

# Transition metal complexes 1

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# Outline

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- ▼ Transition metals and their common oxidation states
- ▼ What is a metal complex?
- ▼ Geometries of complexes
- ▼ Common ligands
- ▼ Isomerism in coordination complexes
- ▼ Naming transition metal complexes

# Transition metals

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																H																	He
Li	Be											B	C	N	O	F	Ne																
Na	Mg											Al	Si	P	S	Cl	Ar																
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr																
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe																
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn																
Fr	Ra	Lr	Db	Jl	Rf	Bh	Hl	Mt																									

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

# Transition metal oxidation states

Sc 3	Ti 3,4	V 2, 3, 4, 5	Cr 2, 3, 4, 6	Mn 2, 3, 4, 6, 7	Fe 2, 3	Co 2, 3	Ni 2	Cu 1, 2	Zn 2
Y 3	Zr 4	Nb 3,4, 5	Mo 2,3,4, 5, 6	Tc 2,3,4, 5,6,7	Ru 2,3,4, 5,6,7, 8	Rh 1, 3	Pd 2, 4	Ag 1	Cd 2
La 3	Hf 4	Ta 3, 4, 5	W 2,3,4, 5, 6	Re 2,3,4, 5,6,7	Os 3,4,5, 6,7,8	Ir 1, 3	Pt 2, 4	Au 1, 3	Hg 1, 2

These are “common” oxidation states. It is not supposed to be an exhaustive list.

Low oxidation states of heavy metals like Ta, Nb, Mo, W and Re tend to be found in compounds containing metal-metal bonds

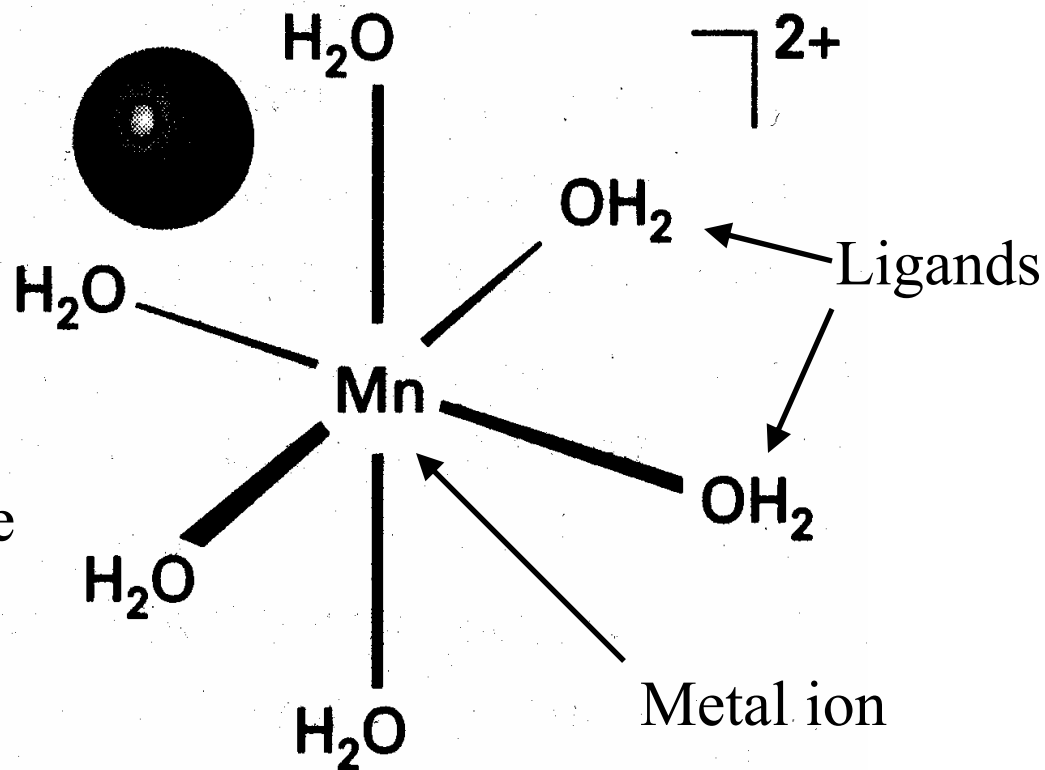
# Transition metal complexes

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- A transition metal complex is species consisting of a transition metal coordinated (bonded to) one or more ligands (neutral or anionic non-metal species)
- Transition metal complexes are important in catalysis, materials synthesis, photochemistry, and biological systems
- Display diverse chemical, optical and magnetic properties

# An example of a complex

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We can view the complex as ligands (Lewis bases) bound to a metal ion (a Lewis acid)



# Coordination numbers

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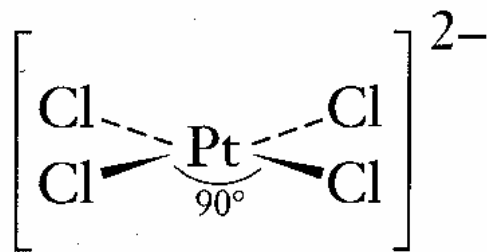
- Transition metal ions usually form complexes with a well defined number of ligands
- Complexes with coordination numbers four and six are the most common, although two and five coordination are also very well established

# Stereochemistry

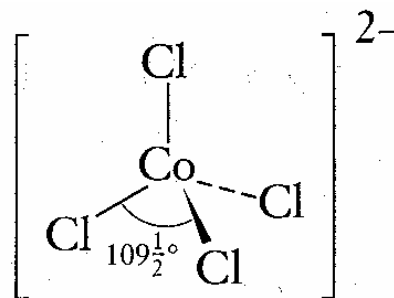
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- Four coordinate transition metal ions adopt either tetrahedral or square planar coordination
  - $\text{FeCl}_4^{2-}$  (tetrahedral),  $\text{AuCl}_4^-$  (square planar)
  - Square planar complexes nearly always involve  $d^8$  metals
- Six coordinate species are nearly always octahedral
- Five coordinate species are either trigonal bipyramidal or square base pyramidal
- Two coordinate species such as  $\text{AgCl}_2^-$  are linear
  - Linear complexes are typically formed by  $d^{10}$  metal ions

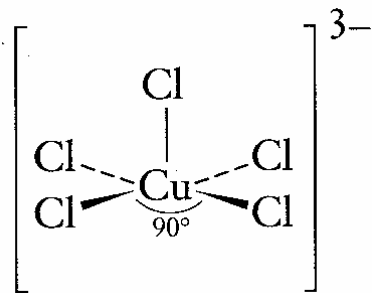
# Example geometries



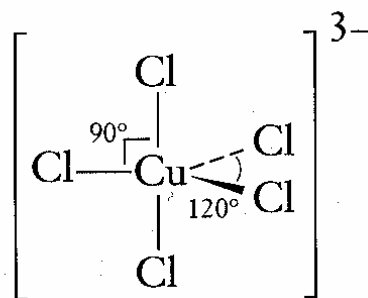
Square planar



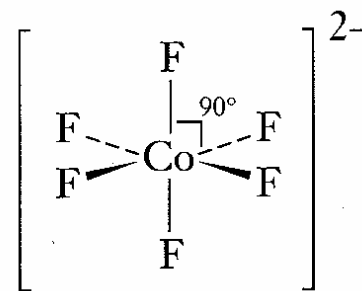
Tetrahedral



Square pyramidal



Trigonal  
bipyramidal



Octahedral

# Ligands

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- Ligands are species (neutral or anionic) bonded to the metal ion
- They may be attached to the metal through a single atom (monodentate) or bound to the metal through two or more atoms (bidentate, tridentate etc.)
- Polydentate ligands are called chelating ligands

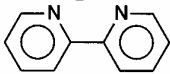
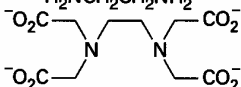
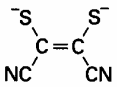
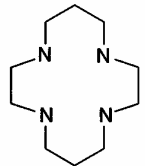
# Example simple ligands

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Neutral Molecules		Anions	
Aqua	H <sub>2</sub> O	Fluoro	F <sup>-</sup>
Ammine	NH <sub>3</sub>	Chloro	Cl <sup>-</sup>
Methylamine	CH <sub>3</sub> NH <sub>2</sub>	Bromo	Br <sup>-</sup>
Carbonyl	CO	Iodo	I <sup>-</sup>
Nitrosyl	NO	Hydroxo	OH <sup>-</sup>
		Cyano	CN <sup>-</sup>

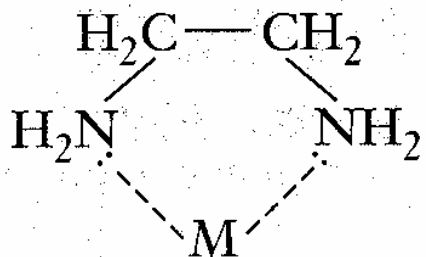
# List of common ligands

Table 7.1 Typical ligands and their names

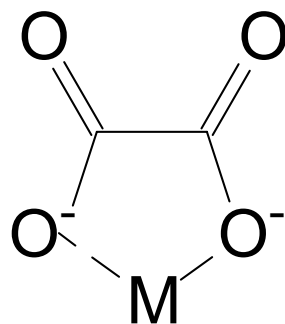
Name	Formula	Abbreviation	Classification
Acetylacetonato	$(\text{CH}_3\text{COCHCOCH}_3)^-$	acac	B(O)
Ammine	$\text{NH}_3$		M(N)
Aqua	$\text{OH}_2$		M(O)
2,2-Bipyridine		bipy	B(N)
Bromo	$\text{Br}^-$		M(Br)
Carbonato	$\text{CO}_3^{2-}$		M(O) or B(O)
Carbonyl	$\text{CO}$		M(C)
Chloro	$\text{Cl}^-$		M(Cl)
Cyano	$\text{CN}^-$		M(C)
Diethylenetriamine	$\text{NH}(\text{C}_2\text{H}_4\text{NH}_2)_2$	dien	T(N)
Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	en	B(N)
Ethylenediaminetetraacetato		edta	S(N,O)
Glycinato	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	gly	B(N,O)
Hydrido	$\text{H}^-$		M
Hydroxo	$\text{OH}^-$		M(O)
Maleonitriledithiolato		mnt	B(S)
Nitrilotriacetato	$\text{N}(\text{CH}_2\text{CO}_2^-)_3$	nta	Te(N,O)
Oxo	$\text{O}^{2-}$		M
Oxalato	$\text{C}_2\text{O}_4^{2-}$	ox	B(O)
Nitrito	$\text{NO}_2^-$		M(O)
Tetraazacyclotetradecane		cyclam	Te(N)
Thiocyanato	$\text{SCN}^-$		M(S)
Isothiocyanato	$\text{SCN}^-$		M(N)
2,2',2''-Triaminotriethylamine	$\text{N}(\text{C}_2\text{H}_4\text{NH}_2)_3$	trien	Te(N)

\*M: monodentate, B: bidentate, T: tridentate, Te: tetradentate, S: sexidentate. The letters in parentheses identify the donor atoms.

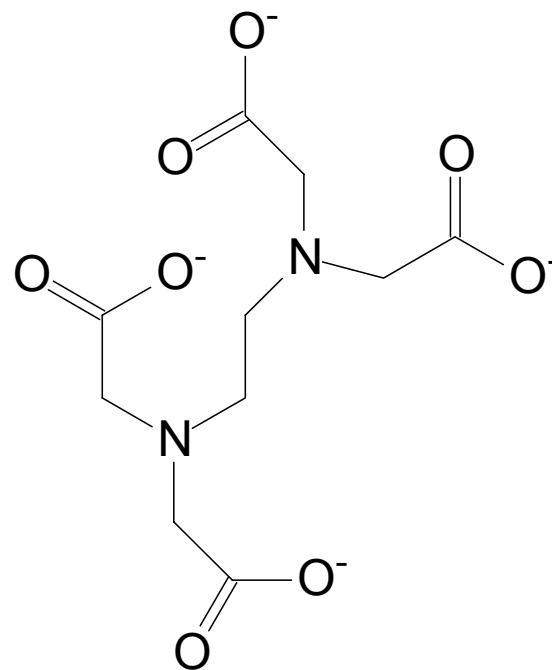
# Example chelating ligands



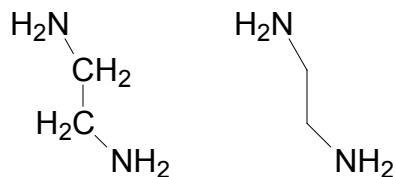
Ethylenediamine  
acting as a bidentate  
ligand



Oxalate acting  
as a bidentate  
ligand



Ethylenediaminetetraacetate  
Can act as hexadentate ligand



Note both of these drawing  
imply the same thing

# Ligands and oxidation state

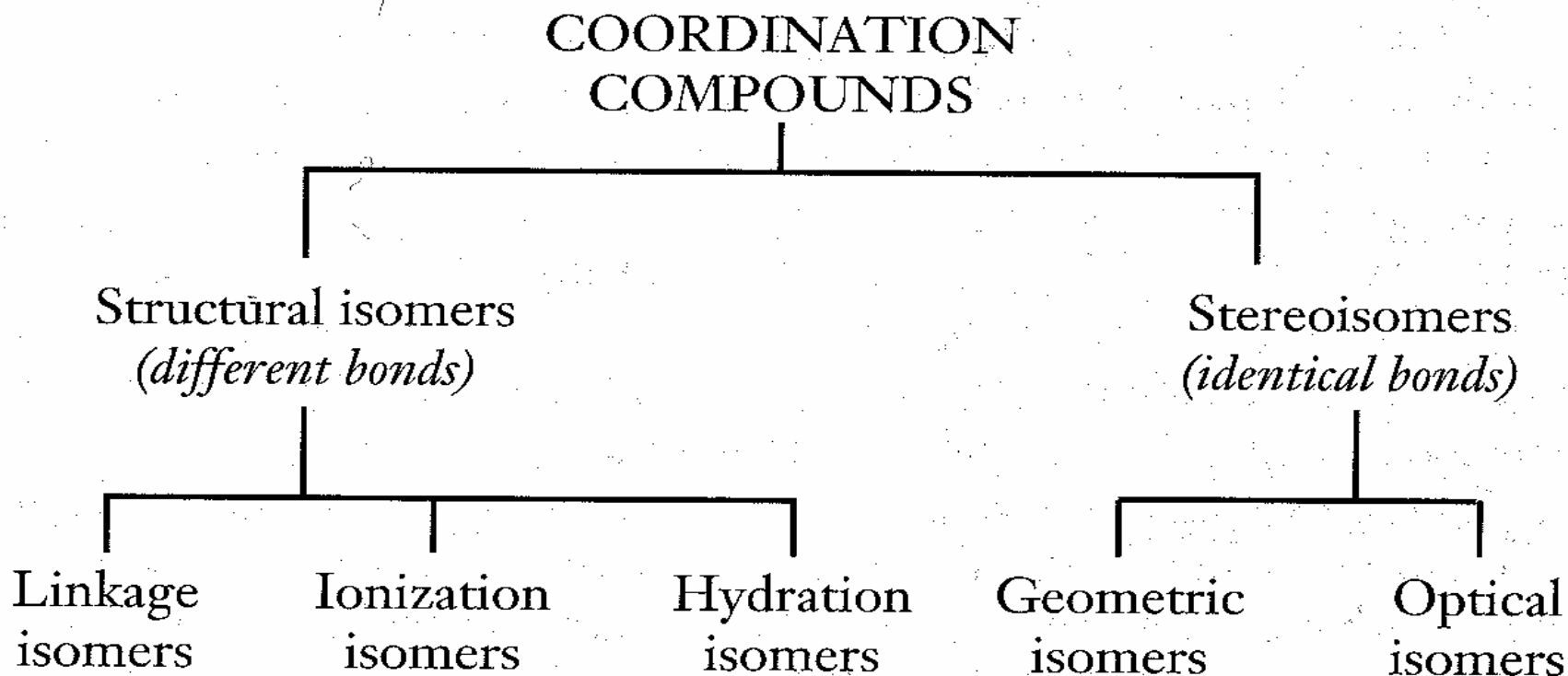
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- Low oxidation state complexes can be stabilized by using ligands such as cyanide and carbon monoxide
- Intermediate oxidation state complexes often have ligands such as chloride, ammonia or water
- High oxidation state complexes usually have fluoride or oxide as ligands

# Isomerism in metal complexes

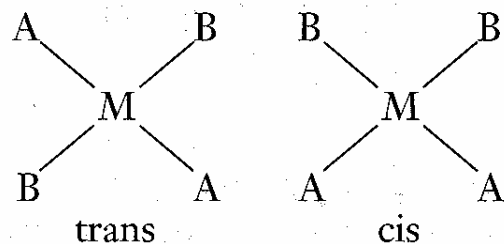
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- Isomers are compounds with the same chemical formula but different structures
  - Note that as they have different structures they will have different physical and chemical properties



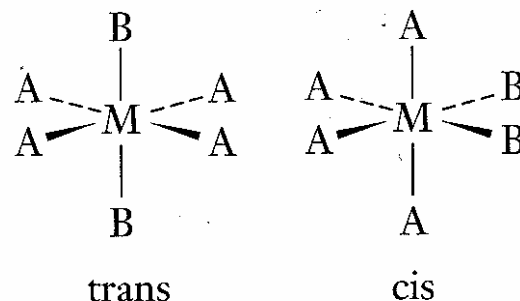
# Geometrical isomers

- Geometrical isomers may exist as distinct compounds because there is no low energy path for their interconversion

