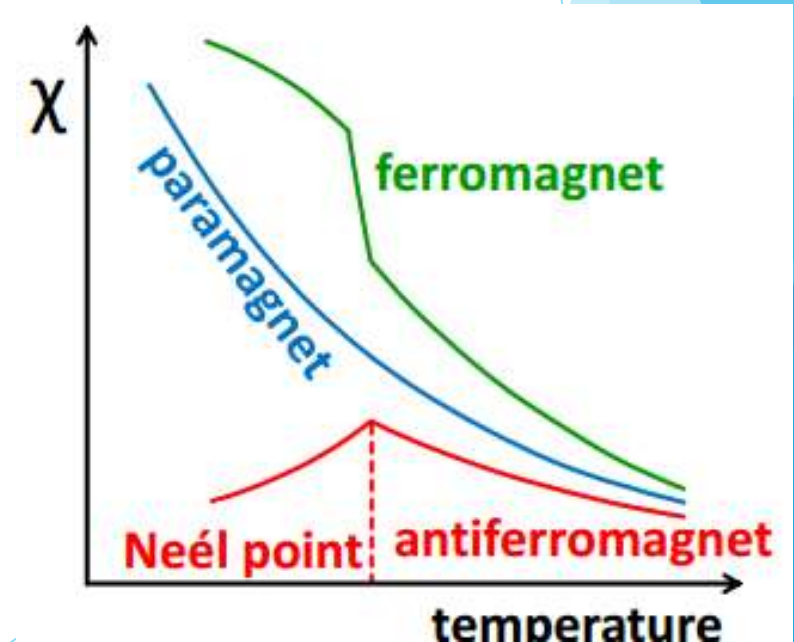


# Ferromagnets

- ▶ Interaction tending to align the spins
- ▶ As T drops,  $\chi$  increases more rapidly than expected due to the spin-spin interaction
- ▶ The curie temperature - thermal randomisation is overcome and all the spins align, sample has net magnetisation

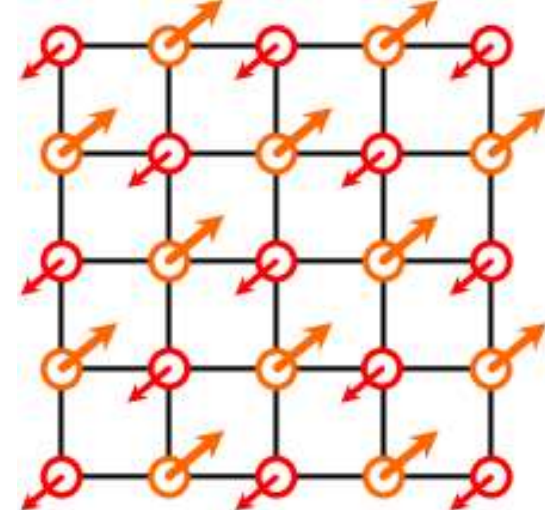
# Antiferromagnets

- ▶ Interaction tending to align neighbouring spins antiparallel
- ▶ As T drops,  $\chi$  decreases more rapidly than expected.
- ▶ Neel temperature - thermal randomisation overcome by coupling and the spins lock down onto the two interpenetrating sublattices with antiparallel alignments
- ▶ Usually result of superexchange



# Ferrimagnets

- ▶ Subclass of antiferromagnets
- ▶ Moments do not cancel due to differences in spin
- ▶ Large moment can persist below critical temperature (Curie temperature)



## Fe<sub>3</sub>O<sub>4</sub> Magnetite

- ▶ Original ferrimagnet, can be permanently magnetised
- ▶ Magnetised by earth's magnetic field
- ▶ Inverse spinel structure
- ▶ Adopted by AB<sub>2</sub>O<sub>4</sub> materials based on face-centred cubic structure of oxide ions

	T <sub>d</sub> sites	O <sub>h</sub> sites	Oxides
per unit cell of fcc structure	<b>8</b>	$(12 \times \frac{1}{4}) + 1 = 4$	$(6 \times \frac{1}{2}) + (8 \times \frac{1}{8}) = 4$
occupied in spinel structure AB <sub>2</sub> O <sub>4</sub>	A <sup>2+</sup>	B <sup>3+</sup> , B <sup>3+</sup>	4 x O <sup>2-</sup>
occupied in inverse spinel B(AB)O <sub>4</sub>	B <sup>3+</sup>	B <sup>3+</sup> , A <sup>2+</sup>	4 x O <sup>2-</sup>
<b>magnetite</b>	<b>Fe<sup>3+</sup></b>	<b>Fe<sup>3+</sup>, Fe<sup>2+</sup></b>	<b>4 x O<sup>2-</sup></b>
<b>spins</b>	<b>↑ S = 5/2</b>	<b>↓ S = 5/2, ↓ S = 2</b>	-

