Fragment Orbitals for Transition Metal Complexes

Introduction

- so far we have concentrated on the MO diagrams for main group elements, and the first 4 lectures will link into your **Main Group chemistry** course
- now we will concentrate on the MO diagrams for TM complexes, and the next 4 lectures will link into your **TM and Organometallic** and your **Crystal Architecture** chemistry courses
- areas we don't have the space to cover are cluster MOs (very interesting!) and extended system MOs (solid state, polymers, conjugated systems). However with the knowledge gained from this course you should be able to delve into these areas if you are interested

Fragment Orbitals of the Metal

- transition metals (TM) are electropositive thus the valence FAOs are high in energy
- the energy levels included for the TMs differ from the main group
  - the active electrons for bonding are in the 3d (or 4d) shell, and thus these AOs are included in the valence MO diagram
  - the occupied 3s and 3p AOs are too deep in energy to participate in bonding and are ignored
  - however the vacant 4s and 4p AOs are very close in energy to the 3dAOs and we do include these AOs in valence MO diagrams that include TMs

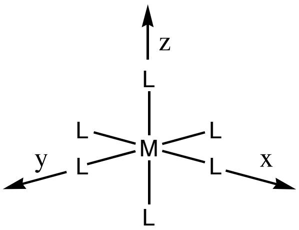


Figure 1 coordinate system

IMPORTANT

- the symmetry labels s, p and d refer to spherical symmetry and in any MO diagram the new symmetry labels for the TM AOs must be determined using the point group symmetry of the molecule and your character tables
  - for example, metals are often in an octahedral environment (six coordinating ligands, **Figure 1**)
  - determining the symmetry of the dAOs is easy; read the symmetry from the character table, dxy, dxz and dyz ⇒ t_{2g} and dx^2-y^2 and dz^2 must be degenerate so we choose ⇒ e_g **Figure 2**
  - the sAO must be totally symmetric ⇒ a_{1g} and pAOs transform as the x, y and z axes ⇒ t_{1u} symmetry

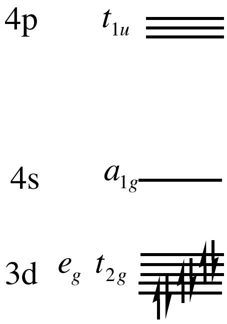


Figure 2 Metal orbital energies and symmetry for the O_h point group

- you should know the shape and phase of the dAOs
  - positive along the axis associated with the label
  - ie dx^2-y^2 positive on x axis and negative on y axis
  - positive in the quadrant associated with the label
  - ie d_{yz} is positive in the positive yz quadrant

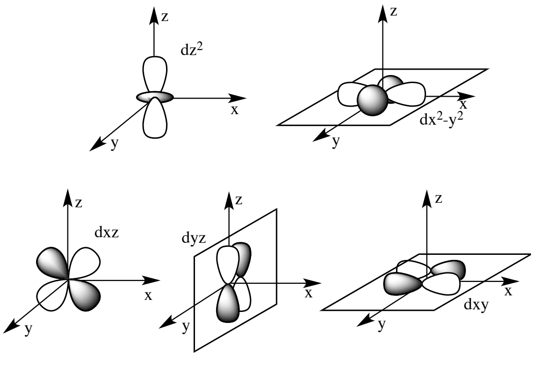


Figure 3 dAOs

Metallic Dimers

- before we move on to octahedral TM complexes we will consider the simpler case of a metallic dimer. Metals do not generally form unsupported dimers, however M-M bonds are a relevant feature of a significant number of multi-centred TM complexes