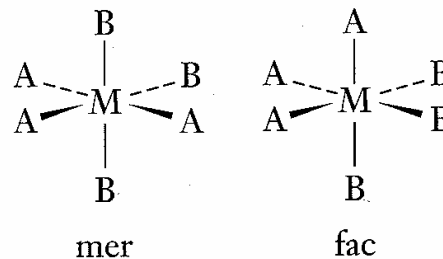


$MA_2B_2$  square planar compounds

Geometrical isomers have different physical and chemical properties



$MA_4B_2$  octahedral compounds

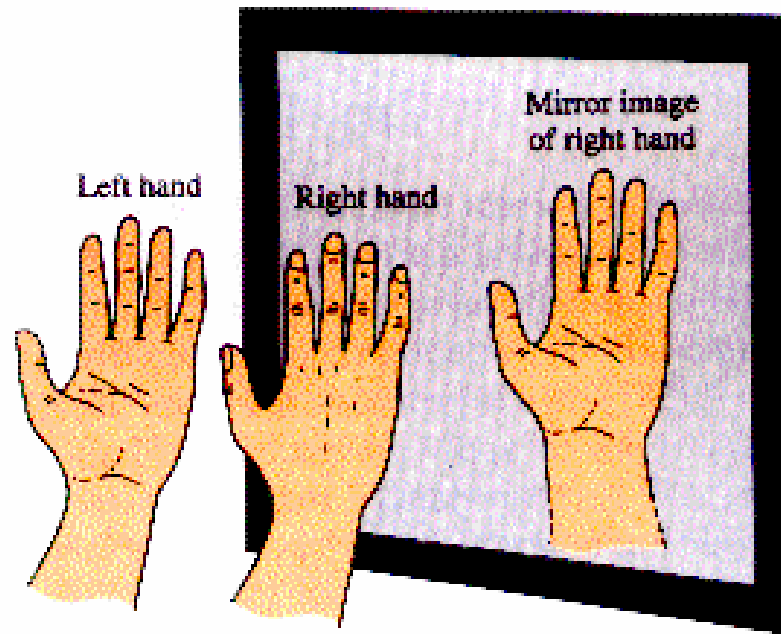


$MA_3B_3$  octahedral compounds

# Chirality

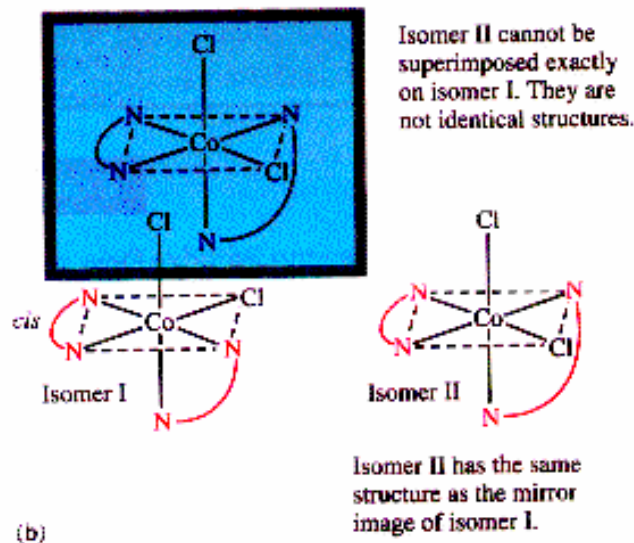
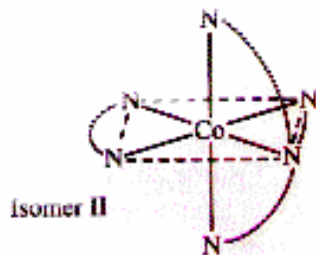
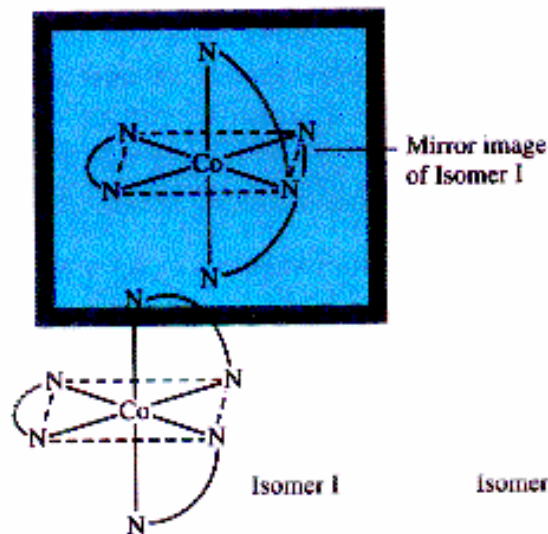
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- Objects that are not superimposable on their mirror images are said to be chiral
  - e.g. left and right hand



# Chiral molecules

- Molecules are not always superimposable on their mirror images
  - If a molecule and its mirror image are not superimposable they are said to be chiral and they are related to one another as enantiomers
    - This is a type of isomerism – optical isomerism



# Properties of chiral molecules

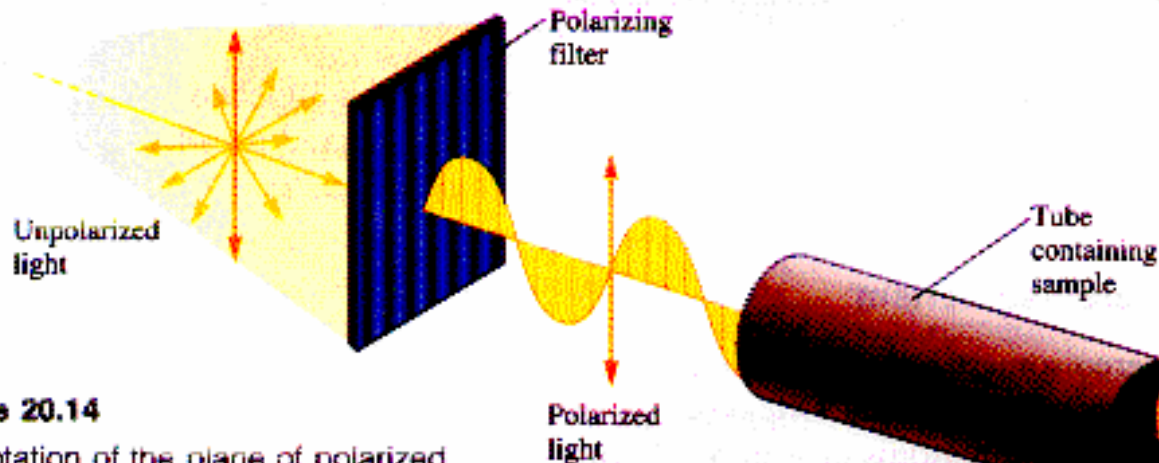
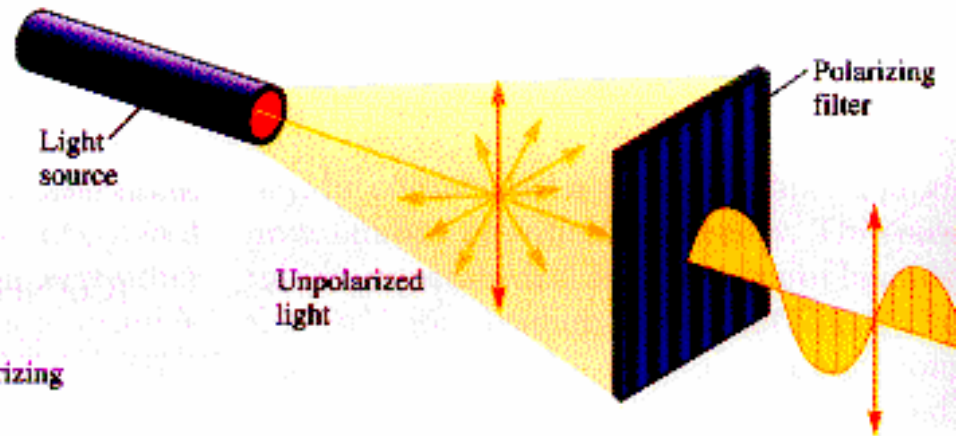
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- Molecules that are related to one another as enantiomers have the same boiling points, densities, colors etc.
  - However, they rotate plane polarized light in opposite directions
  - They react in different ways with other chiral molecules
- As most biological molecules are chiral, this implies that living systems will deal in different ways with species that are related as enantiomers
  - One optical isomer of a drug may be beneficial the other may be lethal

# Optical rotation

**Figure 20.13**

Unpolarized light consists of waves vibrating in many different planes (indicated by the arrows). The polarizing filter blocks all waves except those vibrating in a given plane.



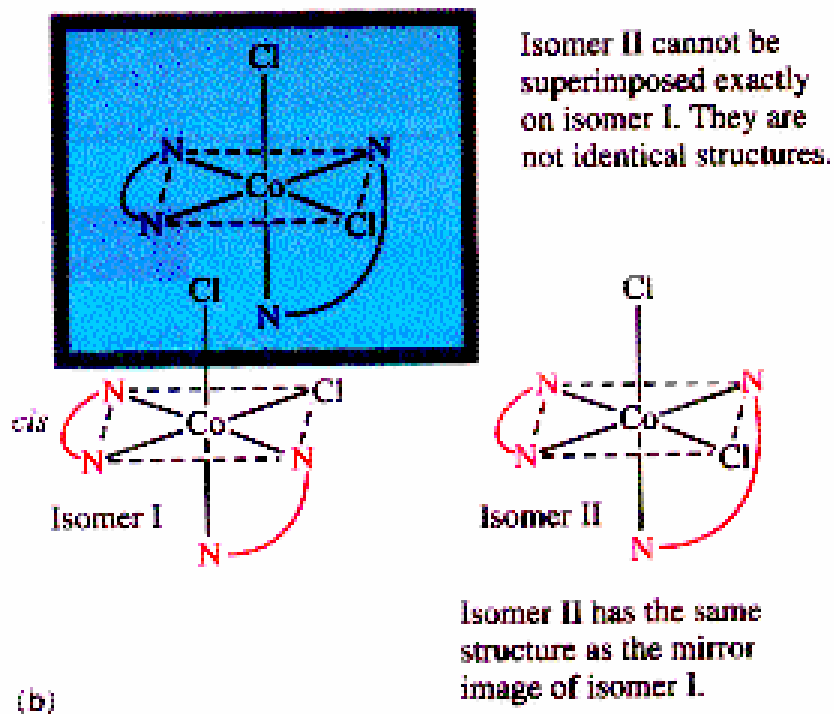
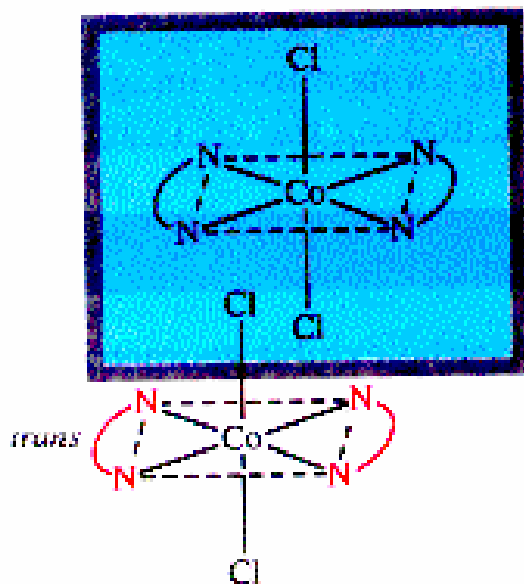
**Figure 20.14**

The rotation of the plane of polarized light by an optically active substance. The angle of rotation is called theta ( $\theta$ ).

Rotated  
polarized light

# Symmetry criteria for chirality

- Molecules that have inversion centers or mirror planes are not chiral



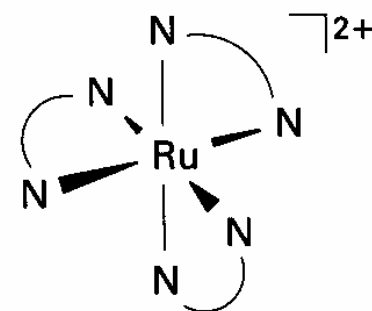
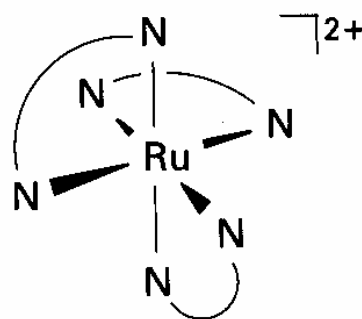
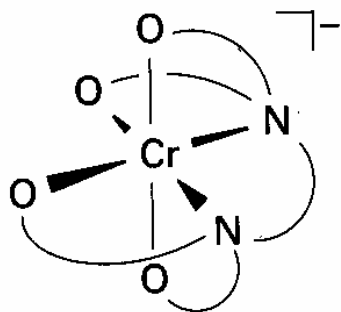
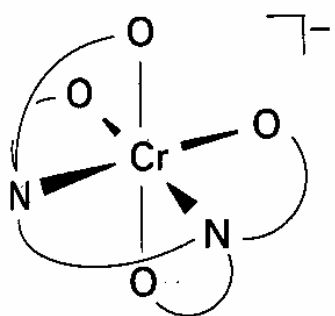
# Optical isomerism in metal complexes

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- Any species that does not have an  $S_n$  axis is chiral
- Common examples include compounds with the formula  $ML_3$  where L is a bidentate ligand
- Even compounds with the formula  $MA_2B_2C_2$  can be optically active

# Examples of optical isomerism

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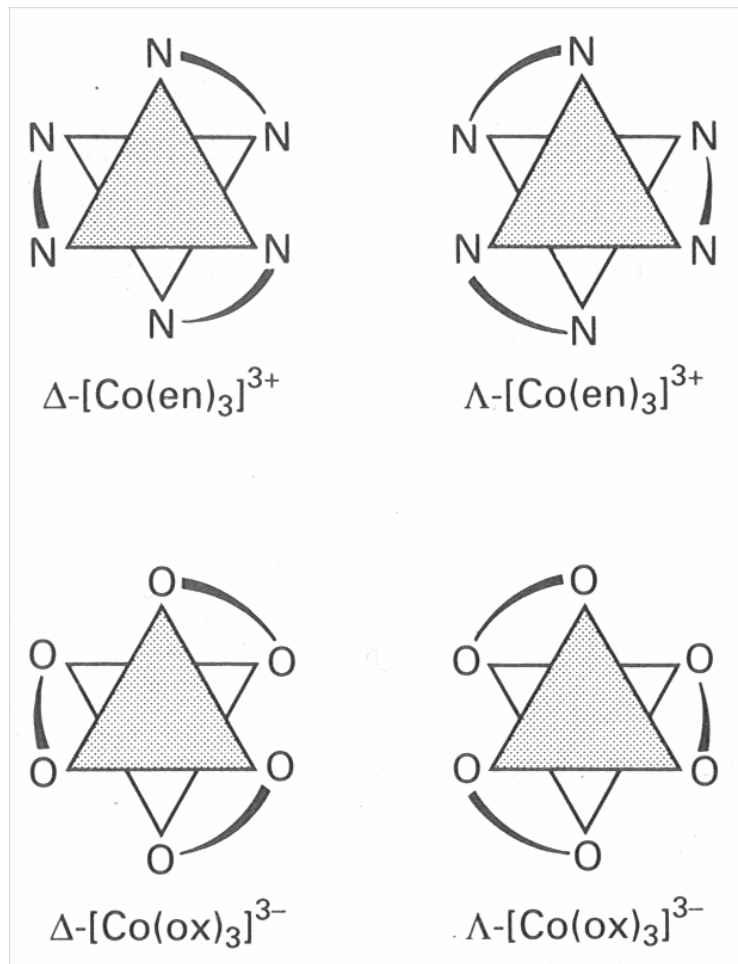


# Naming enantiomers

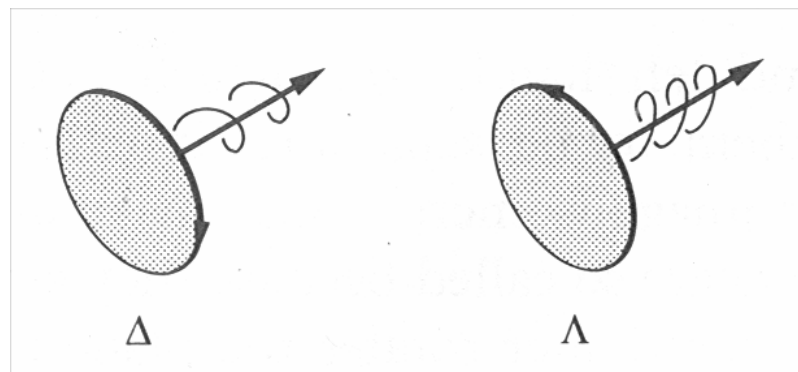
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- d and l are used to denote which way a species rotates plane polarized light (at a specific wavelength)
  - when looking into the light source, d [or (+)] implies the plane of polarization rotates clockwise
- $\Delta$  and  $\Lambda$  are used to denote an absolute configuration (the arrangement of atoms in space). You have to know the structure of the isomer to assign the absolute configuration
  - Complexes with a  $\Delta$  absolute configuration do not always rotate light in a d fashion. In fact the direction in which they rotate the plane of polarized light depends on what wavelength you use

# $\Delta$ and $\Lambda$



To decide if a particular isomer has a Lambda or Delta absolute configuration look down the molecular 3-fold rotation axis and see if the ligand backbones rotate to the left or the right as they go away from you



# Linkage isomerism

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- Some ligands can link to a metal through one of two or more different atoms
  - $\text{NO}_2^-$  can link through oxygen or nitrogen
    - »  $[\text{Co}(\text{ONO})(\text{NH}_3)_5]^+$  and  $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]^+$
  - $\text{NCS}^-$  can link through S or N
  - $\text{SO}_3^{2-}$  can link through O or S

# Ionization and hydration isomerism

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- Ionization isomerism -
  - $[\text{Co}(\text{NH}_3)_5(\text{Br})]\text{SO}_4$  versus  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$
  - or  $[\text{Pt}(\text{NH}_3)_3(\text{Cl})]\text{Br}$  versus  $[\text{Pt}(\text{NH}_3)_3(\text{Br})]\text{Cl}$
- Hydration isomerism
  - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  versus  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  versus  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

# Isolation of isomers

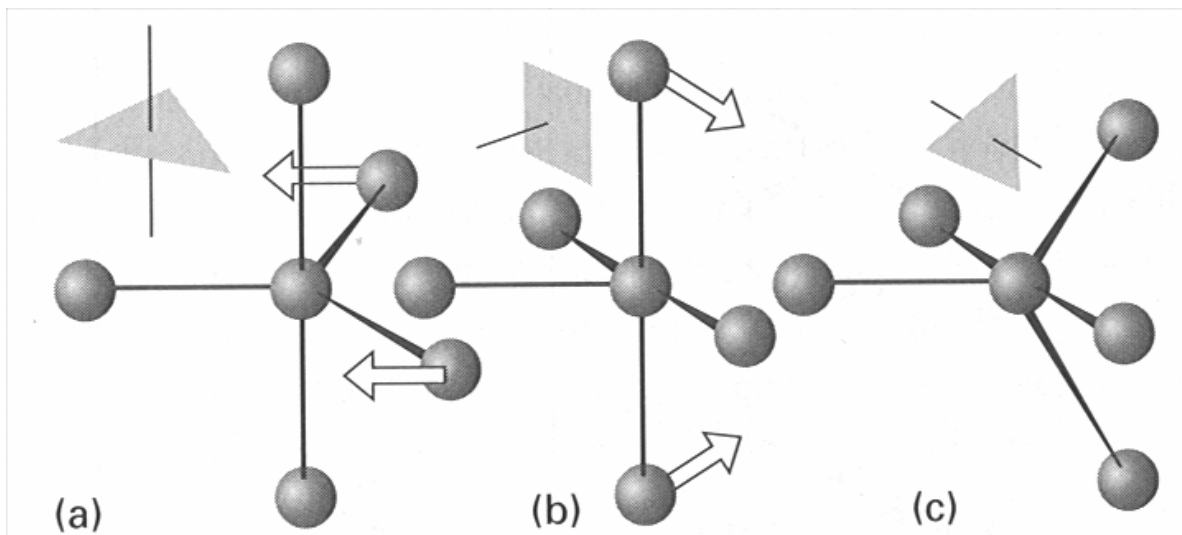
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- Isomers can only be isolated as pure species if there is no easy pathway for the different isomers to interconvert.
  - For there to be no rapid interconversion pathway the ligand-metal bonds must be quite non-labile (ligand should not be able to “drop” off and then reattach somewhere else)
    - » Metal ions like  $\text{Co}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Pt}^{2+}$  do not readily undergo ligand exchange reactions so isomers containing these metal ions can often be isolated
  - The ligands should not be able to move around while still attached to the metal center
    - » This is not usually a problem for coordination complexes, but in some trigonal bipyramidal species axial and equatorial ligands can change places with one another  $\text{Fe}(\text{CO})_5$ ,  $\text{PF}_5$  etc.