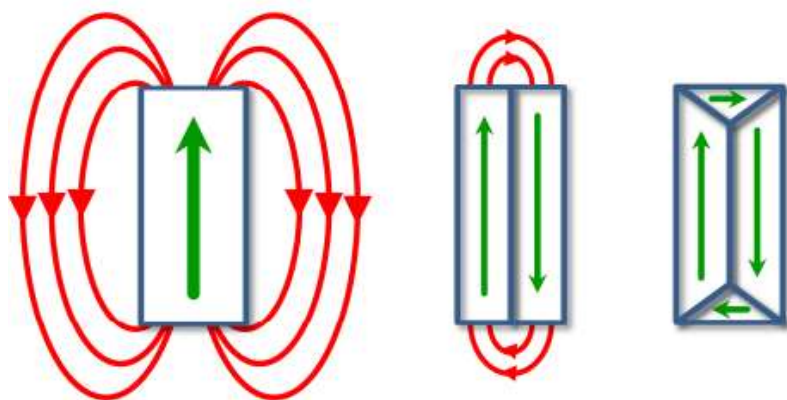
# Domains

- ▶ Ferromagnetic materials, block material, large magnetic moment

## Magnetostatic Energy

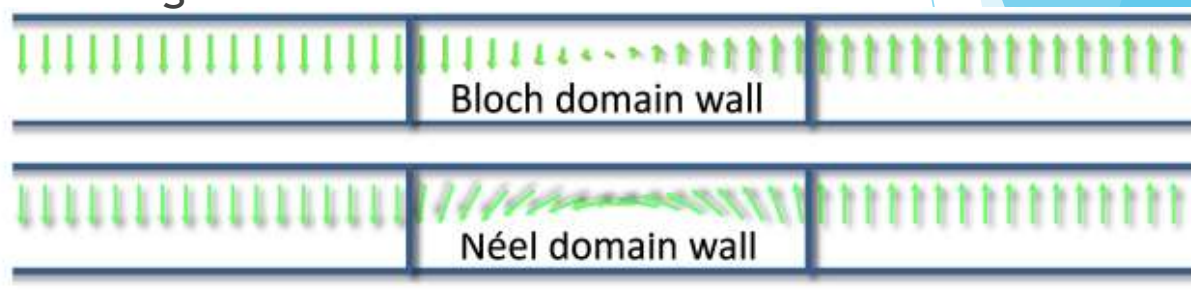
Flux lines have a magnetostatic energy. This can be reduced if the material is divided into domains

Alligning ferromagnetically exchange-coupled spins in an antiparallel fashion is not the most stable arrangement. But the dominant term is the magnetostatic energy and creates the formation of domains.



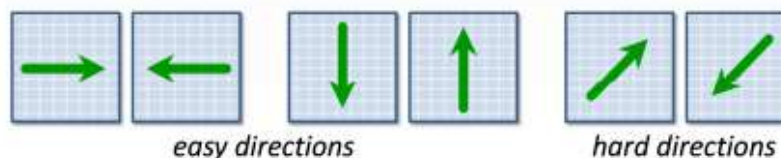
# Domain Boundaries

- ▶ Domain boundaries vary in size - normally a few hundred atoms. The manner in which spin orientation changes also varies



## Magnetocrystalline Energy

- ▶ Dipoles in domains will tend to align one of the easy directions wrt the lattice



# Hysteresis

Applying a magnetic field in a closed domain structure, returning the field to non zero, and then increasing the field in the opposite direction.

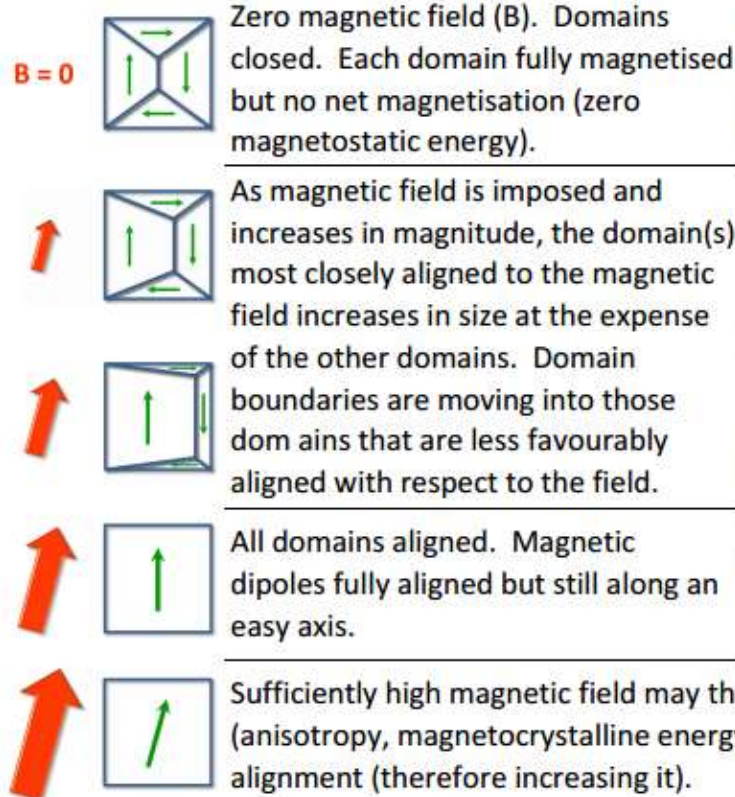
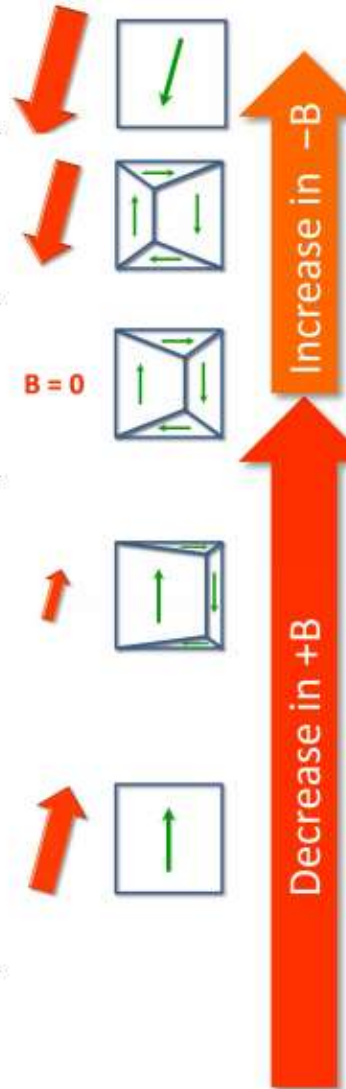
Consider applying an increasing magnetic field to a closed domain structure, returning the field to zero and then increasing the field in the opposite direction. Field is at a non-zero angle to easy directions.

