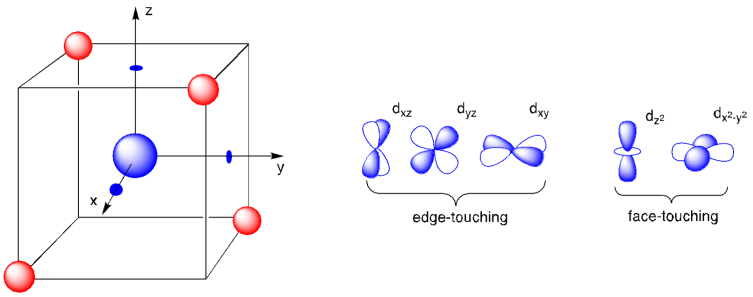
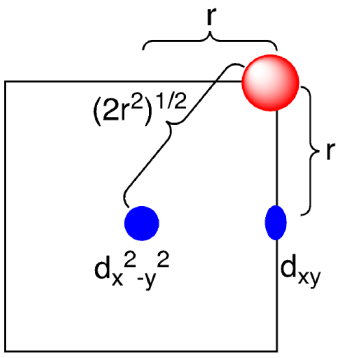
10.3.4: Tetrahedral Complexes

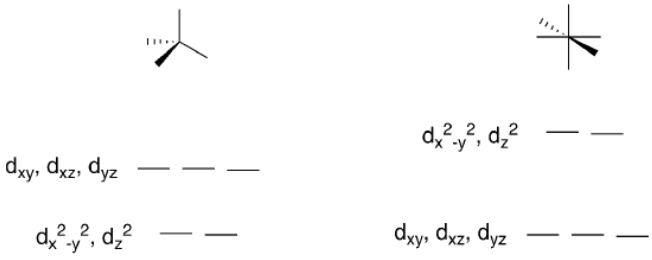
Tetrahedral geometry is even more common in chemistry than square planar geometry. Assessing the orbital interactions in tetrahedral geometry is somewhat more complicated, however, and it is common to proceed directly to a group theory approach. Nevertheless, let's take a look at this geometry and see what we can determine through simple observation before we see the results from a more rigorous approach. To begin, it helps to know that a tetrahedral geometry is defined as having four atoms arranged at alternating corners of a cube around a central atom.



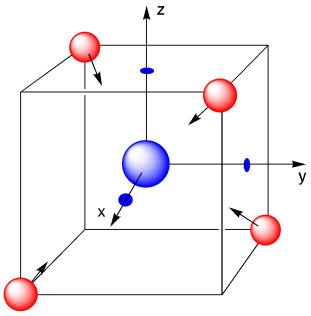
If we consider the orientation of the d orbitals, we find that they fall into two different groups. Although all five orbitals lie off-axis with respect to the ligands, some of them are pointed directly at the edges of the cube (d_{xy}, d_{xz}, d_{yz}) whereas the others point at the faces of the cube ($d_{x^2-y^2}$, d_{z^2}). The edge-touching orbitals lie a little closer to the ligands; we'll define this distance as *r*, which in this case is half the edge length of the cube. The face-touching orbitals are slightly farther away: based on the Pythagorean theorem, they are $r^2 + r^2 = 2\,r^2 = r^2$ away from the ligands.



Based on that simple observation, we might start to think about the dxy, dxz and dyz group as forming the antibonding orbitals upon interaction with the ligands. The dz2 and dx2-y2 would be left as non-bonding orbitals. This result would be exactly the opposite of the octahedral case. We would therefore expect an orbital splitting diagram that is exactly the inverse of the octahedral one. Maybe the splitting between orbital levels would be a little smaller, though, because of the lack of direct overlap between the ligands and the metal orbitals. After all, even the closest set of metal orbitals don't point directly at the ligands like in the octahedral case.

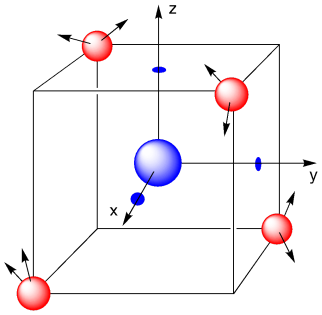


This supposition is confirmed through a group theory approach. We can use vectors pointing along the ligand-metal axes to examine sigma bonding, as shown below. We would subject these vectors to the symmetry transformations in the tetrahedral space group, T_d, shown in the table.



T_d	E	$8C_3$	$6C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ_σ	4	1	0	0	2		$A_1 + T_2$
Γ_π	8	-1	0	0	0		$E + T_1 + T_2$

That analysis leads to the reducible representation for sigma bonding, Γ_σ , shown in the table. This representation reduces to the irreducible representations, $A_1 + T_2$. The d orbitals represented here, the T_2 set, are indeed the d_{xy}, d_{xz} and d_{yz}. The non-bonding d orbitals are the E group, corresponding to d_{z^2} and $d_{x^2-y^2}$.



We can go further with the group theory approach and to determine the reducible representation for pi bonding, Γ_π , also shown in the table. Pi bonding is otherwise even more difficult to assess via simple inspection than was sigma bonding. The resulting representation reduces to $E + T_1 + T_2$. The d orbitals represented here include the expected d_{z^2} and $d_{x^2-y^2}$. Note, however, that they also include the d_{xy}, d_{xz}, and d_{yz} orbitals. That means that in the presence of a pi-donor ligand, the latter set are antibonding with respect to both sigma and pi bonding.

Example 10.3.4.1

Demonstrate these symmetry operations on the drawing of the tetrahedron within a cube shown above.

a. C_3
b. C_2
c. S_4
d. σ_d

Solution