# Berry Pseudorotation

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- Berry pseudorotation provides pathway for the interconversion of different isomeric forms of a trigonal bipyramidal species
  - Axial ligand become equatorial ligands. Process goes via a square based pyramidal intermediate



# Naming of complexes

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- The naming of compounds containing coordination complexes follows a set of well defined rules
  - 1) In a salt, the cation is always named before the anion
  - 2) The names of ligands are given in alphabetical order
    - The names of coordinated anions end “o”, e.g. chloro, cyano etc.
    - The names of neutral ligands and just the name of ligand molecule
    - Some ligands have special names when they are in complexes eg.  $\text{H}_2\text{O}$  – aquo,  $\text{NH}_3$  – ammine
  - 3) The number of ligands that present is indicated by a prefix, di, tri etc. However, if these prefixes are already in the name of the ligand bis, tris, tetrakis etc are used instead
    - Dichloro means two chloride ligands
    - Bisethylenediamine means two ethylenediamine ligands
  - 4) After the ligands we specify the metal and its oxidation state as a roman numeral in brackets
    - Platinum(II) indicates that we have platinum in an oxidation state of two

# Additional rules for naming complexes

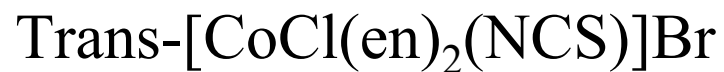
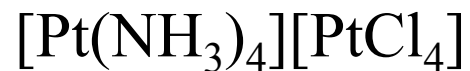
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- If we have ambidentate ligands like  $\text{SCN}^-$  we specify the atom that is binding to the metal
  - For example thiocyanato-S implies bound through sulfur to the metal center
- Sometime a polydentate ligand will bridge between two or metal centers. The notation  $\mu -$  is used to indicate that the ligand is bridging

# Examples

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- Name the following:



# Examples

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- Draw structures for the following:

Tris(ethylenediamine)cobalt(III)nitrate

Potassium dibromobis(oxalato)chromium(III)

# Bonding, optical and magnetic properties

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- Bonding in transition metal compounds
  - 18 electron rule
  - Crystal field theory
  - Molecular orbital approach
- High spin and low spin complexes
  - Magnetic measurements
  - High-spin low-spin equilibria
- Optical spectra
  - d-d transitions for  $d^1$  ions and more complicated cases
  - Spectrochemical series
  - Charge transfer transitions
- Crystal Field Stabilization Energy (CFSE) and trends in ionic radii
- Jahn-Teller distortions

# 18 electron rule

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- Stable low oxidation state complexes are found to have a total of 18 bonding electrons
  - metal electrons plus lone pairs from ligands
- $\text{Ni}(\text{CO})_4$  -  $4s^23d^8$  and 4 lone pairs
- $\text{Fe}(\text{CO})_5$  -  $4s^23d^6$  and 5 lone pairs
- $\text{Cr}(\text{CO})_6$  -  $4s^23d^4$  and 6 lone pairs
- The stability of these 18 electron species can be explained using MO theory
  - Corresponds to filling all the molecular bonding orbitals and none of the antibonding orbitals
- However, the 18 electron rule only works for species with metals in a low oxidation state **NOT FOR MOST COMPLEXES**

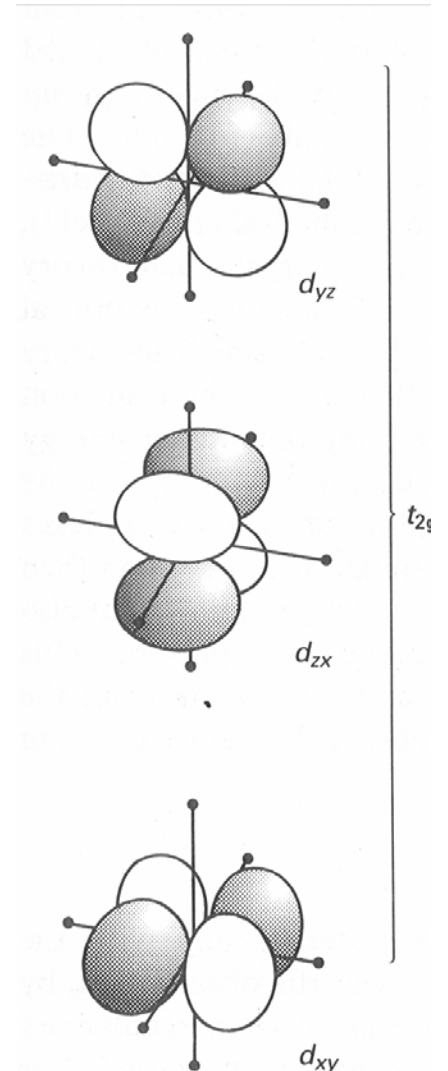
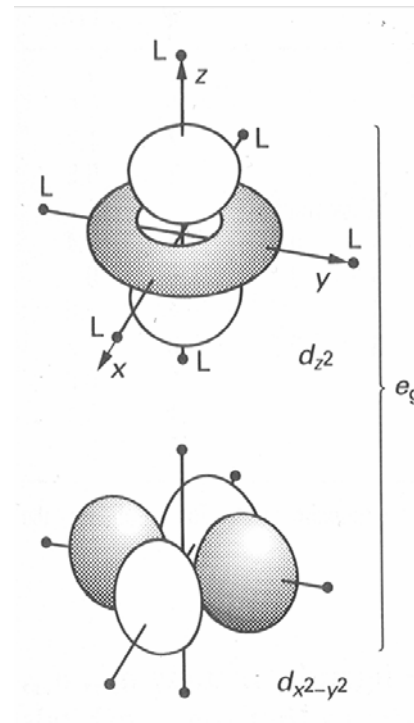
# Bonding in coordination complexes

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- There are two commonly used approaches to describing the bonding in transition metal coordination complexes
  - “Crystal Field Theory” and molecular orbital theory
- Crystal Field Theory is an electrostatic approach where we treat the ligands as point negative charges and ask ourselves what the effect of repulsion between these charges and the d-electrons on the metal ions will be
  - Explains many of the basic physical properties of transition metal complexes but not all of them
- Molecular orbital theory is more complex than crystal field theory, but it allows a more complete explanation of the observed physical properties

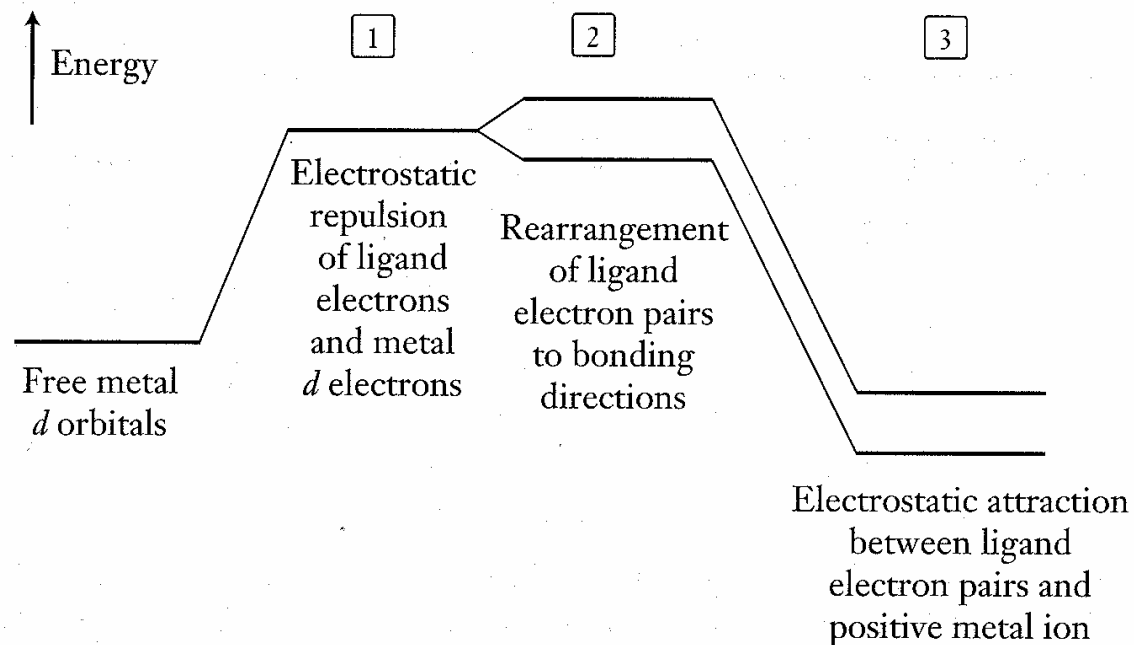
# d-orbitals

- In an isolated gas phase atom or ion, the five d-orbitals associated with a given principle quantum number are degenerate
  - That is they have the same energy as one another



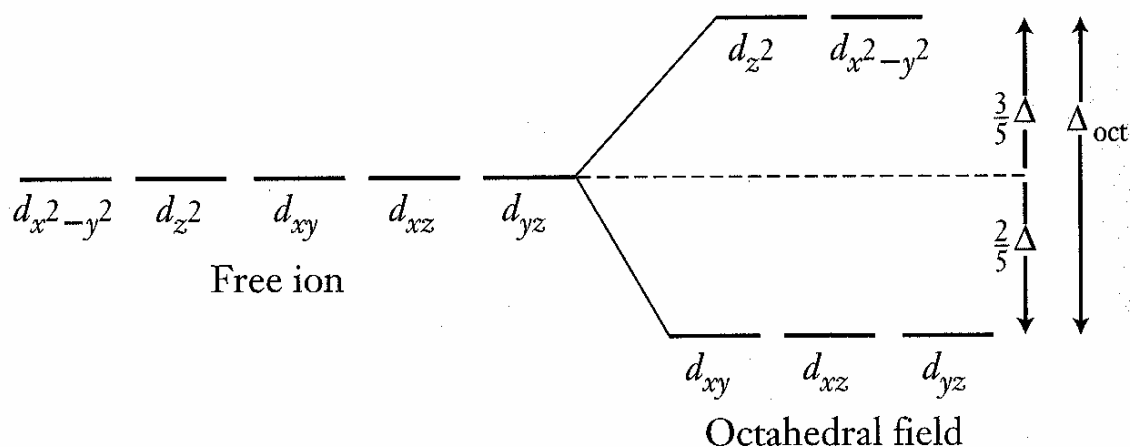
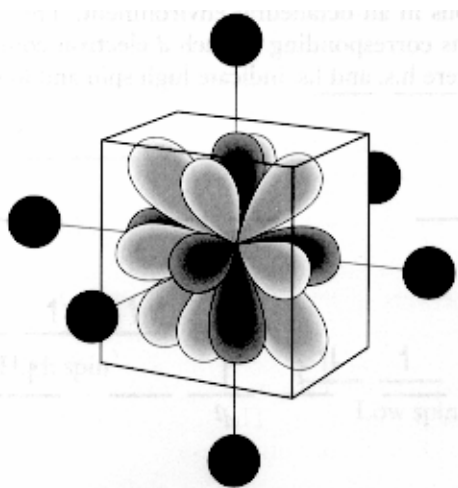
# Crystal Field Theory

- Consider the ligands are point negative charges or as dipoles. How do these charges interact with the electrons in the d-orbitals?



# Octahedral complexes

- Two of the d-orbitals point towards the ligands
  - Repulsion between the ligand electrons and electrons in these two d-orbitals destabilizes them

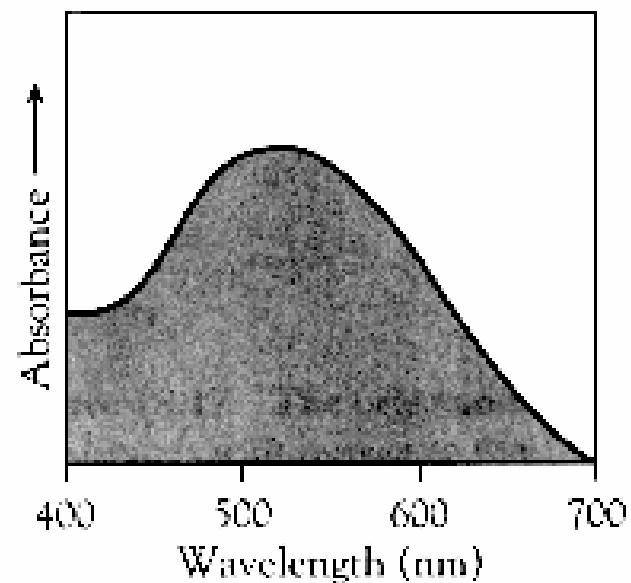
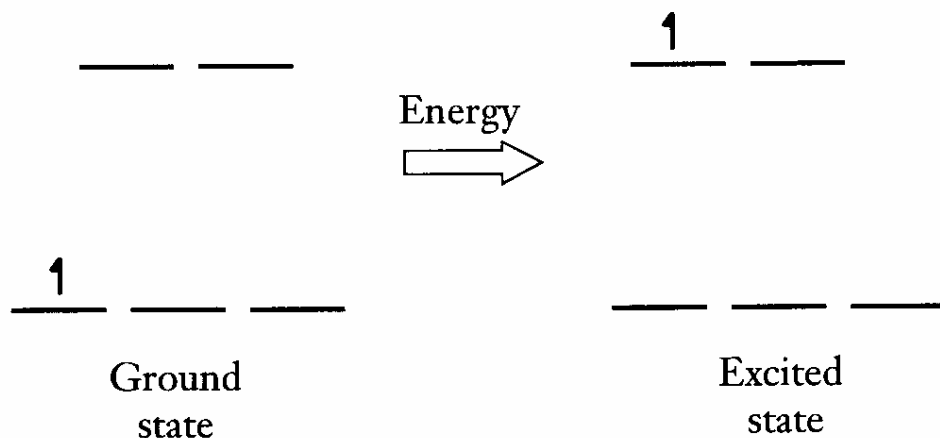


$\Delta_{\text{oct}}$  is referred to as the ligand field splitting for the octahedral complex

# Colors

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- The colors of most transition metal complexes arises as a consequence of the ligand field splitting



# Ligand field splitting

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- The ligand field splitting depends upon the metal, the oxidation state of the metal, and the ligand type
- High oxidation state favors large  $\Delta$ 
  - $\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Fe}^{3+} < \text{Co}^{3+} < \text{Mn}^{4+} < \text{Mo}^{3+} < \text{Rh}^{3+} < \text{Ru}^{3+} < \text{Pd}^{4+} < \text{Ir}^{3+} < \text{Pt}^{4+}$
- Effect of ligand is given by the spectrochemical series
  - $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{CH}_3\text{CN} < \text{NH}_3 < \text{en} < \text{bipy} < \text{phen} < \text{NO}_2^- < \text{PPh}_3 < \text{CN}^- < \text{CO}$

# Ligand field splitting parameters

**Table 6.5** Ligand field splitting parameters  $\Delta_0$  of  $ML_6$  complexes\*

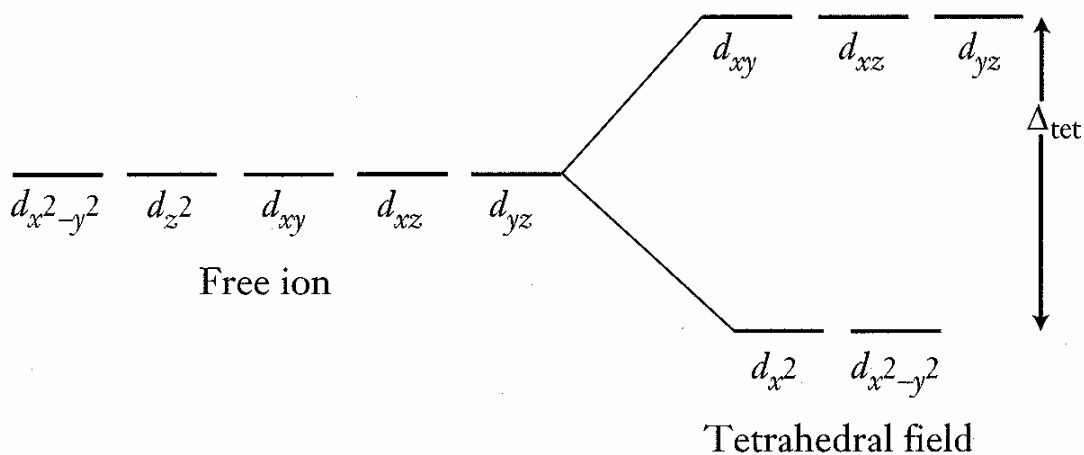
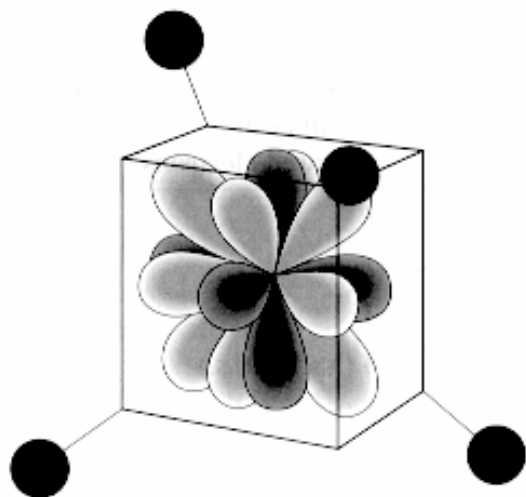
		Ligands				
		$Cl^-$	$H_2O$	$NH_3$	en	$CN^-$
$d^3$	$Cr^{3+}$	13.7	17.4	21.5	21.9	26.6
$d^5$	$Mn^{2+}$	7.5	8.5		10.1	30
	$Fe^{3+}$	11.0	14.3			(35)
$d^6$	$Fe^{2+}$		10.4			(32.8)
	$Co^{3+}$		(20.7)	(22.9)	(23.2)	(34.8)
	$Rh^{3+}$	(20.4)	(27.0)	(34.0)	(34.6)	(45.5)
$d^8$	$Ni^{2+}$	7.5	8.5	10.8	11.5	

\*Values are in multiples of  $1000\text{ cm}^{-1}$ ; entries in parentheses are for low-spin complexes.

Source: H.B. Gray, *Electrons and chemical bonding*, Benjamin, Menlo Park (1965).