At maximum reverse field, the magnetisation now matches the forward field value in magnitude.

Only on reversal of field direction does the magnetisation start decreasing significantly and then reverse in direction.

On return to zero magnetic field, the sample still has significant net (remanent) magnetisation. It's a "magnet" !

As field decreases, minor changes may occur, reducing the net magnetisation slightly but a full reversal of changes does not occur: there is a lag or *hysteresis*. (Reversing the changes in magnetisation will need to be forced by reversing the field.)



Zero magnetic field (B). Domains closed. Each domain fully magnetised but no net magnetisation (zero magnetostatic energy).

As magnetic field is imposed and increases in magnitude, the domain(s) most closely aligned to the magnetic field increases in size at the expense of the other domains. Domain boundaries are moving into those domains that are less favourably aligned with respect to the field.

All domains aligned. Magnetic dipoles fully aligned but still along an easy axis.

Sufficiently high magnetic field may then overcome local symmetry (anisotropy, magnetocrystalline energy) and rotate magnetisation into alignment (therefore increasing it).

# Magnetic Field Scan | Paramagnet

- ▶ Forward and reverse scan on **paramagnetic** molecules, trace is reversible. The remnant magnetisation is zero

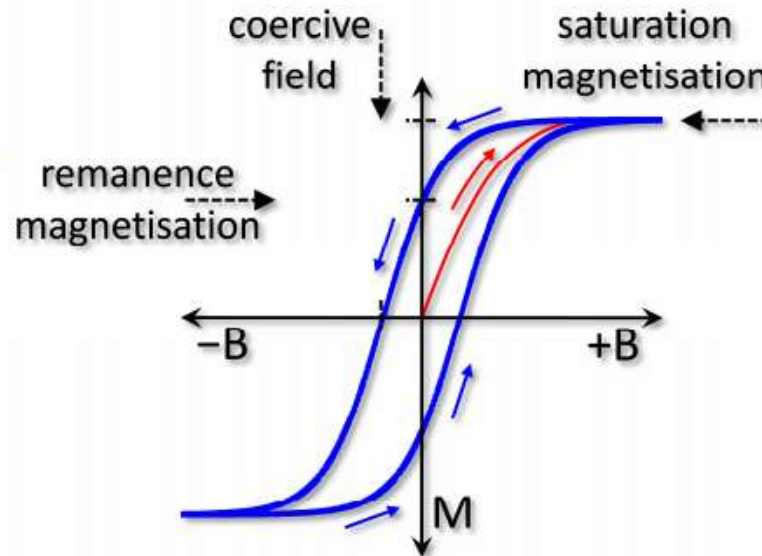
# Hysteresis Loop | Ferromagnets

- ▶ Below the curie temperature, the magnetic field scan of a ferrimagnet results in a lag of magnetisation (hysteresis)
- ▶ First ramp is paramagnetic behaviour

Saturation Magnetisation : Maximum magnetisation

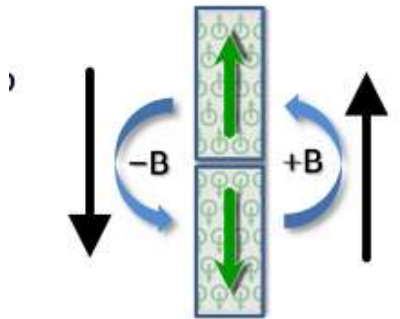
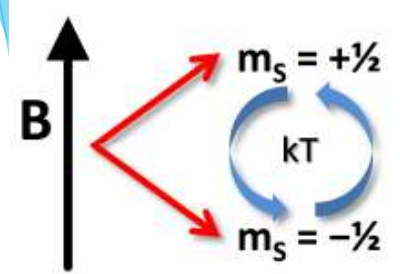
Remanence Magnetisation : Amount of magnetisation left when  $B = 0$

