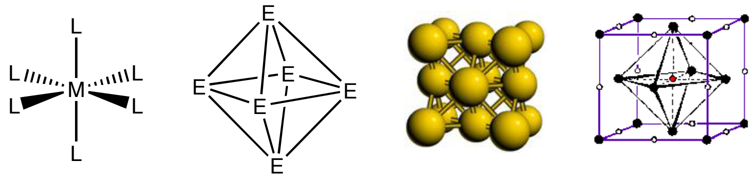
The Octahedral Point Group

2nd year Crystal and Molecular Architecture course

- As an inorganic or materials chemist the octahedral point group is one of the most important, **Figure 1**
  - 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



(a) (b) (c) (d)

Figure 1 (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 2** each places emphasis is on a different aspect of symmetry
  - the "cube" may be less familiar to you, think of the molecular atoms or ligands occupying the centre of each face of the cube and the central main group atom A or metal M lying in the centre of the cube. This view emphasises the C_4 and C_2 axes, **Figure 2(a)**
  - the "double prism" shows a triangular face at the top and then a second rotated relative to this by 60º on the bottom and this view emphasises the C_3 axes, **Figure 2(b)**

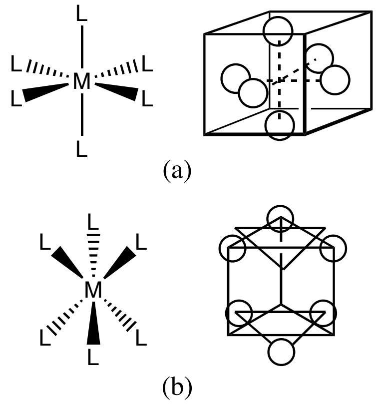


Figure 2 Octahedral geometries

O_h Character Table

- the character table for O_h is given below (**Figure 3**)
- The column headings tell us the key symmetry operations in this group are E $8C_3$ $6C_2$ $6C_4$ $3C_2$ i $6S_4$ $8S_6$ $2\sigma_h$ $6\sigma_d$ and we will now spend some time locating all of these symmetry elements.
- remember from Lecture 1 and the D_{3h} point group
  - 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.

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 3 O_h character table

- E is easy, this is the identity

- there are $8C_3$ operations
  - a C_3 axis passes diagonally through opposite pairs of corners in the cube, **Figure 4**. As each corner is symmetrically equivalent and there are 4 pairs of corners, there are $4C_3$ axes.
  - around each axis there are 3 possible C_3 operations: $C_3^1\ C_3^2\ C_3^3$, however the last operation $C_3^3 = E$ is equivalent to the identity, leaving 2 distinct C_3 operations per axis
  - thus there are 4 C_3 axes each with 2 distinct operations giving $8C_3$ operations in O_h

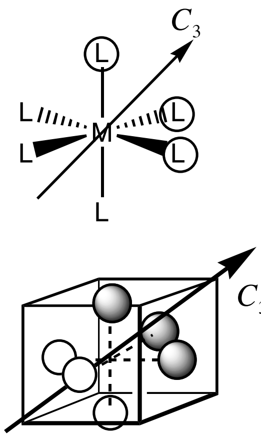


Figure 4 C_3 axes

- there are $6C_2$ operations
  - a C_2 axis lies between each pair of bonds, emerging from the center for each pair of edges in the cube, as there are 6 pairs of edges to the cube there must be $6C_2$ axes, **Figure 5** (only 3 of the 6 axes are shown)
  - $C_2^2 = E$ is equivalent to the identity
  - hence there are $6C_2$ operations in O_h
  - these axes are often identified with a prime or double prime (C'_2) to separate them from axes that pass through bonds (C_2)