# Tetrahedral complexes

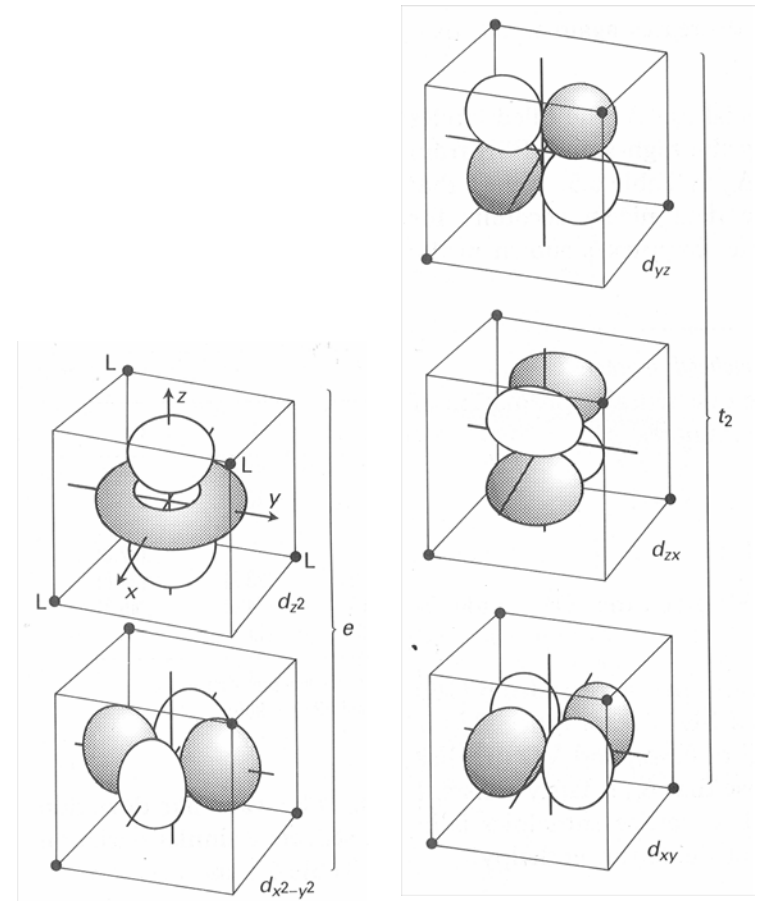
- Three of the d-orbitals point almost towards the ligands. The other two point between the ligands
  - Repulsion between the ligand electrons and electrons in the three d-orbitals that almost point at the ligands destabilizes them



For a given ligand-metal combination,  $\Delta_{tet}$  should be smaller than the  $\Delta_{oct}$  (4/9ths) as there are fewer ligands in the tetrahedral complex and none of them point directly at the d-orbitals

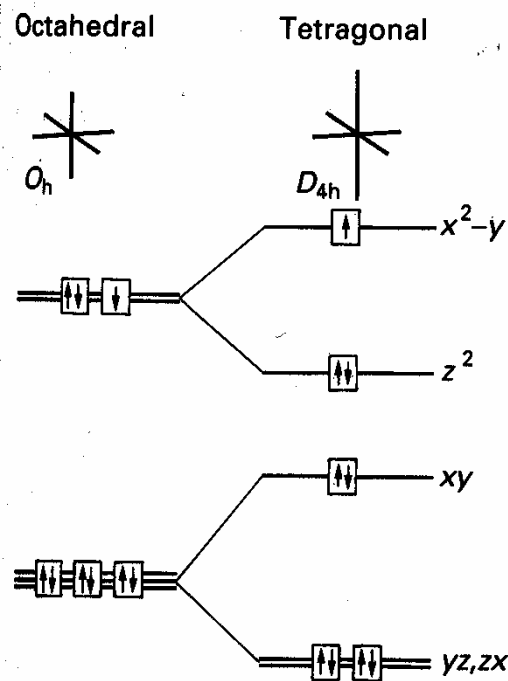
# d-orbitals in tetrahedral complexes

- In a tetrahedral complex the degeneracy of the five d-orbitals is broken to give two degenerate “e” orbitals and three degenerate “t<sub>2</sub>” orbitals
  - While none of the orbitals point directly at the ligands, some of them (t<sub>2</sub>) are oriented so they point more closely towards the ligand positions and hence the electrons in the t<sub>2</sub> orbitals are higher in energy than those in the e orbitals

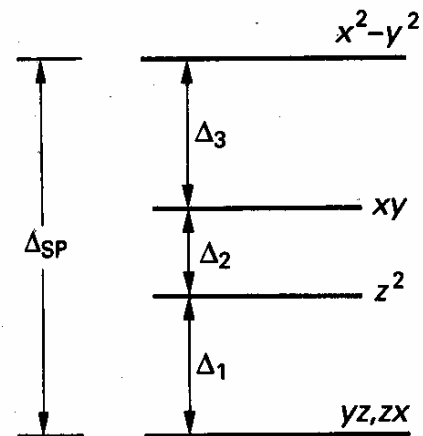


# Tetragonal and square planar complexes

- If we distort an octahedral complex, the degeneracy of the  $e_g$  and  $t_{2g}$  orbitals is broken. As the axial ligands are pulled away from the metal a tetragonal species is formed.
  - The repulsions between the ligands and the d-electrons are different after the distortion. This leads to a further loss of orbital degeneracy
  - In the extreme case where the axial ligands are removed we are left with a square planar complex



**6.16** The effect of tetragonal distortions (compression along  $x$  and  $y$  and extension along  $z$ ) on the energies of  $d$  orbitals. The electron occupation is for a  $d^9$  complex.



**6.17** The orbital splitting parameters for a square-planar complex.

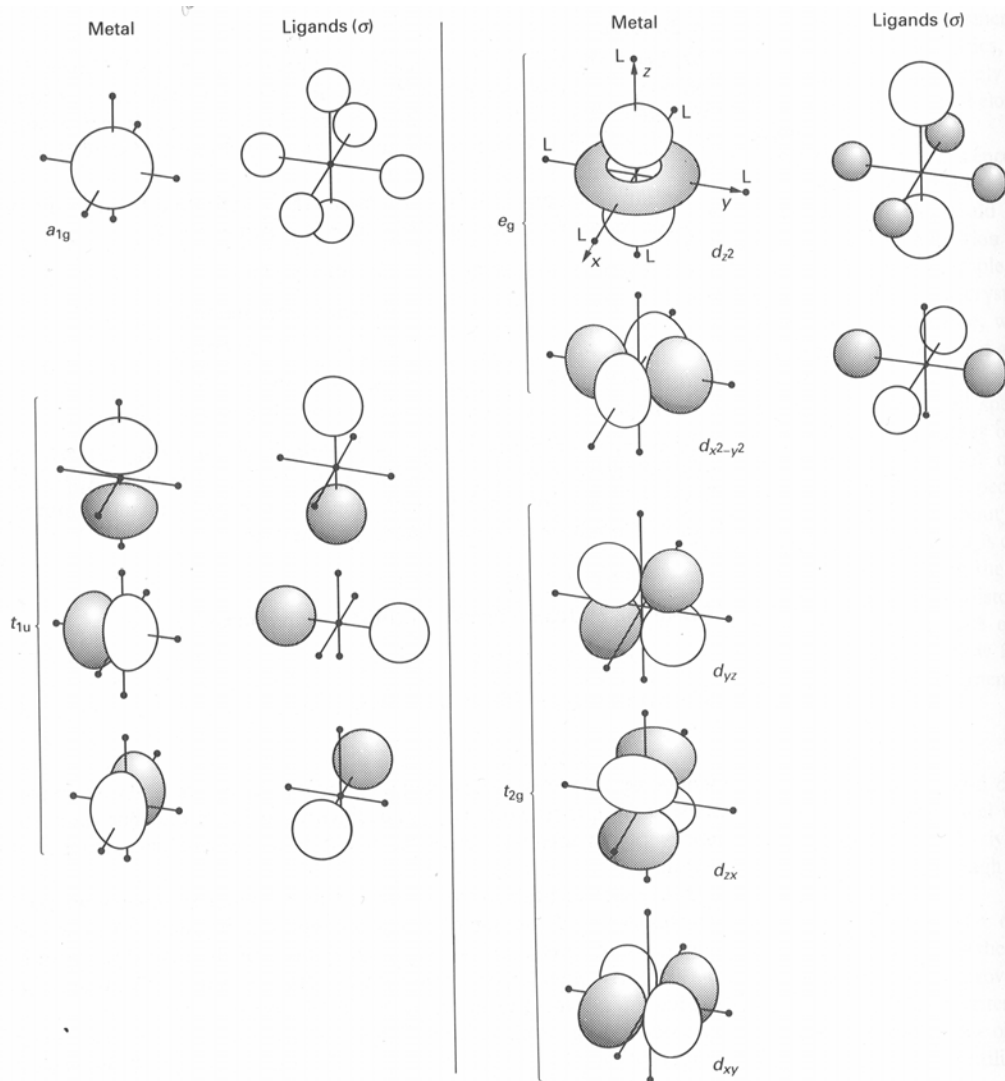
# MO theory

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- Crystal field theory explains many phenomena but not, for instance, the spectrochemical series
  - Why is CO such a strong field ligand (gives big value of  $\Delta$ )?
- MO theory offers a better qualitative picture

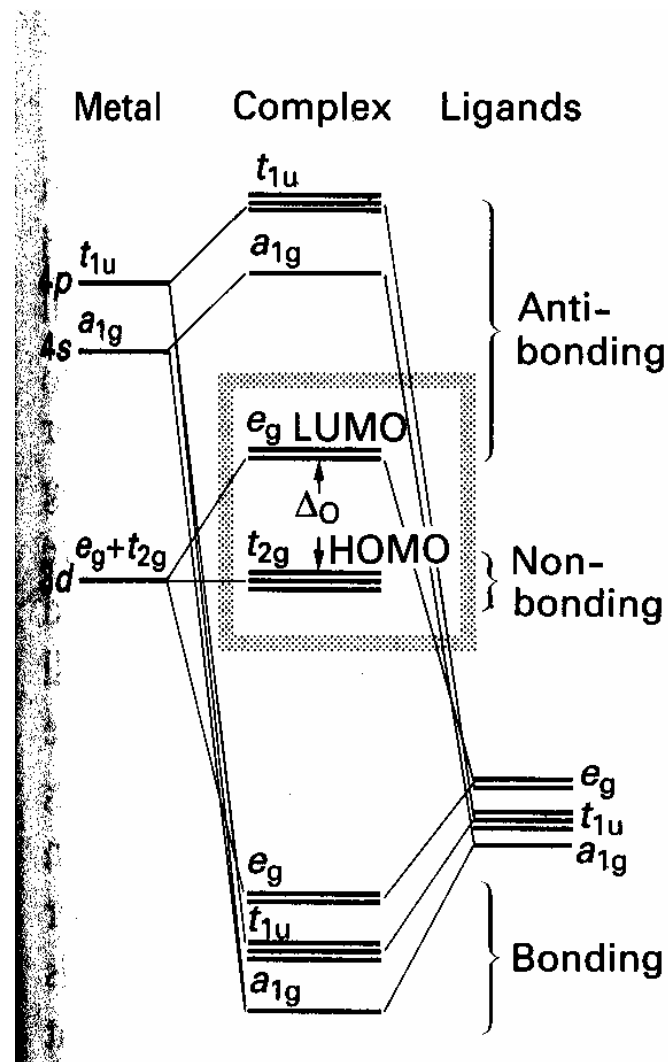
# Octahedral sigma bonded complex

- If the ligands in a complex are only capable of forming bonds with the metal using one lone pair from each ligand, we have to consider the following ligand and metal orbitals when constructing molecular orbitals



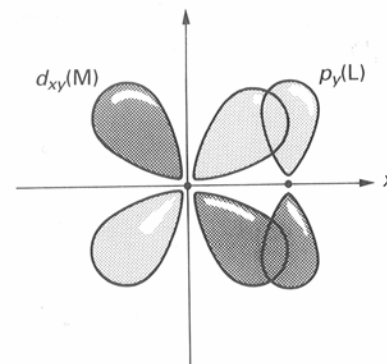
# Orbital energy level diagram for a sigma bonded complex

- With the MO approach to bonding in the complex, the ligand field splitting  $D$  is the energy gap between a set of nonbonding orbitals ( $t_{2g}$ ) and the lowest lying antibonding orbitals ( $e_g$ )
  - As the interaction between the ligand orbitals and the metal orbitals gets stronger, the energy difference between the  $e_g$  bonding and  $e_g$  antibonding orbitals in the complex gets larger so  $\Delta$  also gets larger



# Ligands that can form $\pi$ bonds

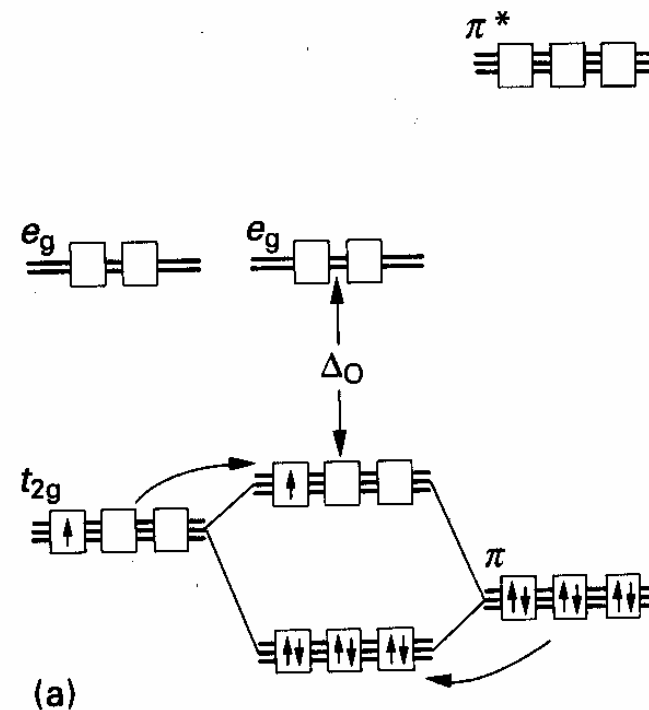
- Many ligands have more than one orbital that can interact with the transition metal ion
  - For example, halide anions have lone pairs in p-orbitals lying perpendicular to the metal ligand axis. These p-orbitals can be involved in bonding as they overlap with some of the metal d-orbitals
  - Molecules like CO and  $\text{CN}^-$  have empty orbitals ( $\pi^*$ ), that do not lie along the metal-ligand axis, that can also be involved in bonding to the metal



**6.21** The  $\pi$  overlap that may occur between a ligand  $p$  orbital perpendicular to the M—L axis and a metal  $d_{xy}$  orbital.

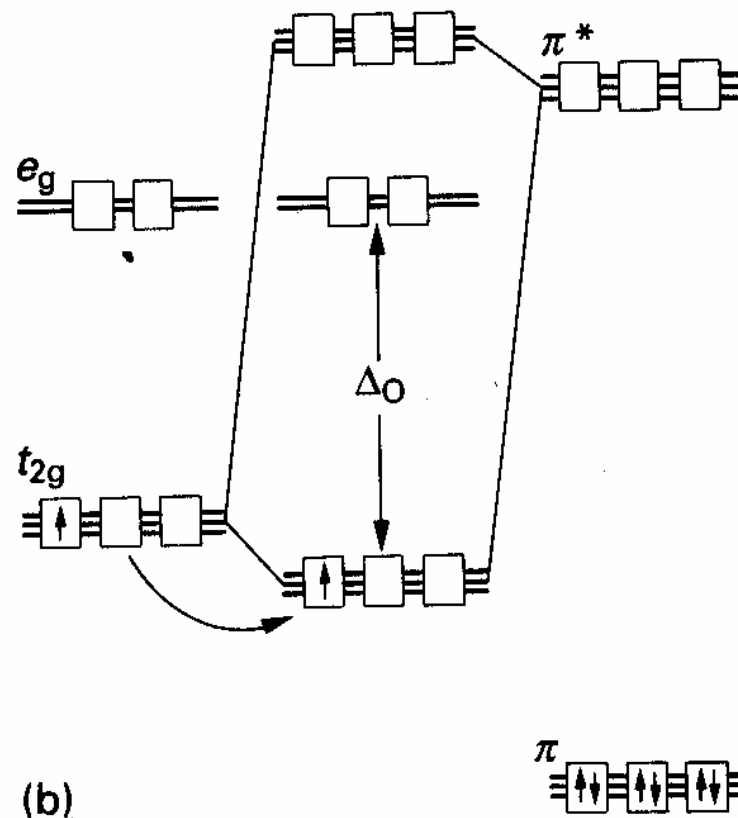
# $\pi$ -donor ligands

- $\pi$ -donor ligands (e.g. halide) give smaller  $\Delta$ 's because the filled  $\pi$  symmetry ligand orbitals interact with the  $t_{2g}$  symmetry orbitals on the metal
  - This is why  $F^-$ ,  $Br^-$ ,  $OH^-$  are weak field ligands (give small  $\Delta$ 's)

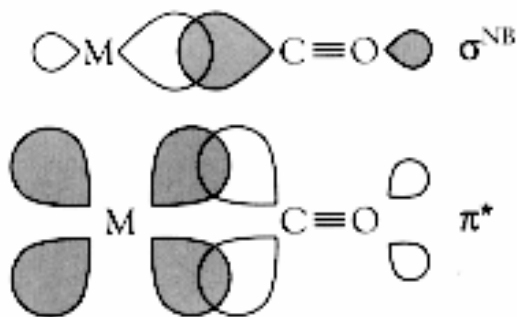


# $\pi$ -acceptor ligands

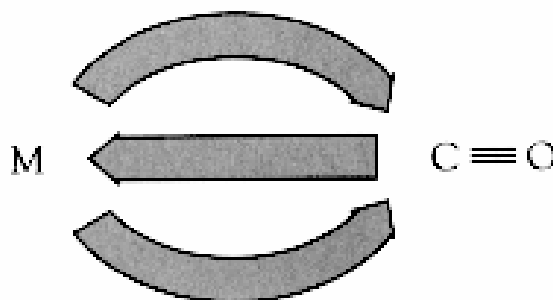
- Ligands with empty  $\pi$ - symmetry orbitals e.g. CO give large  $D$ 's because the empty orbitals on the ligands interact with the  $t_{2g}$  orbitals on the metal and increase  $\Delta$ .



# Carbonyl complexes



**Figure 18.31** The interaction of the HOMO,  $\sigma^{\text{NB}}$ , and the LUMO,  $\pi^*$ , of carbon monoxide with the appropriate  $d$  orbitals of a transition metal ion. The filled orbitals are shaded.



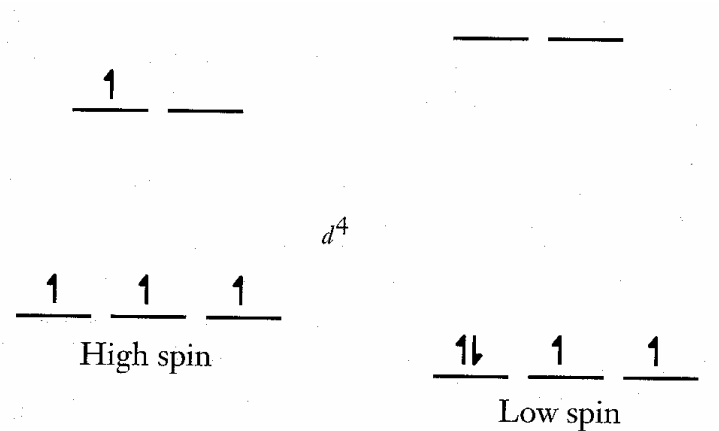
**Figure 18.32** A depiction of the synergistic effect in the bonding of carbon monoxide to a low oxidation state metal ion.