Coercive field : value of  $B$  in opposite direction to demagnetise the sample



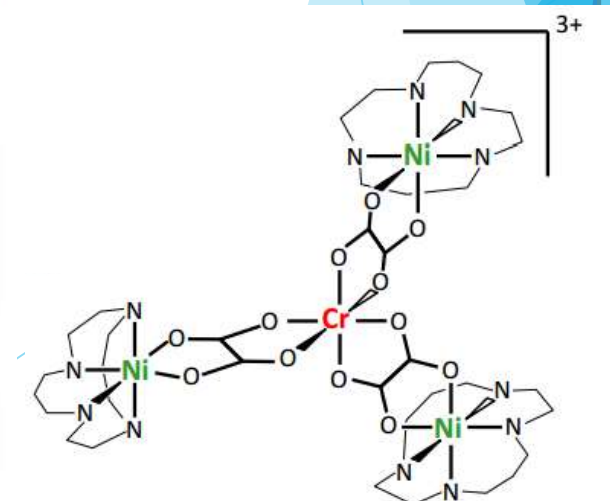
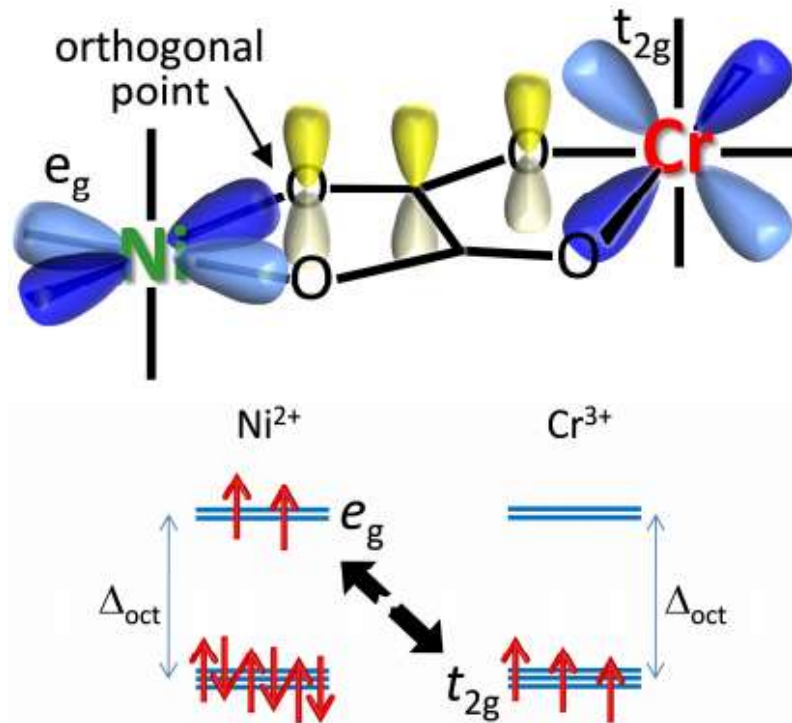
# Single Molecular Magnets & Single Chain Magnets

- ▶ For a **paramagnet** the spins are independent of one another and no molecule is locked into one of the  $+ \frac{1}{2}$  or  $- \frac{1}{2}$  states (dynamic equilibrium)
- ▶ For **ferromagnets** and **ferrimagnets** below their critical temperature, the domains can be locked into one orientation, and thermal energy is insufficient to randomise them.
- ▶ The critical property is inertia, an energy barrier, the reorientation of a large magnetisation at a particular temperature.



## Ferromagnetic Strategy

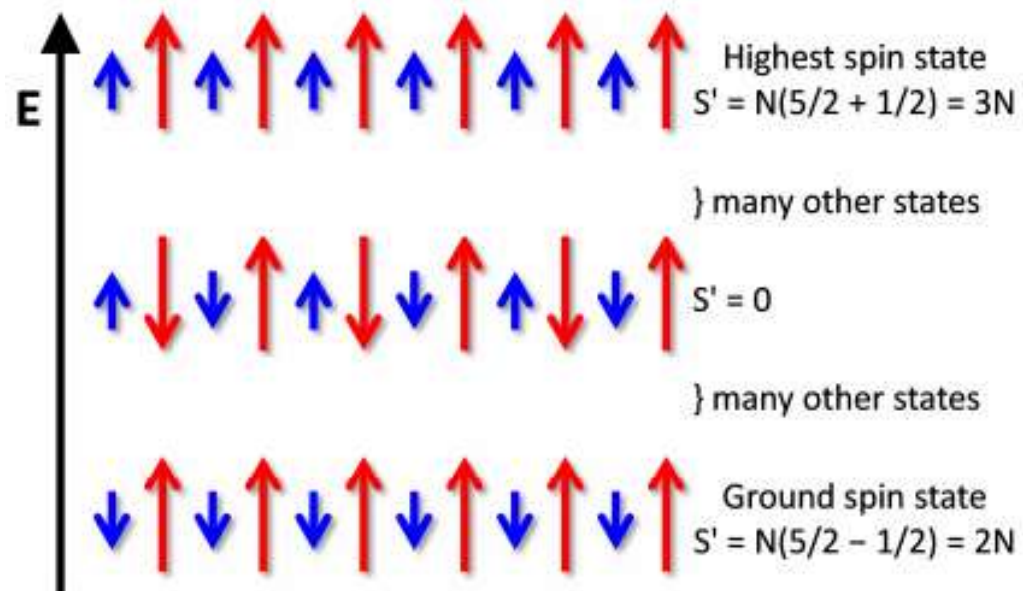
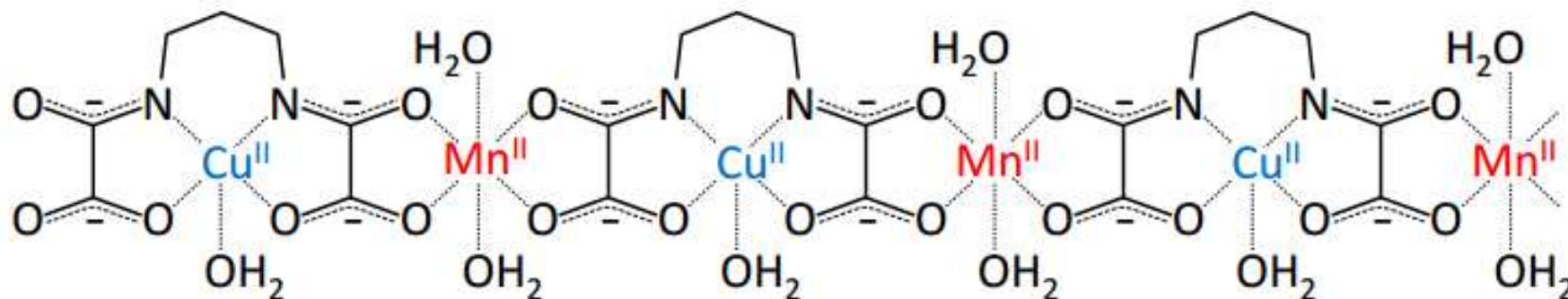
- ▶ Ferromagnetic coupling can only occur if coupling is absolutely orthogonal
- ▶ The oxalate ion can do this
- ▶ “complex as ligand” strategy to create polynuclear structures
- ▶ This results in a large ground state spin which can interact within the extended solid