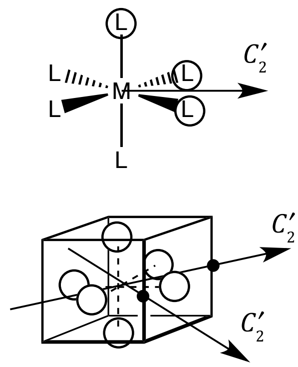


Figure 5 C'_2 axes

- the next two sets of operations are linked, these are the $6C_4$ and $3C_2$ operations, **Figure 6**
  - two coincident C_2 and C_4 axes lie along each bond, emerging from the center of each pair of faces, as there are 3 pairs of faces to each cube, there will be three C_2 and C_4 axes
  - since $C_2^2 = E$ there are $3C_2$ operations in O_h
  - each C_4 axis has 4 possible C_4 operations: $C_4^1\ C_4^2\ C_4^3\ C_4^4$, but $C_4^4 = E$ and the middle operation $C_4^2 = C_2^1$, (C_2^1 is counted first because n=2 is lower than n=4) hence, only C_4^1 and $C_4^3 = C_4^{-1}$ are counted for each C_4 axis.
  - thus there are three distinct C_4 axes each with two operations giving rise to $6C_4$ operations in O_h

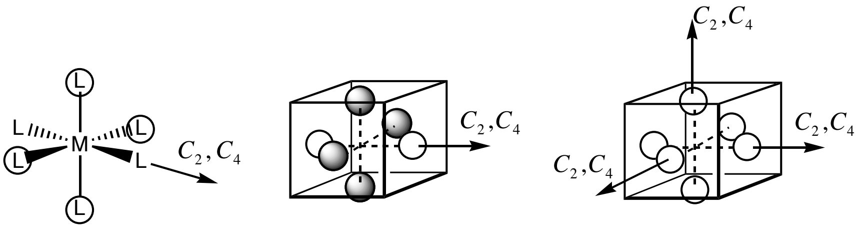


Figure 6 C_2 and C_4 axes

- the inversion point is at the centre of the cube

- there are $6\sigma_d$ operations
  - a σ_d mirror plane passes between bonds, looking from the top, they criss-cross diagonally in both directions on a face of the cube, **Figure 7(a)**
  - as there are 3 pairs of faces each with two mirror planes there are $6\sigma_d$ operations in O_h

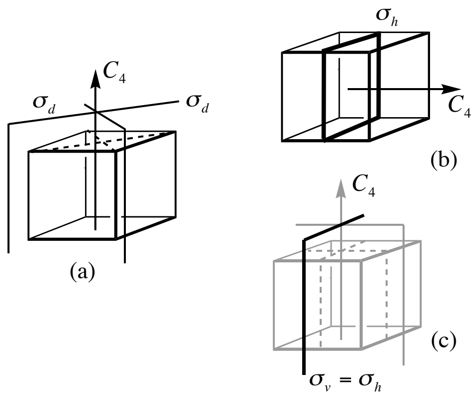


Figure 7 (a) σ_d and (b) σ_h planes

- there are $3\sigma_h$ operations
  - a σ_h mirror plane passes horizontal, or perpendicular to a principle axis (axes of highest C_n) in this case the C_4 axes, thus there are $3C_4$ axes so there must be $3\sigma_h$ mirror planes, **Figure 7(b)**
  - note that each C_4 axis also has two σ_v mirror planes that pass vertically through this axis, however each of these mirror planes is also the σ_h plane for another C_4 axis, and so has already been counted, **Figure 7(c)**

- there are 6S_4 operations
  - each pair of C_4 axis and σ_d mirror plane has an associated improper rotation, the S_4 axis is coincident with the C_4 axis.
  - phase changes are important for improper rotations and it is best to work with pAOs rather than sAO when drawing out these operations. There are two sets of symmetry related orbitals; the equatorial and axial p_π orbitals. These subsets only transform amongst themselves under S_4, **Figure 8**

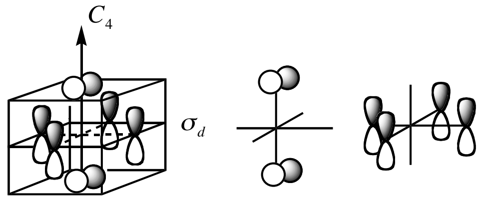


Figure 8 Sets of symmetry related orbitals

  - consider a S_4^1 operation which consists of a rotation of 90º around a C_4 axis and then reflection in the associated σ_h plane.
  - an example of the S_4^1 operation is given in **Figure 9**. For simplicity the effect of the S_4^1 operation has been shown for a single equatorial and axial p_π orbital.
  - notice that if you considered only the equatorial p_π orbitals you might conclude that $S_4^1 = C_2''$, which would be incorrect.