Stable CO complexes are only formed by metal ions that are electron rich. The metal has to have electrons in its  $t_{2g}$  orbitals that can be “donated” to the CO to form a strong bond to the CO

- Carbonyl ligands are strong  $\pi$ -acceptors
  - backbonding (the interaction between the filled  $t_{2g}$  orbitals on the metal and the  $\pi^*$  orbitals on the CO) weakens the C=O bond as seen by vibrational spectroscopy
    - » The CO stretch frequency in a metal complex such as  $\text{Ni}(\text{CO})_4$  is lower than that for molecular CO

# High spin and low spin complexes

- Octahedral complexes with  $d^4$ ,  $d^5$ ,  $d^6$ , and  $d^7$  electron configurations can in principle be in high or low spin states



- If  $\Delta$  is bigger than the energy required for spin pairing the complex will be low spin

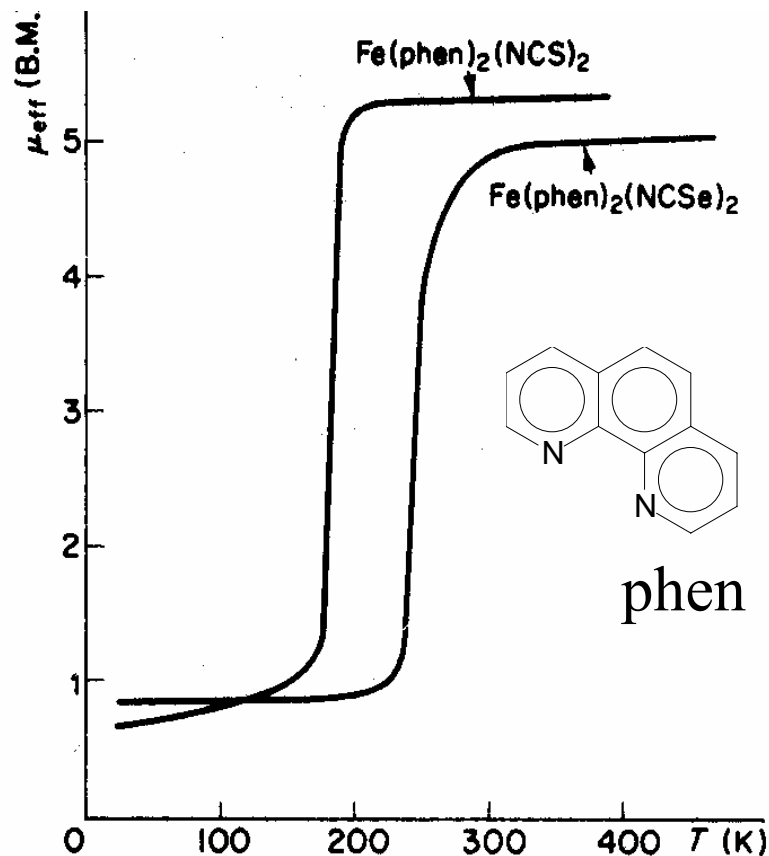
# Factors effecting spin state

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- Both  $\Delta$  and the spin pairing energy depend upon the metal and the ligands.
  - High field ligands,  $\text{CN}^-$  etc, high metal oxidation state, and metals from the 4d and 5d series all favor large  $\Delta$  and hence the formation of low spin complexes
- Tetrahedral complexes can also in principle occur in high and low spin forms.
  - As  $\Delta_{\text{tet}}$  is always less than  $\Delta_{\text{oct}}$ , other things being equal, nearly all tetrahedral complexes are high spin

# High spin-low spin equilibria

- Some coordination complexes show a phase transition from high to low spin as a function of temperature
  - This has been used as a means of information storage for prototype smart cards!
  - Transition presumably occurs because  $\Delta$  is slightly temperature dependent in the solid state



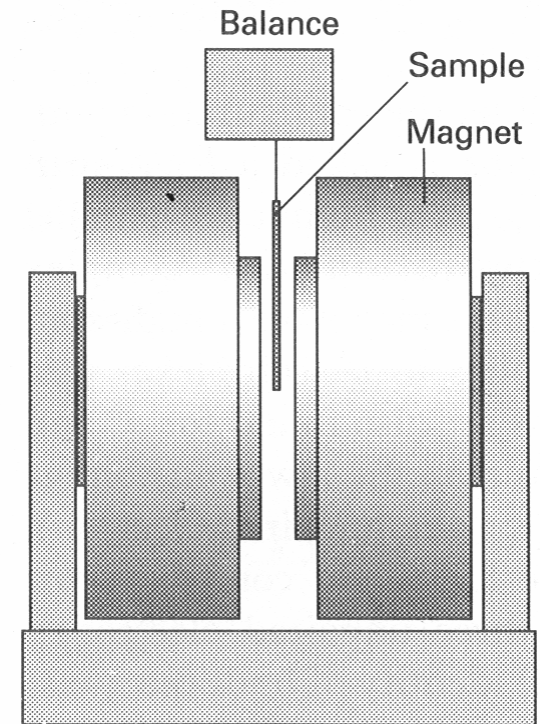
# Experimental methods for determining the spin state

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- The spin state of a complex influences both the absorption spectrum and the magnetic properties of the species
- Absorption spectra are usually harder to interpret than magnetic data
- Both the orbital and spin angular momenta of the electrons influence the magnetic properties of a sample
  - But in coordination complexes the orbital contribution can often be ignored

# Measuring magnetic properties

- We can measure the magnetic properties of a sample by hanging a vial of material from a balance so that it sits partly in a magnetic field
  - The sample will be pulled down into the magnet if it contains unpaired electrons (said to be paramagnetic)
  - It will tend to be pushed out of the field if it contains no unpaired electrons (diamagnetic)
- The amount of material in the vial along with the extent to which the sample is pulled into the magnet allows us to calculate the magnetic susceptibility of the sample
  - Sample with a high magnetic susceptibility is strongly pulled into the magnetic field



**B6.1** A schematic diagram of a Gouy balance.

# Interpreting magnetic measurements

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- The magnetic susceptibility ( $\chi$ ) is measured as a function of temperature
- A magnetic moment ( $\mu$ ) for each metal ion can be obtained from the magnetic susceptibility
  - We can think of the unpaired electrons on each atom as behaving like a little bar magnet. The magnetic moment of an atom or ion is a measure of how strong this bar magnet is.
- Theoretically, for spin only systems  $\mu = 2 [S(S + 1)]^{1/2} \mu_B$ 
  - $\mu_B$  (Bohr magneton) are the units in which the magnetic moment is given
  - $S$  is the total spin angular momentum. It tells you how many unpaired electrons there are
    - $S = 0.5n$ , where  $n$  is the number of parallel spin unpaired electrons in the ion

# Spin only magnetic moments

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Ion	n	S	$\mu/\mu_B$	$\mu/\mu_B$
			Calculated	Experimental
Ti <sup>3+</sup>	1	1/2	1.73	1.7-1.8
V <sup>3+</sup>	2	1	2.83	2.7-2.9
Cr <sup>3+</sup>	3	1 1/2	3.87	3.8
Mn <sup>3+</sup>	4	2	4.90	4.8-4.9
Fe <sup>3+</sup>	5	2 1/2	5.92	5.9

There is reasonable agreement between calculated spin only magnetic moments and those measured for many 3d metal complexes

# Magnetic properties

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- Magnetic susceptibility measurements can be used to tell if a complex is high or low spin
- They can also be used to distinguish between square planar and tetrahedral geometries. Square planar complexes are nearly always low spin  $d^8$  (diamagnetic). If a four coordinate compound is paramagnetic it is probably tetrahedral
  - e.g.  $\text{Ni}(\text{CN})_4^{2-}$  (square planar) is diamagnetic, but  $\text{NiCl}_4^{2-}$  (tetrahedral) is paramagnetic

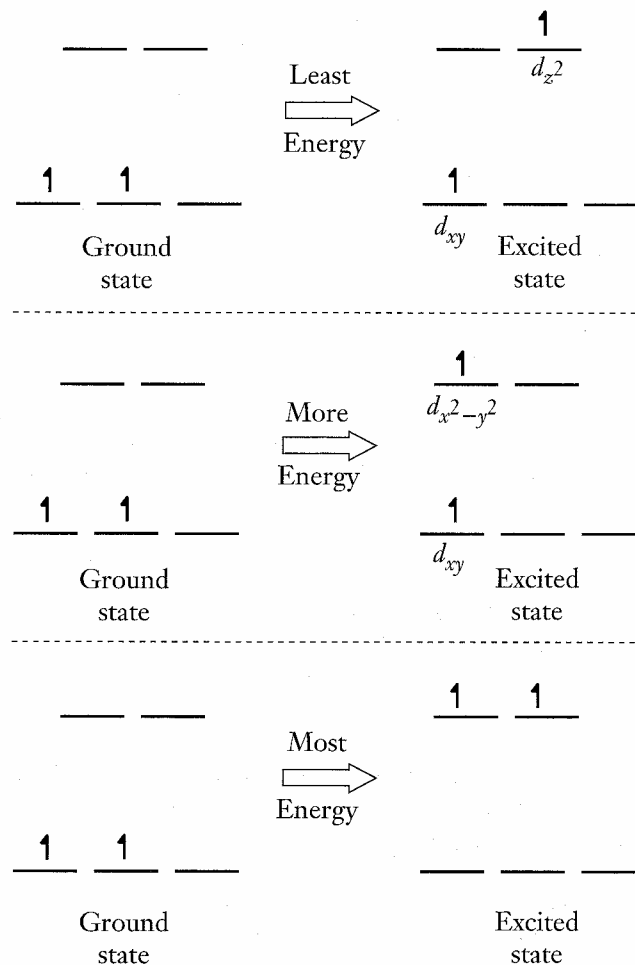
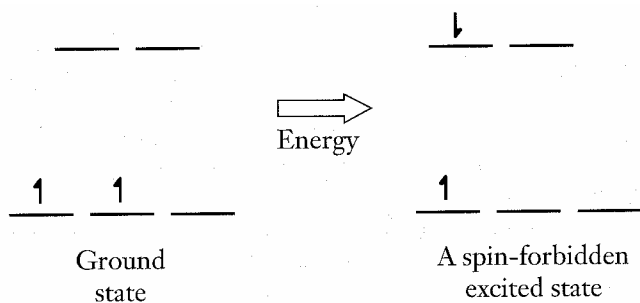
# Electronic spectra

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- TM complexes with more than one d-electron often show absorption bands at multiple wavelengths
  - not just one transition corresponding to  $\Delta$
- The appearance of multiple bands is due to electron-electron repulsion
  - may have more than one state for a given electron configuration

# d<sup>2</sup> complexes

- For complexes with more than one d-electron there are often several allowed transitions



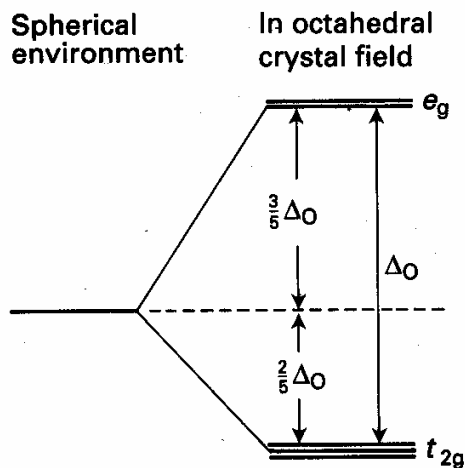
# Charge transfer transitions

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- Some transition metal complexes with no d-electrons are colored
  - This is because there can be electronic transitions in the visible region that do not involve d-electrons
    - »  $\text{MnO}_4^-$  : electrons in filled oxygen based orbitals are excited into empty d-orbitals. This type of Ligand to Metal Charge Transfer band gives rise to the intense purple color of permanganate
    - »  $\text{CrO}_4^{2-}$  : intense yellow color from LMCT band
  - Metal to ligand charge transfer bands also occur in the visible regions for some complexes
  - Charge transfer transitions are often much more probable than d-d transitions. Hence the intense color of  $\text{MnO}_4^-$

# Ligand field stabilization energies

- We can compute a quantity called the Ligand Field Stabilization Energy (LFSE) by comparing the energy of the d-electrons in a species with all five d-orbitals degenerate, to their energy in a complex where the degeneracy of the orbitals has been broken
  - This LFSE can be used to explain some of the properties of transition metal ions



Example calculation: LFSE for high spin  $d^5 = [3 \times (2/5\Delta) - 2 \times (3/5\Delta)] = 0$

Table 6.3. Ligand field stabilization energies\*

$d^n$	Example	Octahedral		Tetrahedral	
		$N$	LFSE	$N$	LFSE
$d^0$	$\text{Ca}^{2+}, \text{Sc}^{3+}$	0	0	0	0
$d^1$	$\text{Ti}^{3+}$	1	0.4	1	0.6
$d^2$	$\text{V}^{3+}$	2	0.8	2	1.2
$d^3$	$\text{Cr}^{3+}, \text{V}^{2+}$	3	1.2	3	0.8
$d^4$	$\text{Cr}^{2+}, \text{Mn}^{3+}$	Strong-field		Weak-field	
		2	1.6	4	0.6
$d^5$	$\text{Mn}^{2+}, \text{Fe}^{3+}$	1	2.0	5	0
$d^6$	$\text{Fe}^{2+}, \text{Co}^{3+}$	0	2.4	4	0.4
$d^7$	$\text{Co}^{2+}$	1	1.8	3	0.8
$d^8$	$\text{Ni}^{2+}$	2	1.2	2	0.8
$d^9$	$\text{Cu}^{2+}$	1	0.6	1	0.4
$d^{10}$	$\text{Cu}^+, \text{Zn}^{2+}$	0	0	0	0

\*  $N$  is the number of unpaired electrons; LFSE is in units of  $\Delta_O$  for octahedra or  $\Delta_T$  for tetrahedra; the calculated relation is  $\Delta_T \approx 0.45\Delta_O$ .

Strong field implies low spin. Weak field implies high spin

# Hydration energies

- The double humped trend that is seen in the hydration enthalpies of TM ions can be explained using the Ligand or Crystal Field Stabilization Energy

CFSE for high spin  $d^4$  is  $\frac{1}{+3/5 \Delta}$

$$= (+3/5 - 2/3 - 2/3 - 2/3)\Delta$$

$$\frac{1}{-2/5 \Delta} \quad \frac{1}{-2/5 \Delta} \quad \frac{1}{-2/5 \Delta}$$

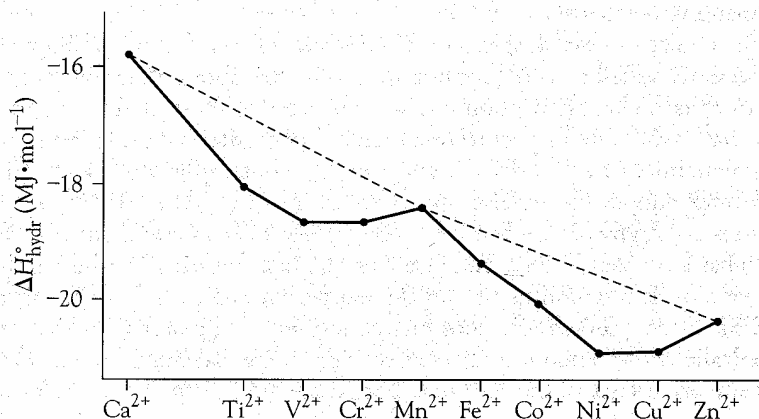
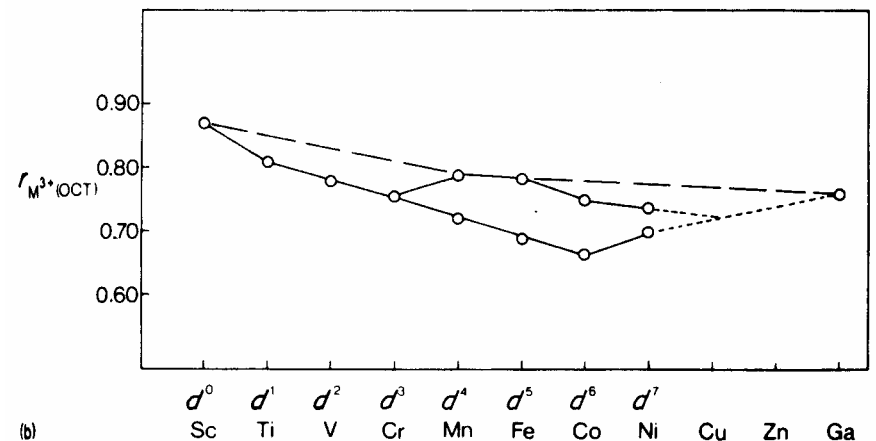
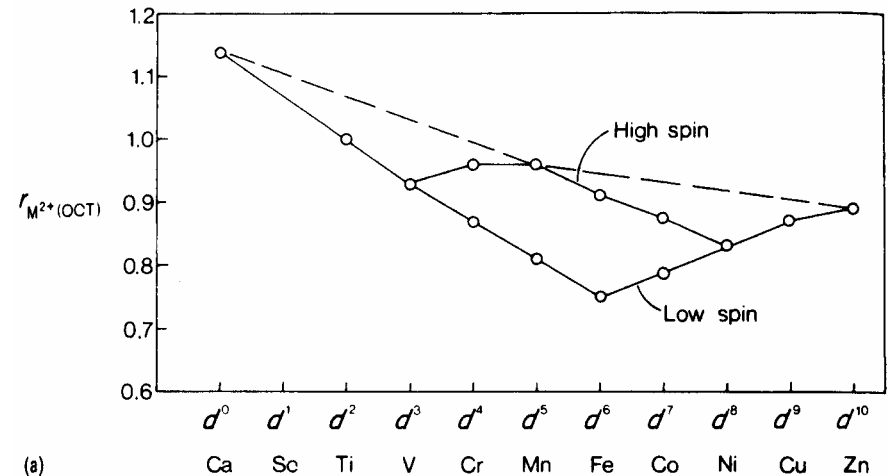


Table 18.3 Crystal field stabilization energies (CFSE) for the dipositive, high spin ions of various Period 4 metals

Ion	Configuration	CFSE
Ca <sup>2+</sup>	$d^0$	$-0.0 \Delta_{\text{oct}}$
—	$d^1$	$-0.4 \Delta_{\text{oct}}$
Ti <sup>2+</sup>	$d^2$	$-0.8 \Delta_{\text{oct}}$
V <sup>2+</sup>	$d^3$	$-1.2 \Delta_{\text{oct}}$
Cr <sup>2+</sup>	$d^4$	$-0.6 \Delta_{\text{oct}}$
Mn <sup>2+</sup>	$d^5$	$-0.0 \Delta_{\text{oct}}$
Fe <sup>2+</sup>	$d^6$	$-0.4 \Delta_{\text{oct}}$
Co <sup>2+</sup>	$d^7$	$-0.8 \Delta_{\text{oct}}$
Ni <sup>2+</sup>	$d^8$	$-1.2 \Delta_{\text{oct}}$
Cu <sup>2+</sup>	$d^9$	$-0.6 \Delta_{\text{oct}}$
Zn <sup>2+</sup>	$d^{10}$	$-0.0 \Delta_{\text{oct}}$