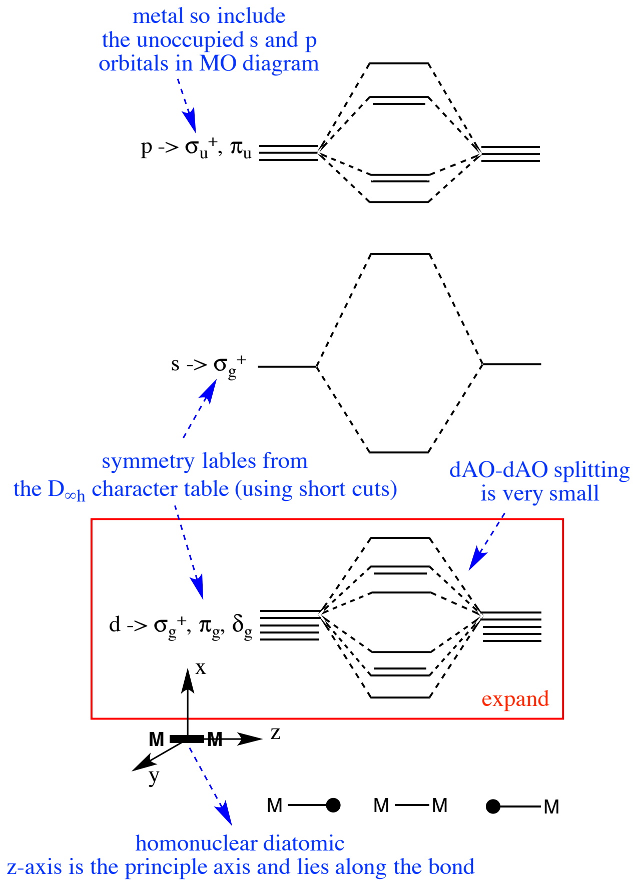


Figure 4 building the M_2 energy diagram

- to understand M-M fragment bonding we start by building a fragment **energy diagram**, **Figure 4**
  - a fragment energy diagram includes all the energy levels and perhaps **some** of the key MOs, this is in contrast to a MO diagram which includes illustrations of **all** MOs.
  - M_2 is a homonuclear diatomic and has $D_{\infty h}$ symmetry, as a first guess orbital symmetries can be read off the character table, dAOs have σ_g^+ π_g and δ_g symmetry labels.
  - d-d AO interactions are very weak compared to sAO and pAO interactions, typically we artificially expand the d-d region of the diagram for ease of interpretation
- **Figure 5** is a MO diagram showing the expanded d-d region of the M_2 energy diagram
  - as with main group elements FOs are combined once in-phase and once out-of-phase

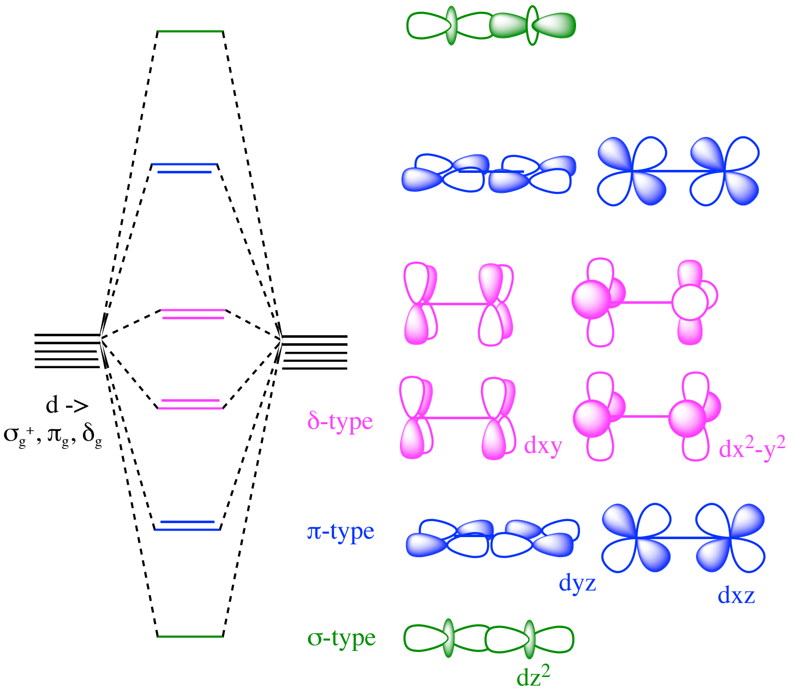


Figure 5 expanded dAO region of the M_2 MO diagram

- determining the symmetry of the final MOs can be daunting initially, however if you know “where to look” and use short-cuts it becomes easier
    - first remember that the labels σ and π are often applied to represent the changes in phase of orbitals on rotation around a bond (**Figure 6**) even when the molecule does not have $D_{\infty h}$ symmetry! (just think of organic chemistry)
    - use the **phase pattern of the orbitals closest to the centre of the bond** where the axis “origin” resides, to determine the MO symmetry, **Figure 7a**