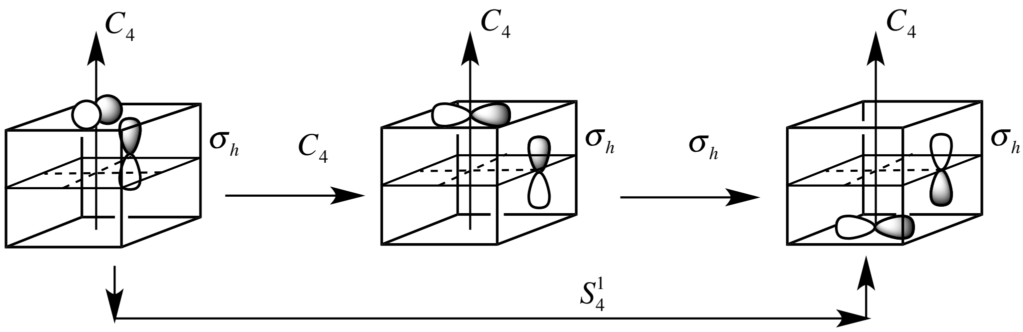


Figure 9 S_4^1 operation

  - working through the various improper rotation symmetry operations (homework) identifies that $S_4^2 = C_2$ and $S_4^4 = E$
  - thus for each S_4 axis there are two unique operations (S_4^1 $S_4^3 = S_4^{-1}$) and hence (as there are 3C_4 axes) there are 6S_4 operations in O_h.

- there are $8S_6$ operations
  - each C_3 axis can also be thought of as having a coincident C_6 and σ_h mirror plane perpendicular to this axis.
  - these are not symmetry elements of O_h because of the staggered arrangement of the three ligands
  - in **Figure 10**, a simplified model is shown with has black dots on the sites that are occupied by ligands
  - consider S_6^1, a rotation of 60° and then reflection in the associated σ_h plane perpendicular to the axis, **Figure 11**

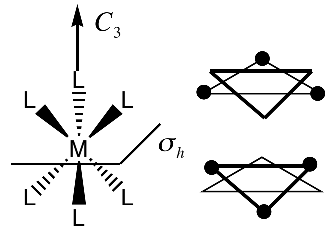


Figure 10 (a) σ_d and (b) σ_h planes

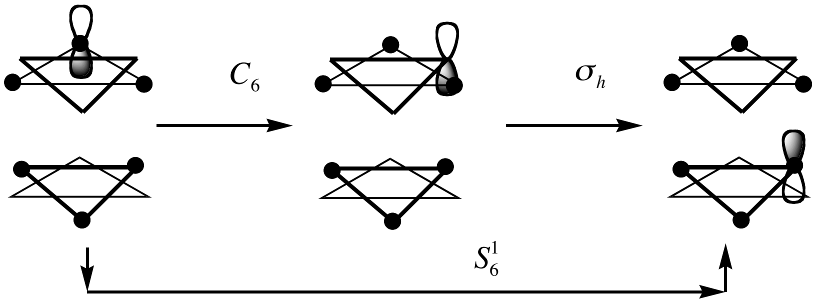


Figure 11 Components of the S_6^1 operation

  - of all the S_6 operations only two are unique S_6^1 and $S_6^5 = S_6^{-1}$ (homework to confirm this)
  - thus for each C_3 axis (of which there are four) there are two associated S_6 operations and hence there are $8S_6$ operations in O_h