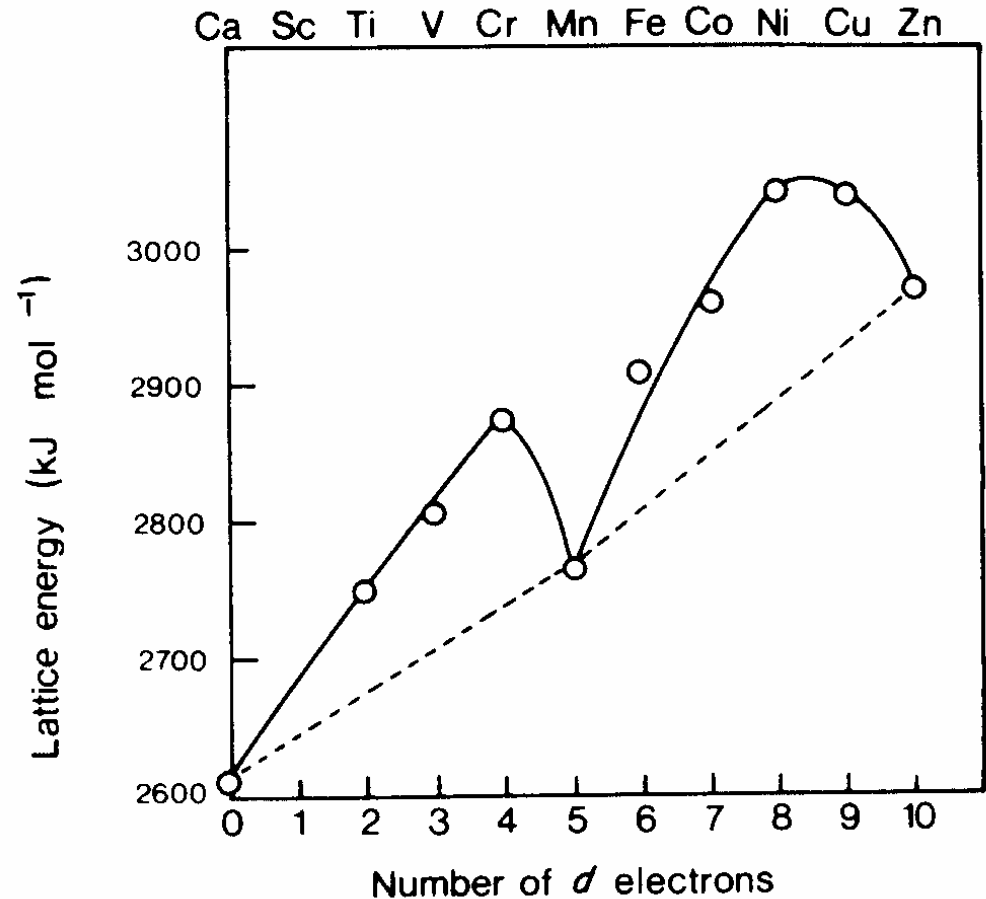
# Ionic radii for 3d metals

- For high spin ions there is a “double humped” trend in ionic radii
  - Due to crystal field stabilization effects



# Lattice energies of 3d oxides MO

- Double humped trend due to CSFE and high spin ions



# LFSE and coordination preferences

- The LFSE for octahedral and tetrahedral sites is different and the magnitude of the difference varies with d-electron configuration
  - Some metal ions show a strong preference for octahedral coordination due to LFSE effects

Table 2.14 *Crystal field stabilization energies (kJ mol<sup>-1</sup>) estimated for transition metal oxides.* (Data from Dunitz and Orgel, *Adv. Inorg Radiochem.*, **2**, 1–60, 1960)

Ion		Octahedral stabilization	Tetrahedral stabilization	Excess octahedral stabilization
Ti <sup>3+</sup>	<i>d</i> <sup>1</sup>	87.4	58.5	28.9
V <sup>3+</sup>	<i>d</i> <sup>2</sup>	160.1	106.6	53.5
Cr <sup>3+</sup>	<i>d</i> <sup>3</sup>	224.5	66.9	157.6
Mn <sup>3+</sup>	<i>d</i> <sup>4</sup>	135.4	40.1	95.3
Fe <sup>3+</sup>	<i>d</i> <sup>5</sup>	0	0	0
Mn <sup>2+</sup>	<i>d</i> <sup>5</sup>	0	0	0
Fe <sup>2+</sup>	<i>d</i> <sup>6</sup>	49.7	33.0	16.7
Co <sup>2+</sup>	<i>d</i> <sup>7</sup>	92.8	61.9	30.9
Ni <sup>2+</sup>	<i>d</i> <sup>8</sup>	122.1	35.9	86.2
Cu <sup>2+</sup>	<i>d</i> <sup>9</sup>	90.3	26.8	63.5

# Degree of inversion in Spinel

- $AB_2O_4$  materials with the Spinel structure have one tetrahedral and two octahedral sites per formula unit
- The fraction of the A cations that are found in the octahedral sites is referred to as the degree of inversion  $\gamma$ 
  - If all the A cations are octahedral the material is an inverse Spinel, and if all the A cations are tetrahedral the Spinel is said to be normal
  - Degree of inversion can be rationalized using CFSE arguments

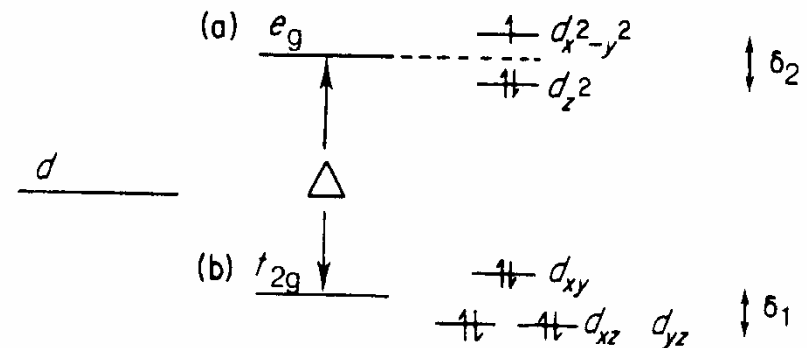
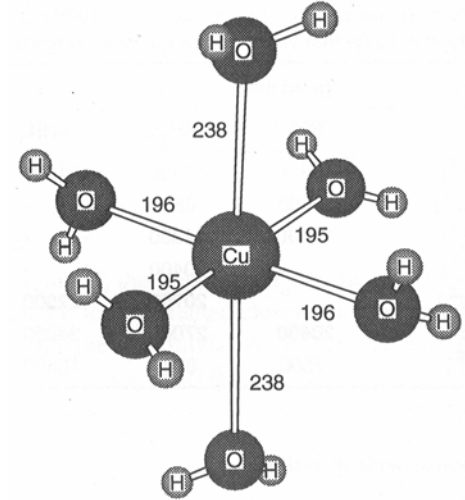
Table 2.15 *The  $\gamma$  parameters of some spinels.* (Greenwood, *Ionic Crystals, Lattice Defects and Nonstoichiometry*, Butterworths, 1968; Dunitz and Orgel, *Adv. Inorg. Radiochem.*, **2**, 1, 1960)

$M^{3+}$	$M^{2+}$	$Mg^{2+}$	$Mn^{2+}$	$Fe^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	$Zn^{2+}$
$Al^{3+}$		0	0.3	0	0	0.75	0.4	0
$Cr^{3+}$		0	0	0	0	0	0	0
$Fe^{3+}$		0.9	0.2	1	1	1	1	0
$Mn^{3+}$		0	0	0.67	0	1	0	0
$Co^{3+}$		—	—	—	0	—	—	0

# Jahn-Teller effect

Jahn-Teller theorem states that any species with an electronically degenerate ground state will distort to remove the degeneracy

- Compounds containing approximately octahedral  $\text{Cu}^{2+}$  ( $d^9 - t_{2g}^6 e_g^3$ ),  $\text{Mn}^{3+}$  ( $d^4 - t_{2g}^3 e_g^1$ ) and L.S.  $\text{Ni}^{3+}$  ( $d^7 - t_{2g}^6 e_g^1$ ) often display distorted coordination environments as the distortion breaks the degeneracy of the octahedral ground state



# Jahn-Teller effect 2

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- Typical distortion of an octahedron leads to 4 + 2 coordination with either 2 short or 2 long bonds
- JT effect important in copper oxide superconductors and manganese CMR materials
- JT effect can also occur for tetrahedrally coordinated species
- JT effect not very strong for “octahedral” compounds with degenerate ground state involving incomplete occupancy of  $t_{2g}$  orbitals

# Reactions of complexes

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- ◆ Reactions of transition metal complexes typically involve the replacement of one ligand by another (substitution) or oxidation or reduction
  - These reactions are all associated with a thermodynamic driving force ( $\Delta G$  determines the equilibrium product distribution) and a rate.
- ◆ Thermodynamics of substitution reactions
  - Formations constants
  - Chelate effect
  - Irving Williams order
- ◆ Kinetics of substitution reactions
  - What factors influence the rate of a reaction?
  - What mechanisms are important?

# Coordination equilibria

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- ◆ Many complex formation reactions are solvent displacements
- ◆  $M(OH_2)_6 + L \rightleftharpoons M(OH_2)_5L + H_2O$
- ◆ These equilibria can be characterized by formation constants
  - $M + L \rightleftharpoons ML \quad K_1 = [ML]/[M][L]$
  - $ML + L \rightleftharpoons ML_2 \quad K_2 = [ML_2]/[ML][L] \dots$
  - Overall formation constant  $\beta_n = K_1 K_2 K_3 \dots K_n$ 
    - »  $\beta_n$  is the equilibrium constant for  $M + nL \rightleftharpoons ML_n$
- ◆ The values of the equilibrium constants depend upon the nature of the metal ion and the ligands

# Trends in formation constants

- ◆ For  $ML_{n-1} + L \rightleftharpoons ML_n$ , typically  $K_1 > K_2 > K_3 > \dots > K_n$ 
  - This can be explained on statistical grounds. The greater the number of ligands that have already been substituted, the smaller the number of open sites for additional substitution

Example data for Ni(II) amines:

$K_n$  is equilibrium constant for  $[Ni(NH_3)_{n-1}(H_2O)_{7-n}]^{2+} + NH_3 \rightleftharpoons [Ni(NH_3)_n(H_2O)_{6-n}]^{2+} + H_2O$

$pK_n$  and hence  $K_n$  decrease as  $n$  goes up as expected, and the ratios  $K_n/K_{n-1}$  are in approximate agreement with those expected on statistical grounds

n	$pK_n$	$K_n/K_{n-1}$	
		Experimental	Statistical
1	-2.72		
2	-2.17	0.28	0.42
3	-1.66	0.31	0.53
4	-1.12	0.29	0.56
5	-0.67	0.35	0.53
6	-0.03	0.2	0.42

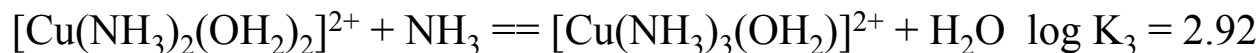
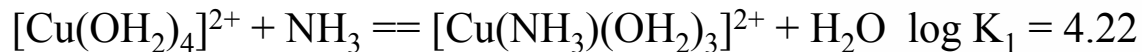
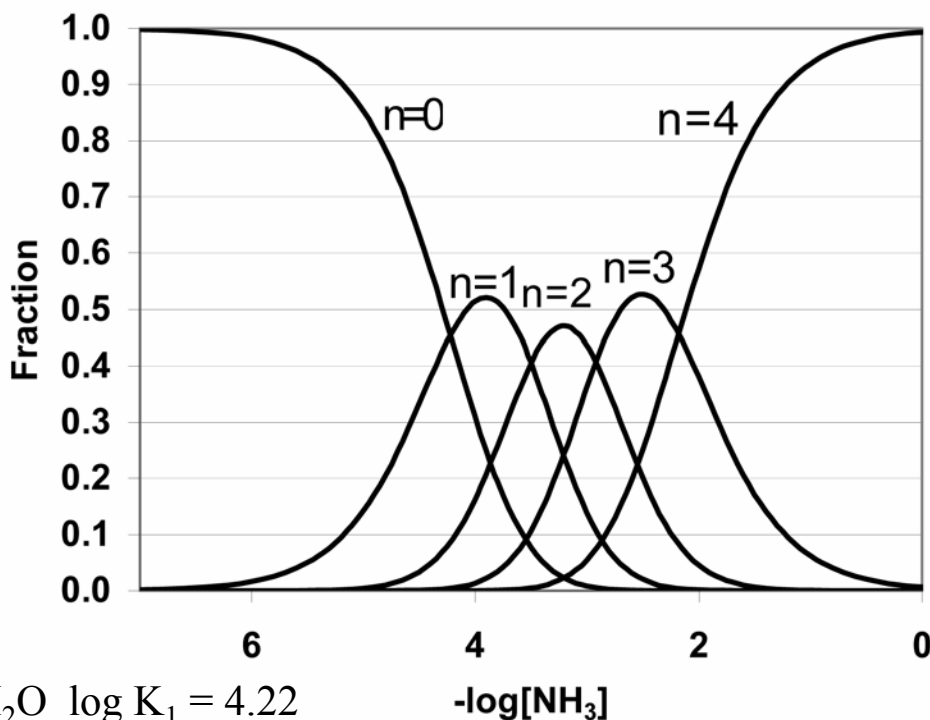
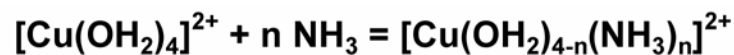
# Statistical treatment of successive $K_n$

---

- ◆ Consider the following substitution reaction in an octahedral complex
  - $\text{MX}_{7-n}\text{L}_{n-1} + \text{L} \rightleftharpoons \text{MX}_{6-n}\text{L}_n + \text{X}$
  - The probability of the forward reaction should be proportional to the number of X ligands available for substitution in the starting material (7-n). The probability of the reverse reaction should be proportional to the number of L ligands available for substitution in the product (n).
  - Assuming that the enthalpy changes associated with each substitution are the same
    - »  $K_n = (7-n)/n$
    - » So  $K_n/K_{n-1} = [(7-n)/n] [(n-1)/(8-n)]$ 
      - ◆ This formula gives the “statistical values” in the previous table

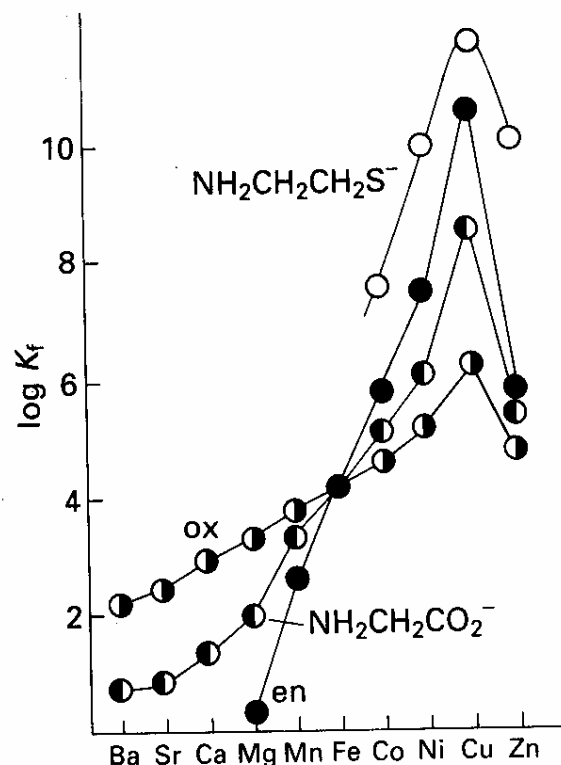
# Effect of successive reactions

- ◆ As with polyprotic acids, the successive replacement of water by other ligands can lead to a complex mixture of species in solution



# The Irving-Williams order

- ◆ The binding of a ligand to a metal depends on the size of the ion, its charge, and the hardness/softness of the donor and acceptor atoms
- ◆ For alkaline earths and first row 2+ ions the following trend is observed:
  - $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$
  - This trend is referred to as the Irving Williams order
  - Note smaller ions in general bind a given ligand more effectively. You would expect this as the smaller ions are expected to be stronger Lewis acids other things being equal



**6.24** The variation of formation constants for the  $\text{M}^{2+}$  ions of the Irving-Williams series.

# Chelate effect

---

- ◆ The equilibrium constants for chelate complexes are usually larger than for similar non-chelate complexes
  - $\text{Ni}(\text{OH}_2)_6^{2+} + 6\text{NH}_3 = \text{Ni}(\text{NH}_3)_6^{2+} + 6\text{H}_2\text{O} \quad \mathbf{K}_1$
  - $\text{Ni}(\text{OH}_2)_6^{2+} + 3\text{en} = \text{Ni}(\text{en})_3^{2+} + 6\text{H}_2\text{O} \quad \mathbf{K}_2$
  - $\mathbf{K}_2 > \mathbf{K}_1$
- ◆ The effect is mainly due to entropic differences between the two reactions

# Thermodynamics and the chelate effect

- ◆ Experiments comparing the thermodynamics of complex formation suggest that the reason chelate complexes are more stable than similar complexes formed with monodentate ligands is entropic

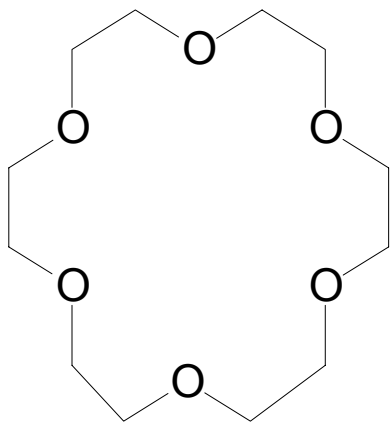
NH <sub>3</sub> complexes				en complexes				Chelate effect		
	$\Delta G$	$\Delta H$	$\Delta S$		$\Delta G$	$\Delta H$	$\Delta S$	$\Delta\Delta G$	$\Delta\Delta H$	$\Delta\Delta S$
[Ni(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	-29.0	-33	-12	[Ni(en)(H <sub>2</sub> O) <sub>4</sub> ] <sup>2+</sup>	-41.9	-38	17	-12.9	-5	29
[Ni(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	-46.3	-65	-63	[Ni(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sup>2+</sup>	-77.2	-77	12	-30.9	-11	74
[Ni(NH <sub>3</sub> ) <sub>6</sub> ] <sup>2+</sup>	-74.2	-92	-58	[Ni(en) <sub>3</sub> ] <sup>2+</sup>	-111.8	-107	29	-50.0	-17	121

$\Delta G$ ,  $\Delta H$  and  $\Delta S$  are for reactions involving replacement of water by amines.  $\Delta\Delta G$ ,  $\Delta\Delta H$  and  $\Delta\Delta S$  is the difference between the values for the ammonia and en complexes

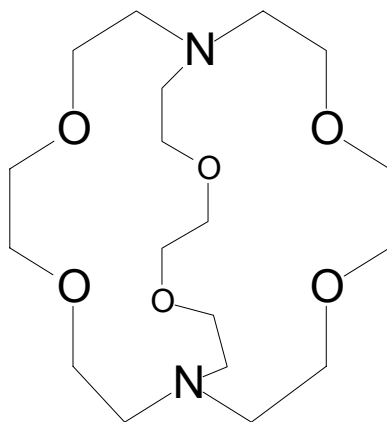
# Macrocyclic ligands

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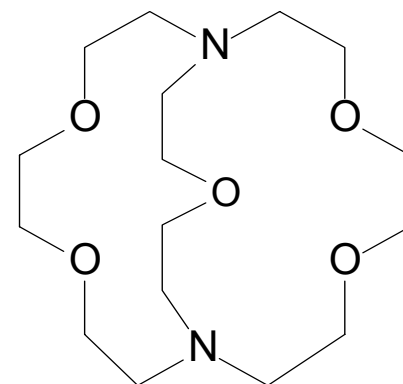
- ◆ Ligands such as crown ethers and cryptands are referred to macrocyclic ligands as they consist of rings of atoms that are studded with Lewis base donor sites.
  - They often display very high affinities for metal ion binding and they are to some extent size selective
    - » Preferentially bind ions in a certain size range