IMPORTANT

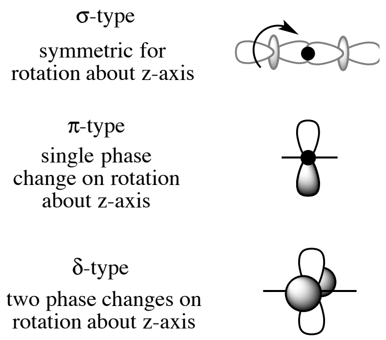


Figure 6 symmetry labels

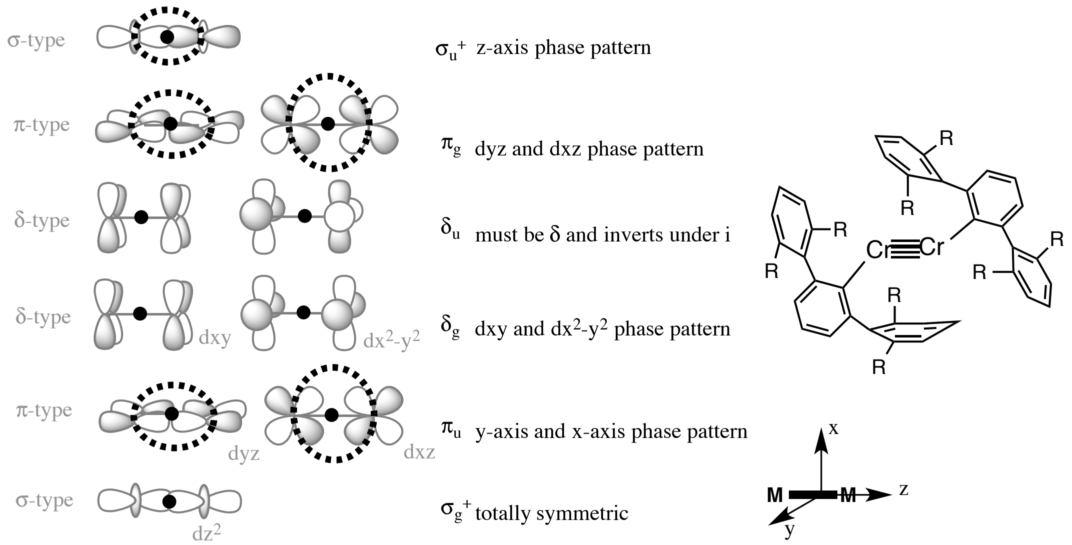


Figure 7 (a) symmetry labels of the MOs for M_2. Axis origin shown by black dot in the centre of the bond, and (b) the first ambient conditions stable quintuple bond R=isopropyl.

- The quintuple M-M bond!! (bond order of 5)
    - understanding the MO structure of TMs lead to the prediction of M-M dimers that could bond orders of 4, 5 and 6!
    - in a metal if all the bonding dAO MOs are occupied (and all the antibonding MOs are vacant) then the bond order can potentially reach a maximum of 5, the “electronic configuration” for the **dAO based manifold** of MOs is $\sigma^2\pi^4\delta^4$, (**Figure 8**)
    - a quintuple bond at ambient temperature was first reported for a stable dichromium compound in 2005 (**Figure 7b**), links to the original Science paper on my web-site
    - if the higher 4s (or 5s) also interact and the bonding MO is occupied a potential bond order of 6 can be obtained
    - $[Re_2Cl_8]^{2-}$ forms a quadruple M-M bond, and Mo_2 and W_2 form a sextuple bond at very low temperatures.