# Single Chain Magnet

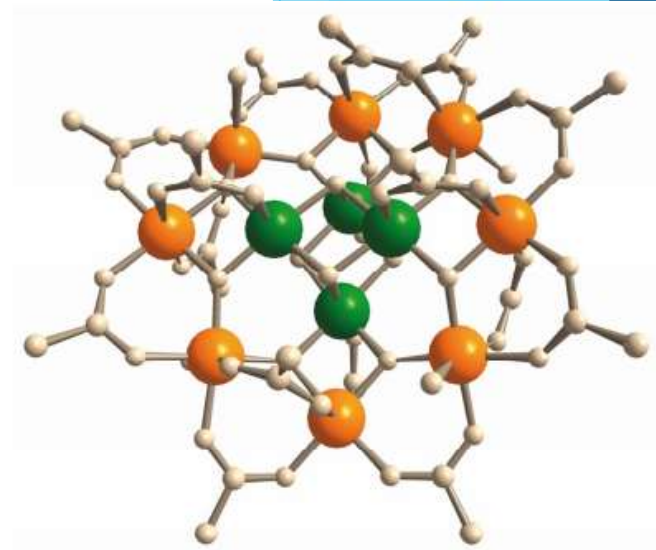
- ▶ Example of Ferrimagnetic strategy to produce large spins
- ▶ Accepting the inevitability of antiferromagnetic ligand mediated coupling but using alternating spins of very different magnitudes so as to maximise uncanceled net spin



Results in a large ladder of spin states  
 Interactions between chains add another level of complexity, can be altered by adding substituents to the bridging ligands

# Single Molecule Magnet

- ▶  $Mn_{12}$  can be the smallest molecular magnet
- ▶ Single chain magnets - units with large spins, tetranuclear molecules and extended chains. Exhibit molecular magnet behaviour, such as hysteresis, often have very low critical temperature.
- ▶ Challenge is to raise this temperature
- ▶ This compound has the specific structure to show non-paramagnetic behaviour
- ▶ A molecule containing lots of Fe ions won't show hysteresis



↑ 8 x Mn(III) high-spin  $d^4$   $S = 2$   
couple to give sub-ring of  $S' = 16$

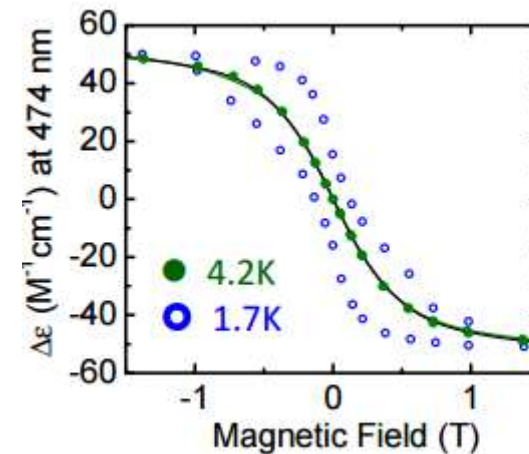
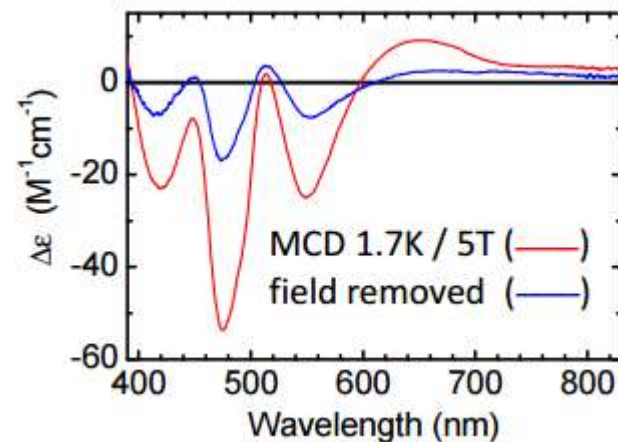
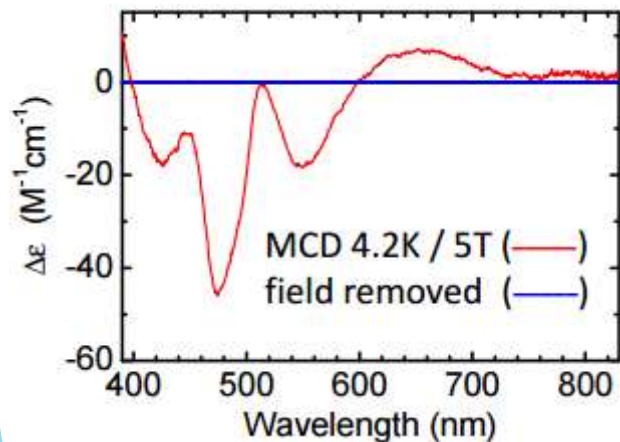
↓ 4 x Mn(IV) high-spin  $d^3$   $S = 3/2$   
couple to give sub-ring of  $S'' = 6$