18-crown-6



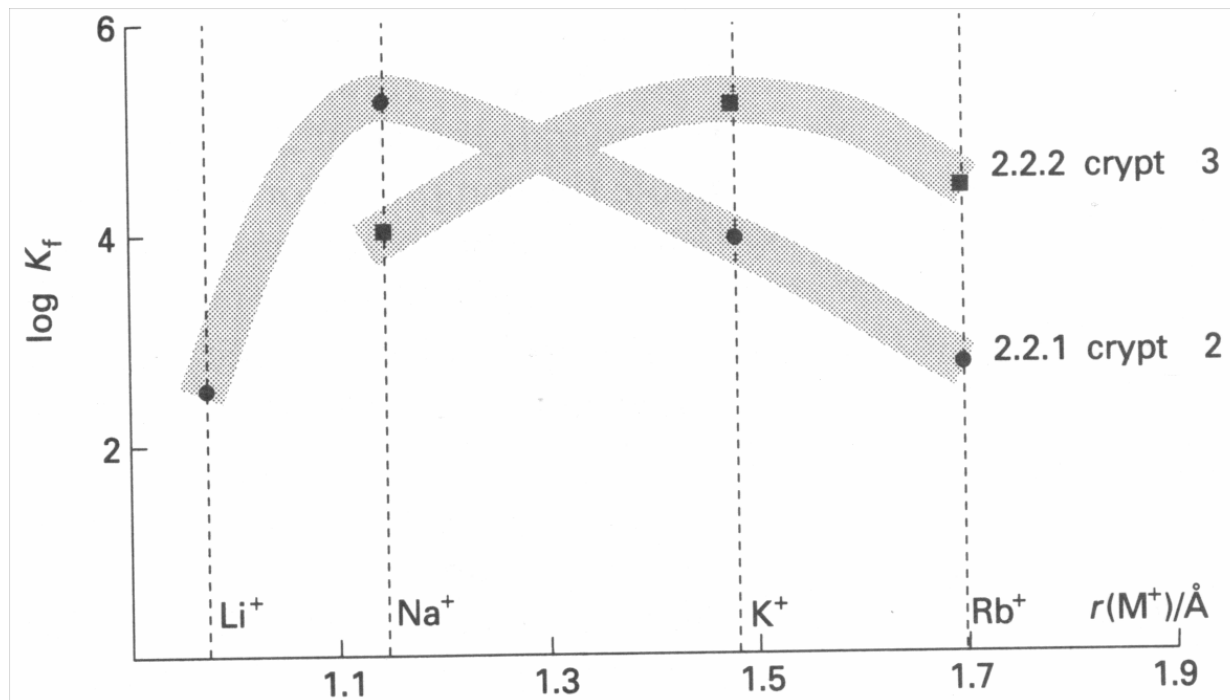
2.2.2-cryptand



2.2.1-cryptand

# Size selectivity of binding

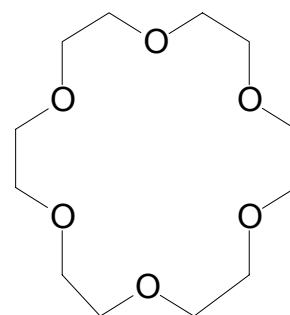
- ◆ For alkali metal ions, different cryptand ligands bind most strongly the metal that best fits inside the ligand



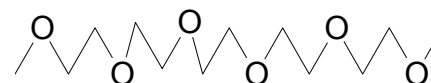
# Thermodynamics of macrocycle binding

- ◆ Compare the binding of a macrocyclic ligand with a similar open chain ligand to try and understand why the macrocycle binds metals so well

		Na <sup>+</sup>	K <sup>+</sup>	Ba <sup>2+</sup>
<b>Log K<sub>1</sub></b>	18-C-6	4.36	6.06	7.04
	pentaglyme	1.44	2.1	2.3
	$\Delta\log K$	2.92	3.96	4.74
<b><math>\Delta H</math></b>	18-C-6	-35.1	-56.0	-43.5
	pentaglyme	-16.7	-36.4	-23.8
	$\Delta\Delta H$	-18.4	-19.6	-19.7
<b><math>\Delta S</math></b>	18-C-6	-33	-17	-13
	pentaglyme	-29	-84	-33
	$\Delta\Delta S$	-4	13	20



18-C-6



pentaglyme

Binding of the macrocycle is favored enthalpically as the crown ether is already prefolded into almost the right shape to bind to the metal. The process of folding the glyme ligand up around the metal introduces repulsions between different ligand atoms and this is enthalpically unfavorable

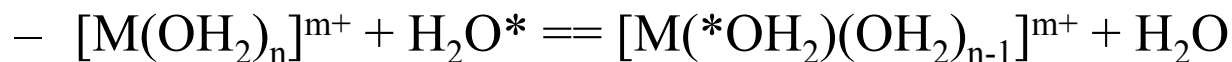
# Rates of reaction

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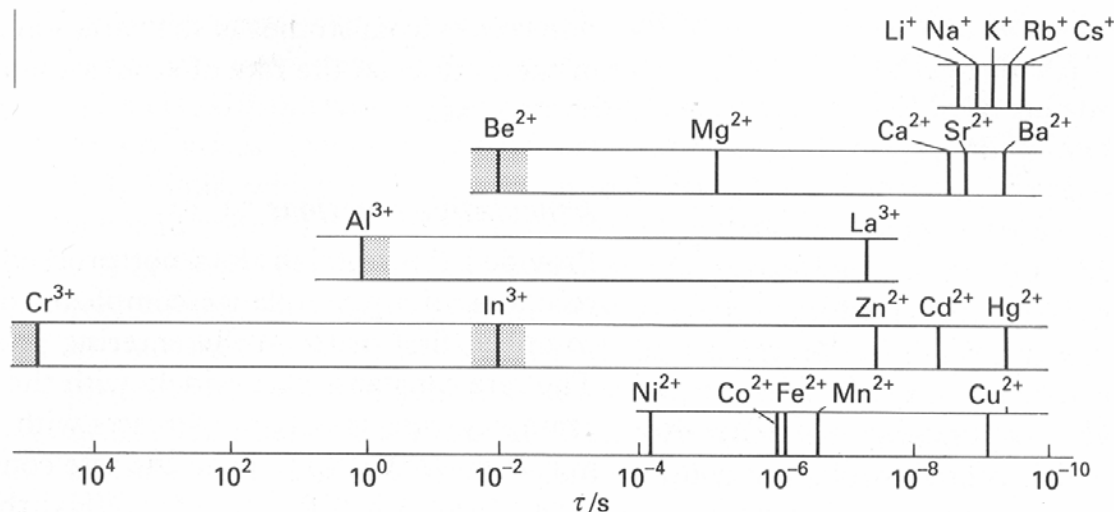
- ◆ Reactions involving transition metal complexes do not all occur at the same rate. Many reactions are very fast, but some are incredibly slow
  - Complexes that undergo ligand replacement rapidly are said to be labile
  - Complexes that undergo ligand replacement very slowly are said to be inert
- ◆ The reactivity of a complex in a ligand substitution reaction can be rationalized by considering a combination of charge/size ratio for the cation and the LFSE of the starting complex

# Water exchange rates

- ◆ The exchange of water between the bulk solvent and the coordination sphere of the aquo complex of a metal ion is a reaction with no enthalpy change. The determination of its rate provides a useful guide to the lability or inertness of complexes involving different metal ions



- » The rate of this reaction can be followed by using isotopically labelled bulk water and monitoring how fast the isotope is incorporated into the complex



High charge and small size favor slow ligand exchange. Metals showing high LFSE in their aquo complexes also show slow exchange

# Reaction mechanisms

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- ◆ Balanced chemical equations are typically written to communicate what the reactants and products are. However, in order to understand why you get certain products and why a reaction occurs at a given rate it is sometimes necessary to understand how the reaction occurs
- ◆ A description of how a reaction occurs is referred to as a reaction mechanism

# Mechanism of substitution reactions

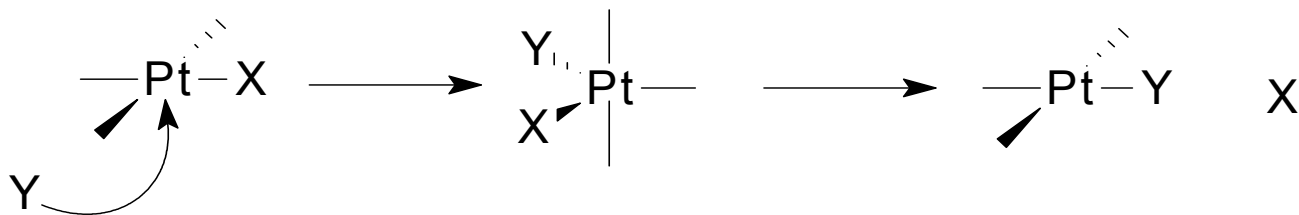
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- ◆ Ligand substitution reactions in transition metal complexes are examples of nucleophilic substitutions
  - This is a very common type of reaction in inorganic, organic and biochemistry. The nucleophile is an electron donor (Lewis base) that attacks (forms a bond with) an electron deficient site in a molecule.
- ◆ There are two extreme possibilities describing how the substitution occurs
  - We could imagine the nucleophile forming a bond with the atom that it is attacking before the group that it is ultimately going to replace has started to leave, and then the leaving group leaves. This mechanism would be described as associative and it is often referred to as an  $S_N2$  reaction (substitution nucleophilic bimolecular)
  - Alternatively we could view the reaction as involving the loss of the leaving group from the substrate. Followed later by the nucleophile coming in and making a bond to the metal center. This would be described as a dissociative reaction and denoted  $S_N1$

# Associative reactions

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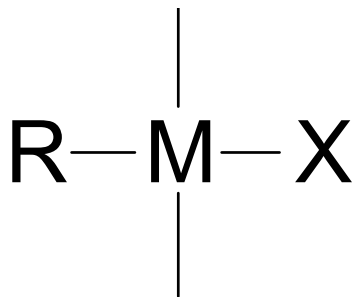
- ◆ Many square planar Pt(II) species react via an associative mechanism
  - $\text{trans [PtClX(py)}_2\text{]} + \text{Y} \rightarrow \text{trans [PtClY(py)}_2\text{]} + \text{X}$
- ◆ It is observed that the rate of this type of reaction is strongly dependent on the nucleophile (Y) and almost independent of the leaving group (X)
  - This strongly suggests that the rate limiting step in the reaction involves the formation of a Pt-Y bond and that Pt-X bond breaking is not part of the rate limiting step



# The trans effect

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- ◆ The rates of substitution in square planar complexes depend strongly on the nature of the ligand trans to the leaving group
- ◆ Rates are enhanced by good  $\sigma$  donors and  $\pi$  acceptors



Rate at which X can be replaced by Y depends on the nature of R. R is trans to X

# Mechanism of the trans effect

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- ◆ The trans effect can arise because the trans ligand either stabilizes the transition state or destabilizes the starting complex
- ◆  $\pi$  acceptors help remove charge from the transition state and stabilize it
- ◆  $\sigma$  donors weaken the bond between the leaving group and the metal center and destabilize the starting complex

# Stereoselective synthesis using the trans effect

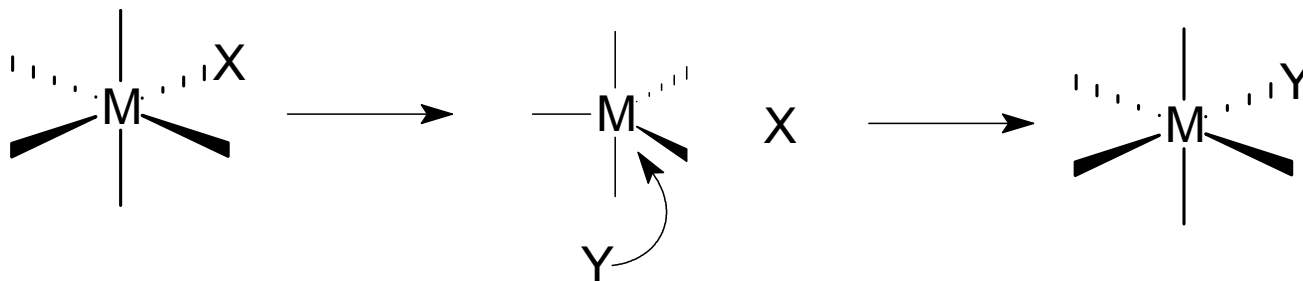
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- ◆ The trans effect can be exploited to make particular isomers of a complex in high purity (selectively)
- ◆ To make trans -[PtCl<sub>2</sub>(NH<sub>3</sub>)(PPh<sub>3</sub>)]
  - 1) [PtCl<sub>4</sub>]<sup>2-</sup> + PPh<sub>3</sub> ----> [PtCl<sub>3</sub>(PPh<sub>3</sub>)]<sup>-</sup> + Cl<sup>-</sup>
  - 2) [PtCl<sub>3</sub>(PPh<sub>3</sub>)]<sup>-</sup> + NH<sub>3</sub> -----> trans[PtCl<sub>2</sub>(NH<sub>3</sub>)(PPh<sub>3</sub>)] + Cl<sup>-</sup>
- ◆ To make cis -[PtCl<sub>2</sub>(NH<sub>3</sub>)(PPh<sub>3</sub>)]
  - 1) [PtCl<sub>4</sub>]<sup>2-</sup> + NH<sub>3</sub> ----> [PtCl<sub>3</sub>(NH<sub>3</sub>)]<sup>-</sup> + Cl<sup>-</sup>
  - 2) [PtCl<sub>3</sub>(NH<sub>3</sub>)]<sup>-</sup> + PPh<sub>3</sub> -----> cis [PtCl<sub>2</sub>(NH<sub>3</sub>)(PPh<sub>3</sub>)] + Cl<sup>-</sup>

# Dissociative reactions

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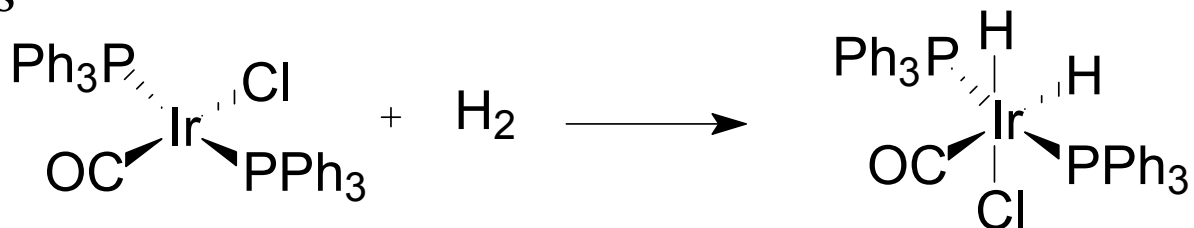
- ◆ Substitution in many octahedral complexes go via a dissociative mechanism
  - Rates depend strongly on the leaving group and only slightly on the nucleophile suggesting that the rate limiting step involves breaking the metal leaving group bond



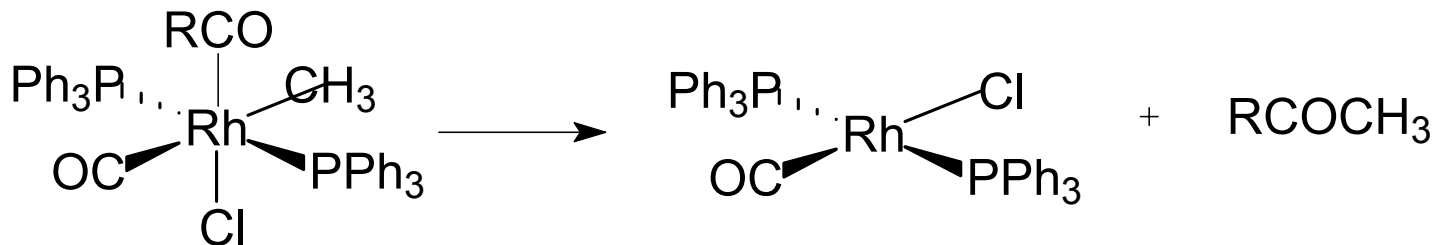
Intermediate has a lower coordination number than the reactant – hence dissociative

# Oxidative addition and reductive elimination

- ◆ These reactions are important in the operation of many industrial catalysts
- ◆ Oxidative addition is a reaction where the coordination number of the metal increases at the same time as its formal oxidation state increases



- ◆ Reductive elimination is a reaction where the coordination number of the metal decreases at the same time as its formal oxidation state decreases



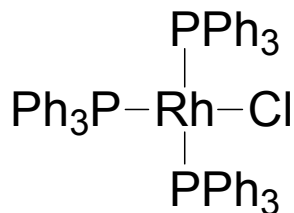
# Catalysts

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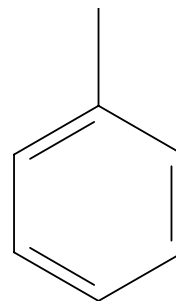
- ◆ A catalyst is a substance that speeds up a reaction. It can not alter the equilibrium constant for a reaction, it can only effect how quickly equilibrium is achieved
- ◆ Catalysts are very widely used industrially
  - Select a catalyst that speeds up only the reaction that you want. This minimizes the amount of unwanted biproducts and produce the desired material rapidly.
- ◆ Two general types of catalyst are used: homogeneous and heterogeneous
  - A homogeneous catalyst exists in the same phase as the reactants and products. So if a reaction was carried out in solution, the catalytically active species would also be in solution
  - A heterogeneous catalyst exists in a different phase from the reactants and products. Typically, the catalysts is a solid and the reactants and products are liquids/gases. The reaction takes place at the solid surface

# Example homogeneous catalysts

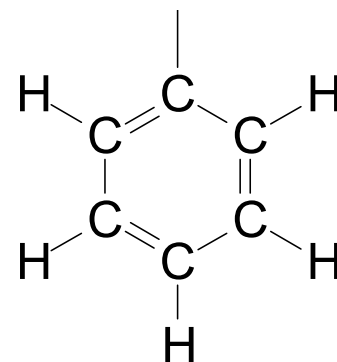
- ◆ Industrial homogeneous catalysts are typically coordination complexes or organometallics



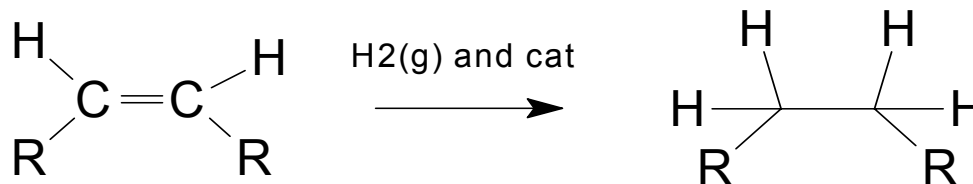
$\text{PPh}_3$ , is  
triphenylphosphine  
Ph is a phenyl group



or



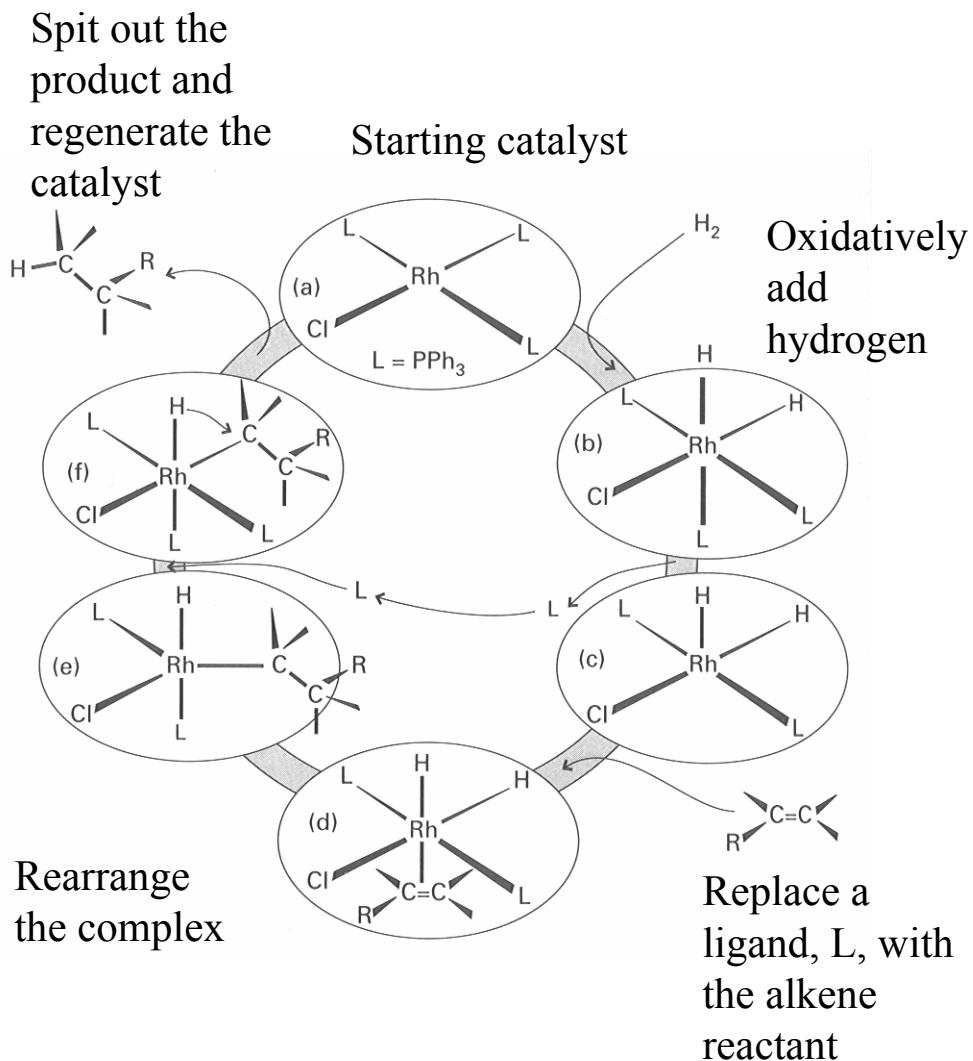
Wilkinson's catalyst. Used  
for hydrogenations