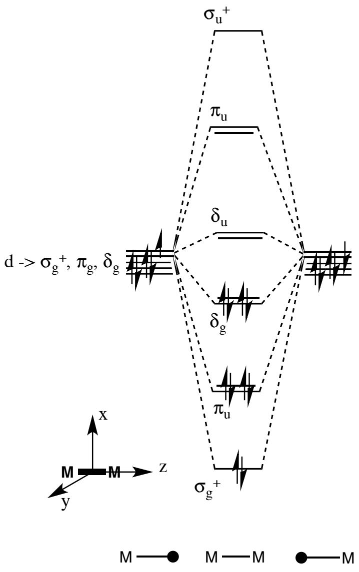


Figure 8 quintuple M-M bond

Ligand Fragment Orbitals and Symmetry Adapted Orbitals

- symmetry can be used to determine **symmetry adapted** orbitals

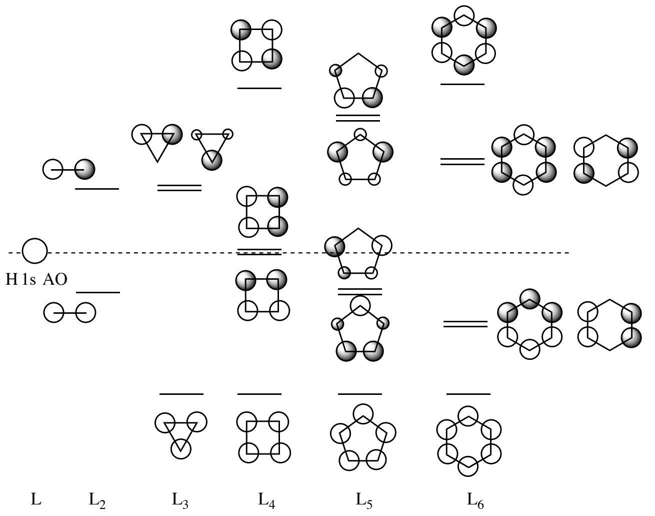


Figure 9 symmetry adapted orbitals for a ring

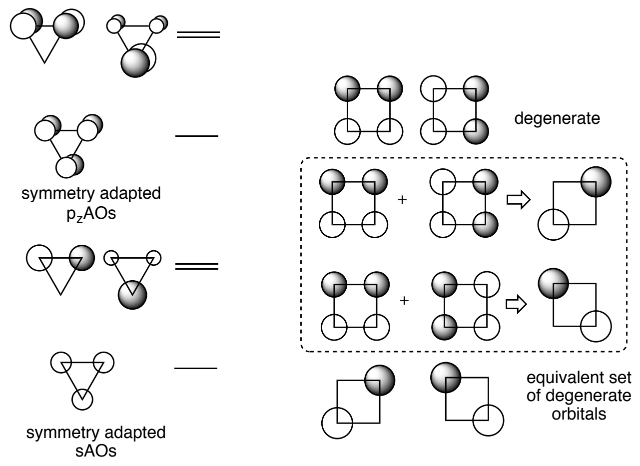


Figure 10 symmetry adapted FOs based on pAOs, and mixing of degenerate orbitals

- if you want to know more about how these are derived look on my web-site under the first problems class
- from **Figure 9** you need to **know** the symmetry adapted orbitals up to L_4 and you should be **familar** with those up to L_6
  - symmetry adapted orbitals are general and can be used with any type of MO diagram; organic, main group and TM
  - you have already meet those for L_2 and L_3, we will be using those for L_4 in the next few lectures
- useful facts about symmetry adapted orbitals:
  - once you know the symmetry adapted orbitals for the sAOs you also know them for the p_zAOs, **Figure 10a**
  - degenerate orbitals can be "rotated" or "mixed" with no cost in energy, you will see this most often for the degenerate symmetry adapted orbitals of L_4, **Figure 10b**

- the L_6 orbitals above are for a planar molecule like benzene. However in a TM the L_6 orbitals are 3D!