$S'$  and  $S''$  then couple *antiferromagnetically* to give the complex an overall spin of **10**.

MCD

4.2 K

1.7 K



# Electrical Conductivity

## Conductivity

$\sigma = n e \mu$  (number of current carrying species x electron charge x mobility)

Ionic conduction can occur with ions, but we are only concerned with electrons and holes

## Band Theory

Imagine an alkali metal (group 1 - conductors)

In an extended array of solid each s AO contributes to a MO. The number of AO you overlap must be the number of MO you get out. Hence a band rather than discrete energy levels

Same applies to p and d orbitals

Extra MO only fills the current set, it does not raise and lower the maximum and minimum levels

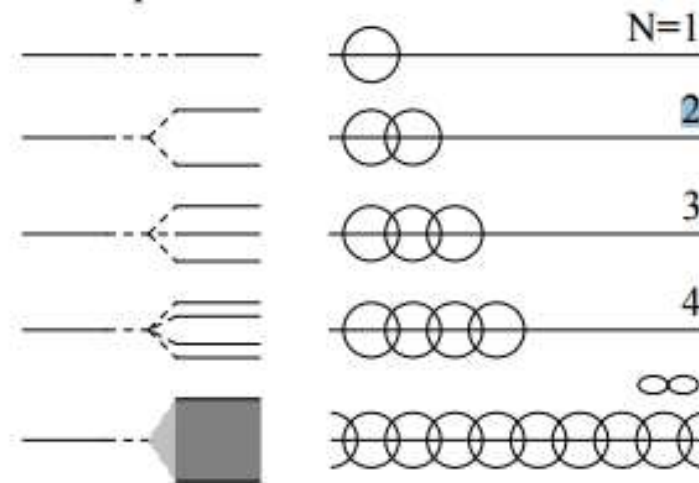
For alkali metal, there are N electrons and N orbitals

Each orbital takes 2 electrons

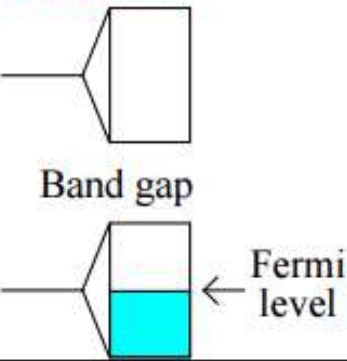
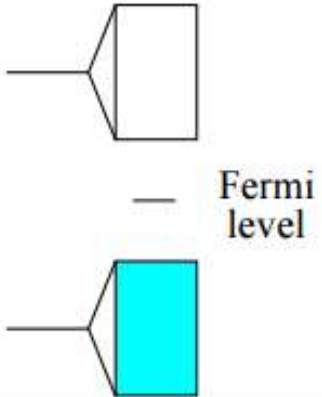
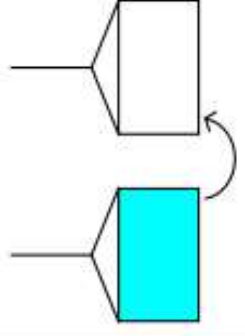
Therefore only lowest N/2 orbitals are filled.

Highest filled orbital is the **Fermi Level**

Example of an *s*-band:

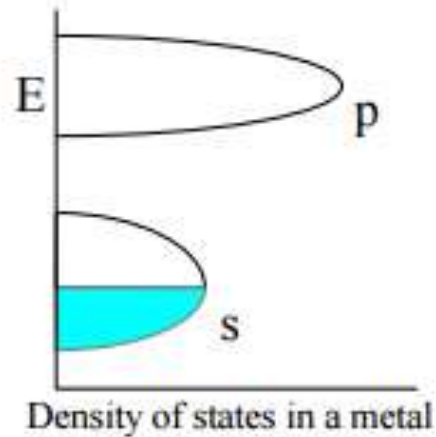


# Band Theory

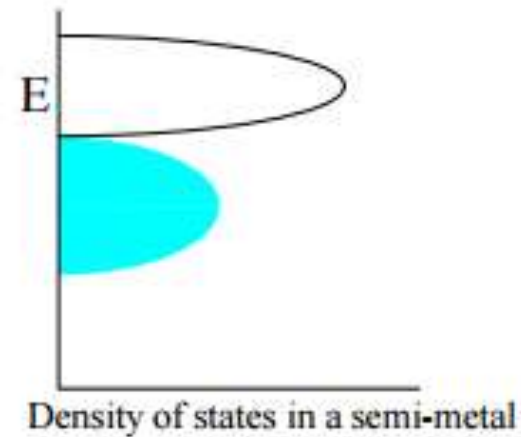
<p><b>conductor</b></p>  <p>The diagram shows two energy bands. The lower band is partially filled with blue, and the Fermi level (indicated by a horizontal line) is within this band. The upper band is empty. A label 'Band gap' points to the space between the two bands.</p>	<p>Because Fermi level lies within band, there are unfilled orbitals within a negligible energy range. Imparts mobility to electrons. Electrical <b>conductivity</b> thus a property of <i>partially filled bands</i> in the metal. Mobility of electron 'sea' in metals imparts properties- high electrical and thermal conductivity, lustre and malleability.</p>
<p><b>insulator</b></p>  <p>The diagram shows two energy bands. The lower band is completely filled with blue, and the Fermi level (indicated by a horizontal line) is at the top of this band. The upper band is empty. A label 'Fermi level' points to the top of the lower band.</p>	<p>When atom provides TWO electrons, Fermi level is at top of full band and material is an <b>insulator</b>. e.g. diamond or solid helium! Band gaps <math>&gt;3.0\text{eV}</math>.</p>
<p><b>semi-conductor</b></p>  <p>The diagram shows two energy bands. The lower band is completely filled with blue, and the Fermi level (indicated by a horizontal line) is in the band gap between the two bands. An arrow points from the top of the lower band to the upper band, indicating the excitation of electrons.</p>	<p>If the gap to next empty band is within thermal excitation (<math>&lt;3\text{eV}</math>), then electrons reach higher band and positive holes left behind act as charge carriers and substance is an intrinsic <b>semi-conductor</b>. Thus conductivity of semi-conductor rises with temperature. Example is silicon with same <i>structure</i> as diamond but smaller band gap.</p>

# Band Theory

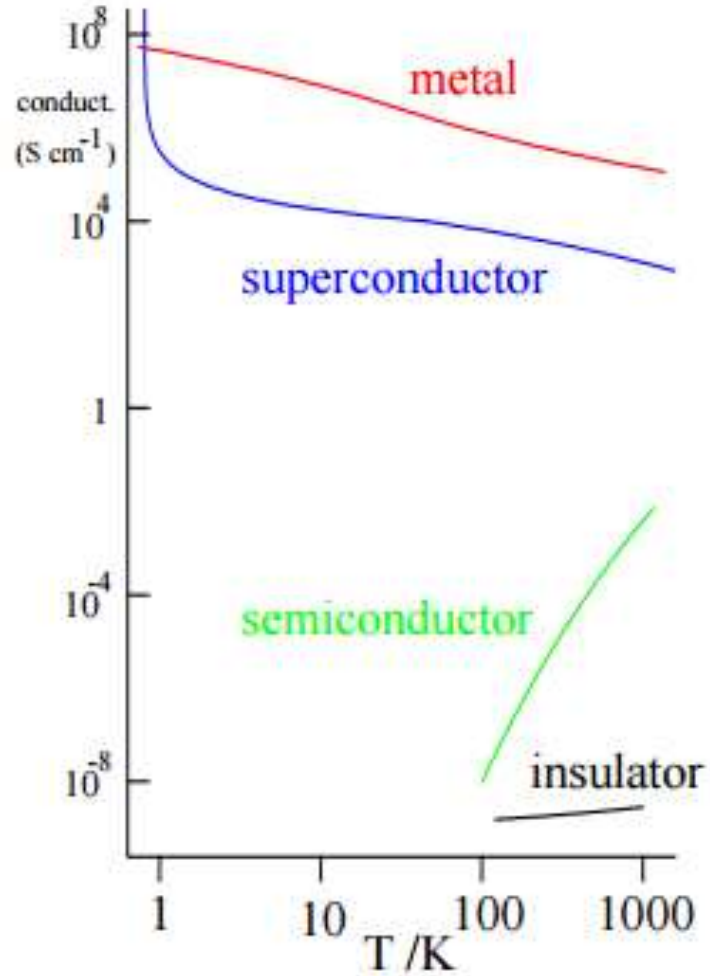
Direct evidence for band structure is obtained from photoelectron and x-ray emission spectroscopies which give bands very broad *cf.* molecular species.



**Density of states** is greater at the extremes of a band for the one-dimensional case but for a three-dimensional system is greater at energies in the middle of the band.  
Graphite- sheet semi-metal.



# Band Theory



Conductors and semi-conductors: contrasting temperature dependence.