R – some additional organic group

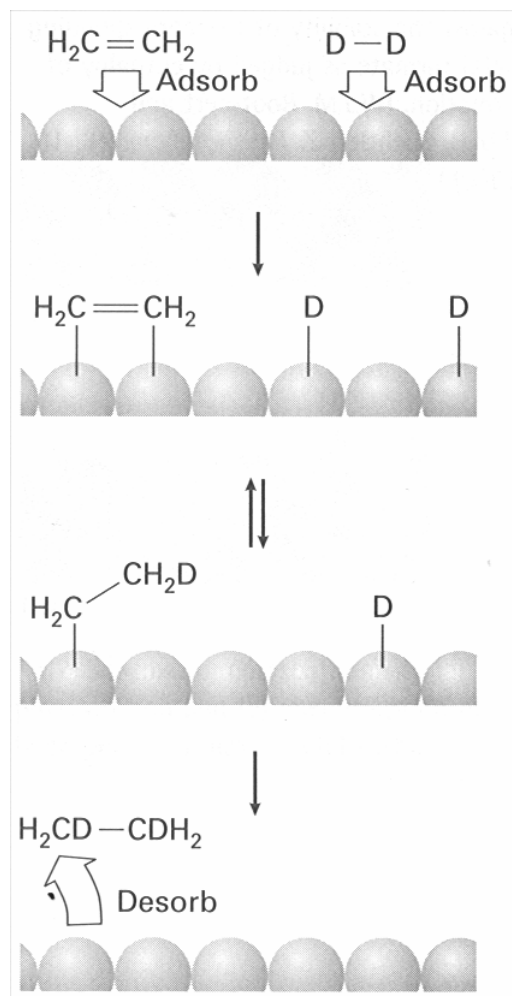
# A catalytic cycle

- ◆ We can represent the mechanism by which a catalyst such as Wilkinson's catalysts does a reaction using a catalytic cycle: a series of reaction steps that take the reactants to products and regenerate the catalytically active species



# Example heterogeneous catalyst

- ◆ Heterogeneous catalysts operate by virtue of reactions that occur on the surface of the catalyst



Metal absorbs the starting compounds and breaks the D-D bond

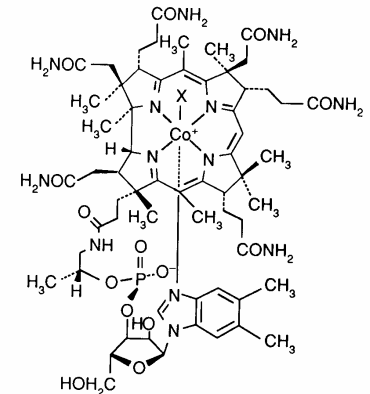
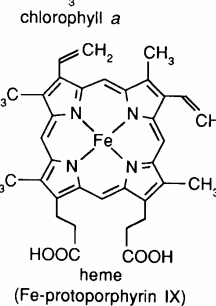
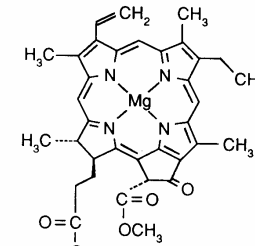
D atoms on the surface react with the adsorbed alkene

Surface D atom and alkyl group react and product is desorbed

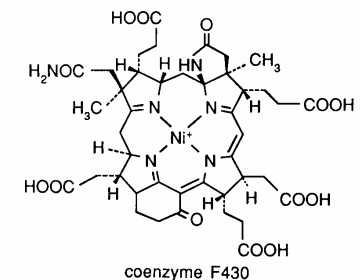
Hydrogenation (deuteration) using a metal catalyst

# Coordination complexes and transition metals in biological systems

- ◆ Metal complexes and transition metals are of considerable importance in biological systems
  - Responsible for many biological redox processes
  - Useful for oxygen transport
  - Useful in various drugs
  - Can be highly toxic



vitamin B<sub>12</sub> (X = CN)

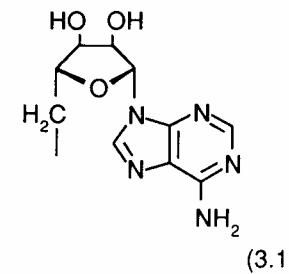
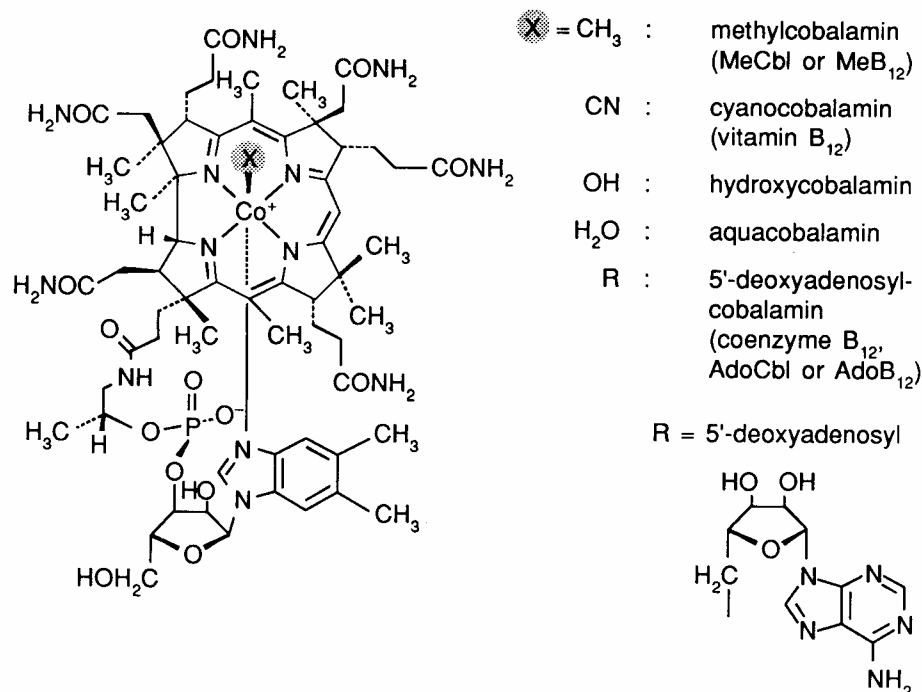


# Vitamin B<sub>12</sub>

◆ Vitamin B<sub>12</sub> is a cobalt containing complex

– The cyanocomplex is not the biologically active species. X = R or CH<sub>3</sub> are involved in biological redox processes and alkylation reaction

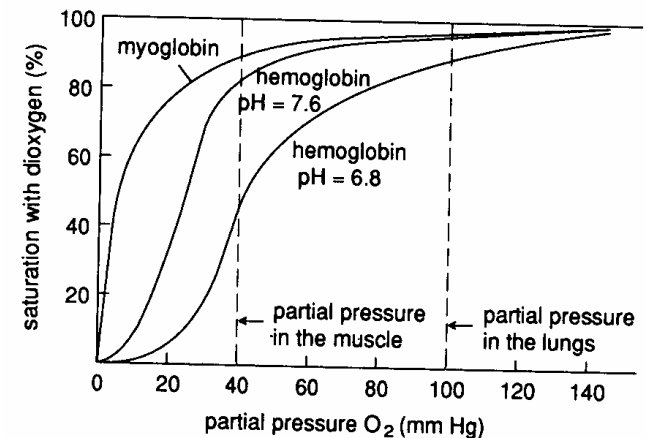
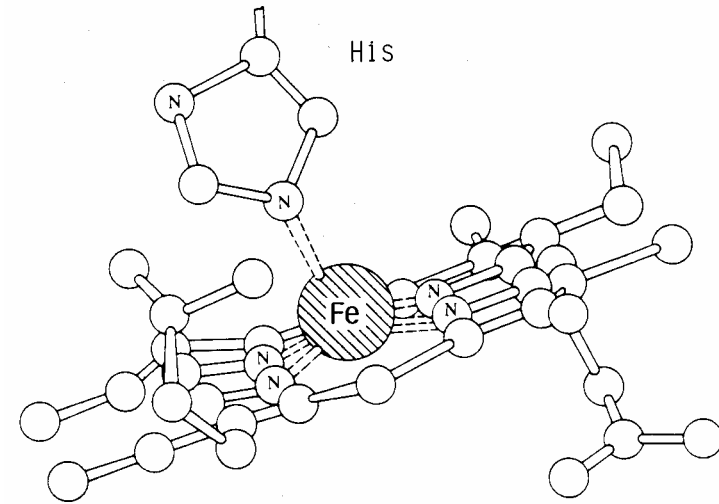
◆ Cobalt containing species is a coenzyme - it does its biological job with the aid of an apoenzyme



Note that the presence of a cobalt carbon bond makes many of these species examples of organometallics

# Oxygen transport

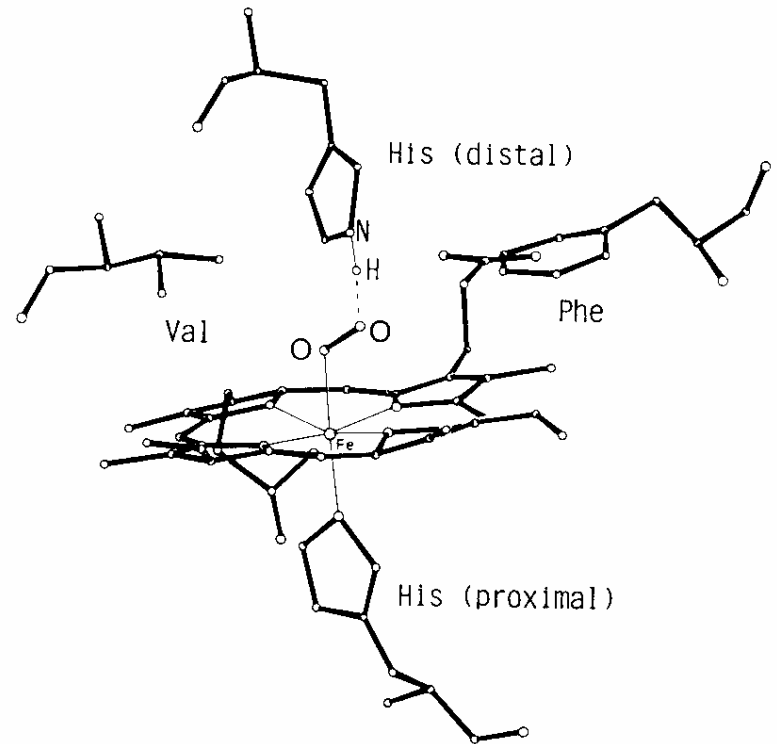
- ◆ The iron containing proteins hemoglobin and myoglobin are involved in oxygen transport
  - Hemoglobin moves oxygen through the body
  - Myoglobin stores and moves oxygen within muscle
  - Hemoglobin has a lower oxygen affinity than myoglobin and its oxygen binding is pH dependent. This provides a mechanism for oxygen transfer from hemoglobin to myoglobin in the muscle



# Oxygen binding in myoglobin

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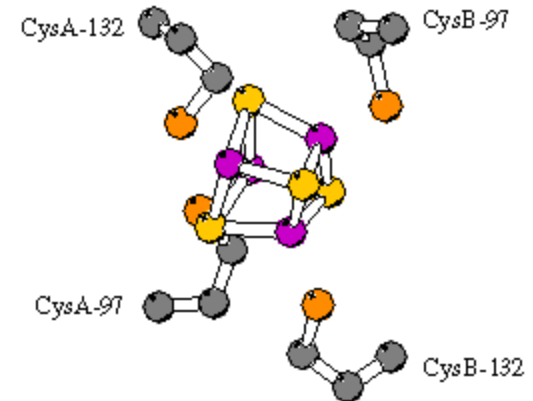
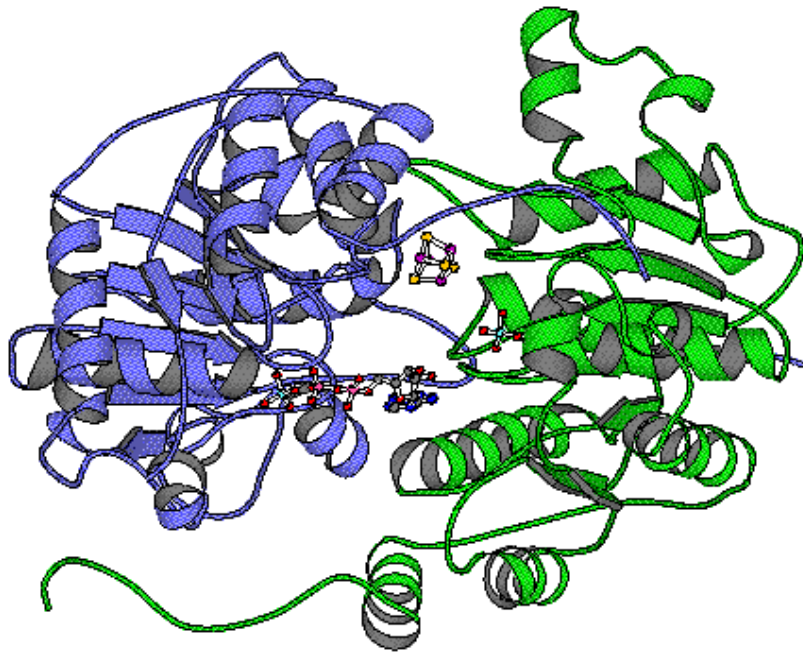
- ◆ Oxygen binds to the metal center end on, but it sits at an angle to the plane of the porphyrin ring ligand.
  - Oxygen binding in this mode is efficient
- ◆ CO also binds at an angle to the ring. This reduces the binding efficiency for CO and slightly reduces your chances of CO poisoning



# Nitrogen fixation

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- ◆ Plants use metalloproteins to convert gaseous nitrogen to useful nitrogen compounds. Some of these proteins include clusters with an  $\text{Fe}_4\text{S}_4$  core

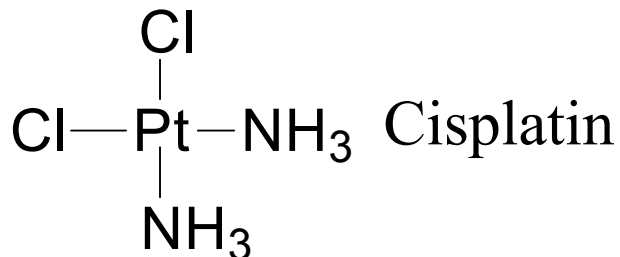


# Anticancer drugs

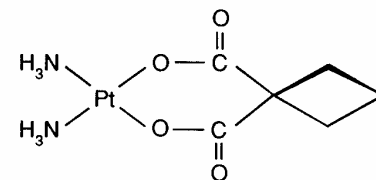
- ◆ The platinum complexes cisplatin and carboplatin are widely used anticancer agents.

Cisplatin is very useful for testicular cancers.

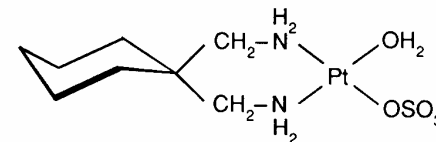
They bind to DNA and prevent replication.



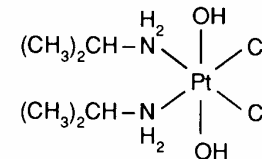
carboplatin: *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II)



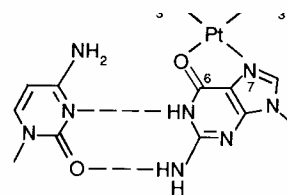
spiroplatin: aqua-1,1-bis(amino-methyl)cyclohexanesulfatoplatinum(II)



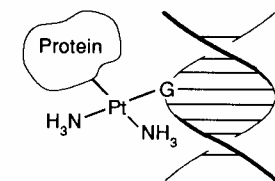
iproplatin, CHIP: *cis*-dichlorobis(isopropylamine)-*trans*-dihydroxoplatinum(IV)



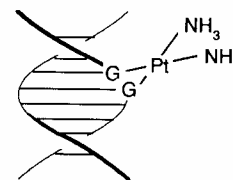
(19.4)



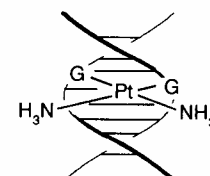
chelate coordination to a guanine base



DNA-protein cross-linking



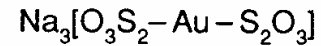
1,2-intrastrand cross-linking



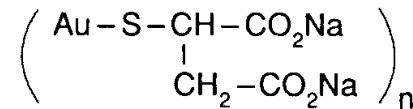
interstrand cross-linking

# Anti arthritis drugs

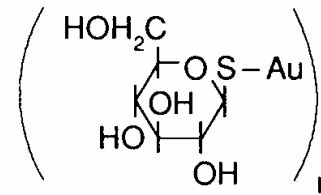
- ◆ Some gold compounds have been employed to treat arthritis.



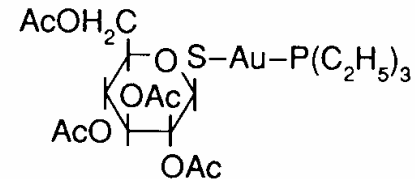
trisodiumgold(I)bis(thiosulfate)  
( 'sanocrysin' )



disodiumgold(I)thiomalate ( 'myochrisin' )



gold(I)thiogluucose ( 'solganol' )



(2,3,4,6-tetrakis-O-acetyl-1-thio-β-D-glucopyranosido)gold(I)triethylphosphine ( 'auranofin', 'ridaura<sup>®</sup>' )