IMPORTANT

- the symmetry adapted L_6 orbitals for ligands in an octahedral (O_h) complex are shown in **Figure 11,** you need to **know** these orbitals.
  - there are tricks to help you remember!
  - the first MO is all in-phase and totally symmetric ⇒ a_{1g}
  - the next three MOs have the same phase pattern as the x, y, z-axes ⇒ t_{1u}
  - the next MO has the same phase pattern as a dz^2 AO ⇒ e_g
  - the last MO has the same phase pattern as a dx^2-y^2 AO ⇒ e_g

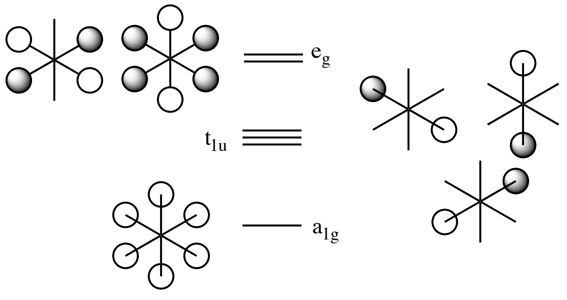


Figure 11 symmetry adapted orbitals for octahedral ligands

Isolobal Analogy

- many ligands can be approximated by the orbital diagrams we have already seen; E_2, ER_2, ER_3, for example CO, OH_2 and NH_3 and the more complex analogues EX, EX_2 and EX_3 (X=an element with pAOs)
- to form the TM MO diagram we use the MO diagrams of the ligands as fragments
- however, not all of the orbitals of a ligand will interact with a central TM, the energy of the TM dAOs is high, typically only the highest energy FOs of a ligand contribute to the TM diagram

IMPORTANT

- for many ligands the key MO is an orbital which has **"sigma" like characteristics**
  - for example in $[Co(NH_3)_6]^{3+}$ the HOMO of the ammonia molecule, has σ-like characteristics, **Figure 12**
  - however the high energy orbital must have the right symmetry to interact, so it is not always the HOMO, for example, in the case of OH_2 it is the HOMO-1 that is important

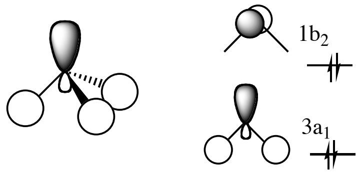


Figure 12 the HOMO of EH_3 and HOMO-2 of EH_2 ligands

- we say these σ-like orbitals are **isolobal** to the simpler sAOs
  - from the perspective of the metal "looking out toward" the ligand, the ligand FO looks like an sAO.
  - isolobal with the orbitals of EH_3 are those of NH_3, NR_3, PH_3, PR_3 and even CR_3 and SiR_3 where there is only a single electron in this FO
- we build the TM MO diagram using a symmetry adapted combination of the ligand σ-like FOs, **Figure 13**, compare this diagram with **Figure 11**.
  - these symmetry adapted sigma orbitals are very important, we will be using them extensively, **memorize them!**

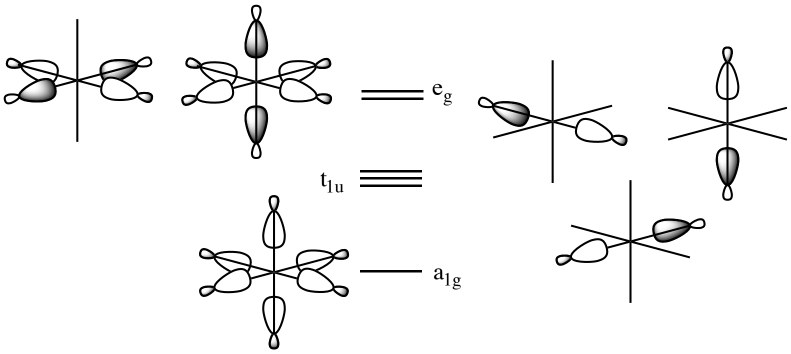


Figure 13 isolobal symmetry adapted orbitals for octahedral ligands

- what energy ordering can we expect for the ligand orbitals?
  - the orbitals are "two bonds" apart, ie they are distant and so will not interact strongly, thus they will all be very close in energy
  - the a_{1g} is totally bonding and will lie deepest due to through space interactions
  - the t_{1u} FO are essentially non-bonding
  - the e_g FOs will be slightly higher in energy due to through space antibonding interactions
- ligands that have π and π^* FOs are also important, we will be looking at these in a later lecture