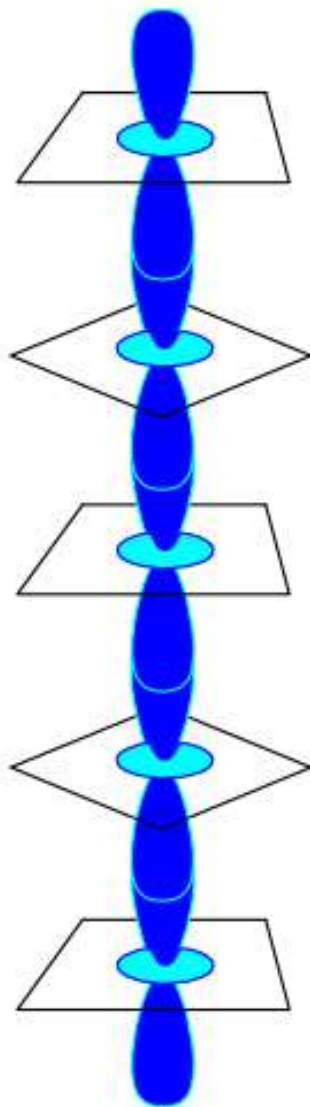
**Conductor:** as temperature rises, electrical resistance rises. Electron described as travelling wave which is scattered by lattice vibrations disrupting the required uniformity of the orbital wavefunctions.

**Semi-conductors:** thermal increase in number of *charge carriers* more than offsets above effect:- increase in conductivity.

Generally, metal conductivity at room temperature is higher than semiconductor but it is not the magnitude that distinguishes the two.

# One-dimensional solid

## One-dimensional solid



$\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$  (=KCP) :  
white non-conductor with long  
(3.48 Å vs. metal 2.78 Å) Pt-Pt lengths.

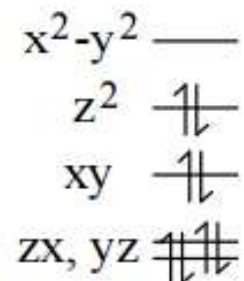
1842: discovered under oxidising conditions appears bronze  
and conducts electricity.

Contains substoichiometric  $\text{Br}^-$  or  $\text{Cl}^-$   
i.e.  $\text{Pt}(\text{II}) \rightarrow \text{Pt}(2.3)$  and formula  
is  $\text{K}_2\text{Pt}(\text{CN})_4\text{X}_{0.3} \cdot 3\text{H}_2\text{O}$  with Pt-Pt at 2.88/2.87 Å.

Calculation shows a one-dimensional band structure is  
optimum at these stoichiometries and gives metallic  
properties.

(Whangbo & Hoffmann (1978) JACS **101** 6093)

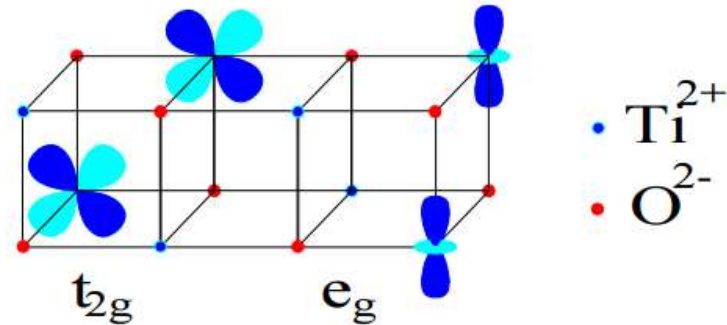
Square-planar Pt(II): band is formed from  $5d_{z^2}$  orbitals,  
which are full until partial oxidation occurs.



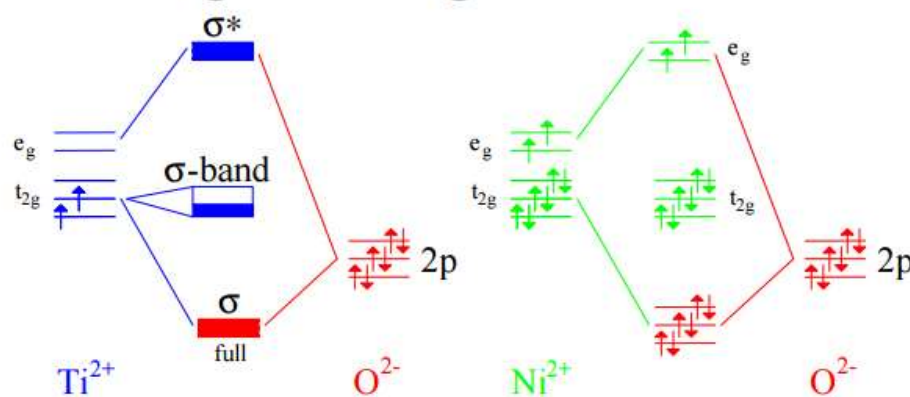
# First row transition metals with rock salt structure

1<sup>st</sup> row TM M(II) oxides with rocksalt structure

TiO	VO	CrO	MnO	FeO	CoO	NiO
	V(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup> violet					Ni(H <sub>2</sub> O) <sub>6</sub> <sup>2+</sup> green
	VO black					NiO green
d <sup>2</sup> partially occupy t <sub>2g</sub>						d <sup>8</sup> partially occupy e <sub>g</sub>
diffuse d-orbitals						contracted d-orbitals
high electronic conductivity (10 <sup>3</sup> (Ωcm) <sup>-1</sup> )	high electronic conductivity			defects/impurities? semi-conductor properties		insulator, no metallic properties



Shows conductivity



Does not show conductivity