The Octahedral Point Group

- to understand TM bonding we need to understand the O_h point group (**Figure 14**) as this will determine the symmetry of the orbitals.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	h=48
A_{1g}	1	1	1	1	1	1	1	1	1	1	$(x^2+y^2+z^2)$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
Eg	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
Eu	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(T_x, T_y, T_x)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

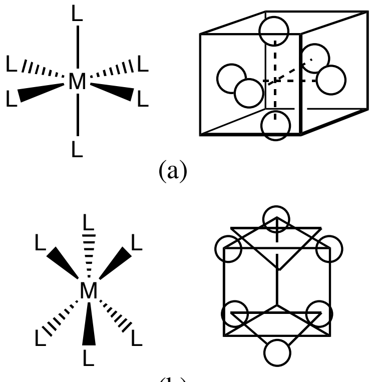
Figure 14 O_h character table

- as an inorganic or materials chemist the octahedral point group is one of the most important, **Figure 15**
  - a vast number of TM or organometallic compounds are octahedral, or are complexes that can be related to octahedral such as square planar
  - many clusters can be understood using symmetry arguments developed from octahedral cage clusters.
  - an octahedral arrangement is one of the fundamental building blocks for solid state structures particularly that for the face centred cubic cell.
  - the centre of a “cube” of atoms is the equivalent of an octahedral interstitial site for solid state structures

2nd year Crystal and Molecular Architecture course

Figure 15 (a) transition metals compounds, (b) cluster compounds, (c) face centred cubic (d) octahedral interstical sites

- there are two useful ways of drawing an octahedral molecule, **Figure 16** each places emphasis is on a different aspect of symmetry
  - a "cube" where the molecular atoms or ligands occupying the centre of each face, emphasising the C_4 and C_2 axes, **Figure 16(a)**
  - the "double prism" emphasises the C_3 axes, **Figure 16(b)**



(a)

(b)

Figure 16 Octahedral geometries

- the key symmetry operations in this group are E $8C_3$ $6C_2$ $6C_4$ $3C_2$ i $6S_4$ $8S_6$ $2\sigma_h$ $6\sigma_d$
  - remember from Lecture 1 and the D_{3h} point group that the number in front tells us the number symmetry elements
  - there can be multiple symmetry elements (ie $3C_2$ axes in D_{3h}) or there can be a single element with multiple operations (ie $2C_3$ where C_3^1, C_3^2 operations about a single C_3 axis are counted in D_{3h})
  - only *new unique* symmetry operations are counted in a character table, thus if a symmetry element has already been found (and recorded in the symmetry operations to the left) it is not added to the character table.
- I expect you to **know and be able to show all the operations of the O_h point group**, if you need some help there is an extra document on the web-site that steps through these in detail!

Decent in Symmetry

- TM complexes are not always octahedral
  - mixed σ-donor ligand complexes can occur such as $[Co(H_2O)_2(NH_3)_4]^{3+}$
  - some complexes have only 4 σ-donor ligands, for example $NiCl(PPh_3)_2$
  - it is important to be able to determine the MO and energy diagrams for complexes with a lower symmetry than O_h
- a higher symmetry group has more symmetry operations, a lower symmetry group has fewer symmetry operations
  - a lower symmetry group can be a **sub-group** of a higher symmetry group
  - when different symmetry elements are lost, different sub-groups occur
  - we say there has been a **descent** in symmetry, **Table 1**

C_{2v}	C_2	C_s							
C_{3v}	C_3	C_s							
C_{4v}	C_4	C_{2v}							
D_{3h}	C_{3h}	C_{3v}							
	D_3	C_3	also	C_{2v}					
D_{4h}	D_{2d}	D_{2h}	D_2	C_{4h}	C_{4v}	C_{2v}			
	D_4	C_4	S_4	C_{2h}	C_2	C_s	C_i		
D_{6h}	D_{3d}	D_{2h}	C_{6v}	C_{3v}	C_{2v}	C_{2h}			
	D_6	D_{3h}	C_{6h}	C_6	C_{3h}	D_3	S_6	D_2	C_3
T_d	D_{2d}	C_{3v}	C_{2v}	also	S_4	D_2	C_3	C_2	C_s
O_h	T_d	D_{4h}	D_4	D_{2d}	C_{4h}	C_{4v}	D_{2h}	D_2	C_{2h}
	D_{3d}	D_3	C_{3v}	S_6	C_3	also	C_4	S_4	C_{2v}

Table 1 A selection of examples showing descent in symmetry, descent after C_{2v}, C_{3v} are assumed for the higher point groups.

- for example, the D_{3h} point group has many different sub-groups: C_{3h}, C_{3v}, C_3, C_s, D_3, C_3, C_{2v} and C_2
  - the D_3 point group has operations E, C_3 and C_2 where the symmetry elements σ_h, S_3 and σ_v have been lost
  - the C_{3h} point group has operations E, C_3, σ_h and S_3 where the symmetry elements σ_v and C_2 have been lost

- you have already seen descent in symmetry in action in the correlation diagrams ($D_{\infty h}$->C_{2v} and D_{3h}->C_{3v}), the effect of a distortion is to eliminate one or more symmetry elements
- in the context of TM chemistry we are interested in the descent of symmetry of the octahedral point group, **Figure 17**
- as the ligands in the TM complex are differentiated the symmetry drops
- we work out the reduction in symmetry of the FOs and then MOs from O_h to the new point group

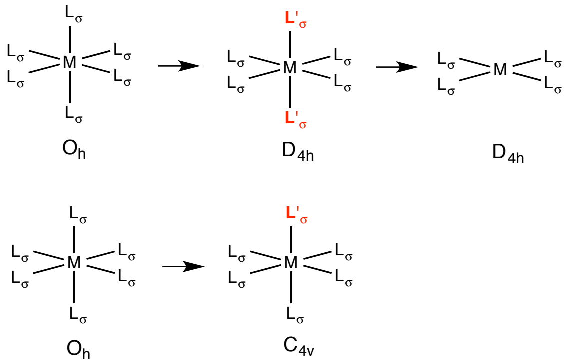


Figure 17 drop in symmetry for TM complexes

Key Points

- be able to draw MO diagrams that include dAOs
- be able to explain σ, π and δ interactions for dAOs
- be able to draw energy and/or MO diagrams for homonuclear and heteronuclear diatomics including M_2, MM' and ME (as well as EE' and E_2) where M,M' are metals and E,E' are main group elements.
- be able to discuss bond order with respect to diatomic molecules, and be able to explain why bond order cannot be extended to larger molecules
- be able to draw and use the ligand symmetry adapted fragment orbitals for rings L_n n=1-4, and L_6 in an octahedral arrangement
- be able to explain and use the isolobal analogy
- be able to explain why the octahedral point group is very important for inorganic chemistry
- be able to locate all of the symmetry elements of the O_h point group and be able to draw diagrams showing the action of the O_h point group symmetry operations on molecules and fragment orbitals
- be able to describe a descent in symmetry

Self-Study Problems / Exam Preparation

- Draw the MO diagram for Mo_2 and show that a sextuple bond order is potentially possible.
- Use the long method to show that the M_2 dimer dxz/dyz combination of AOs has π_u symmetry.
- Clearly show using diagrams that $S_4^2 = C_2$ and $S_4^4 = E$ Thus, showing that there are 2 unique operations per S_4 axis in the O_h point group.
- Clearly show using diagrams that S_6^1 and $S_6^5 = S_6^{-1}$ are the only unique operations for each S_6 axis in the O_h point group.
- Which symmetry operations are lost from the D_{6h} point group to generate the C_{3v} point group?