Lecture II: Shapes and Symmetry of Molecules

01-15-2020

Last time, we spoke about tetrahedral and octahedral molecules. Why do they adopt that shape? What other shapes are available and when do they happen?

VSEPR (Valence Shell Electron Pair Repulsion) or the repulsion theory states that the coordination sphere of the central atom adopts the shape that minimizes the repulsion of electron pairs—positions them as far as possible from each other. Lone electron pairs also count in these considerations.

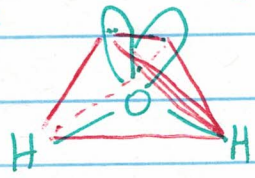
A) Divalent AB_2 system

linear geometry $B-\overset{180^\circ}{A}-B$ $O=C=O$ $H-C\equiv C-H$ } sp-hybridized carbon atoms

Relatively rare with main group elements, but $BeCl_2$ would be an example

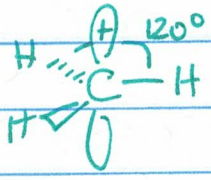
bent geometry

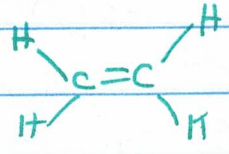
But this is in fact a variant of tetrahedral binding geometry, once two lone pairs are considered too:

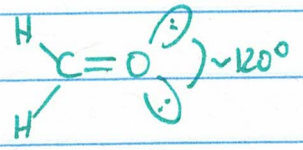


B) Trivalent AB_3 System

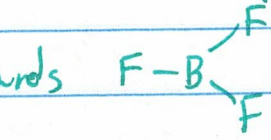
Common for sp^2-hybridized C, N, and O:





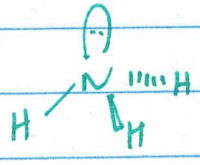


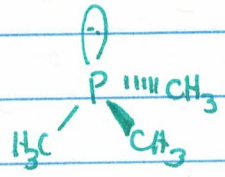
trigonal planar geometry



Also common for electron-deficient boron compounds $F-B(F)-F$

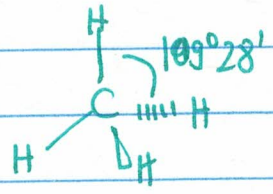
Trigonal pyramid geometry is adopted in NH_3 and its derivatives, as well as in phosphines, but it is also a variant of tetrahedral (tetravalent) geometry:

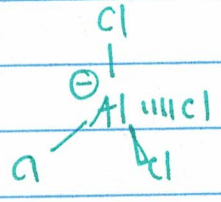


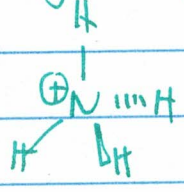


C) Tetravalent AB_4 Systems

Extremely common in organic chemistry — this is the preferred geometry for sp^3 carbon atoms — is the tetrahedral geometry





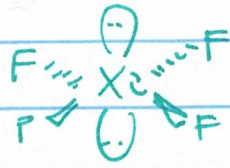


Often seen also in compounds with free el pairs: NH_3, H_2O, ROH

Common in anions: $SO_4^{2\ominus}$ $ClO_4^{\ominus}$ $PO_4^{3\ominus}$

Si^{4+}, Ge^{4+}, Pb^{4+}, Sn^{4+}, $BF_4^{\ominus}$ etc. etc.

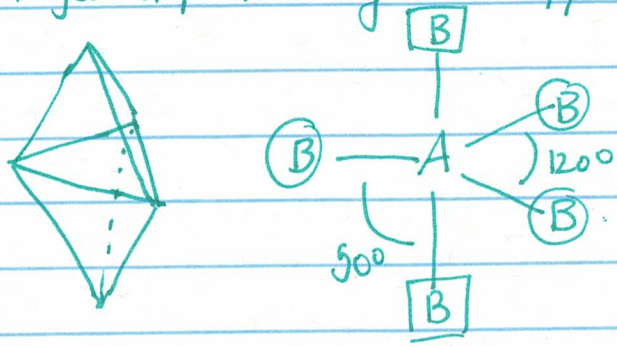
Square planar geometry is rarely seen outside of transition metals, but it is generally caused by some electron density outside of the plane:



In fact octahedral!

D) Pentavalent AB_5 Systems

We leave the domain of organic chemistry now. The most common geometry is trigonal bipyramid:

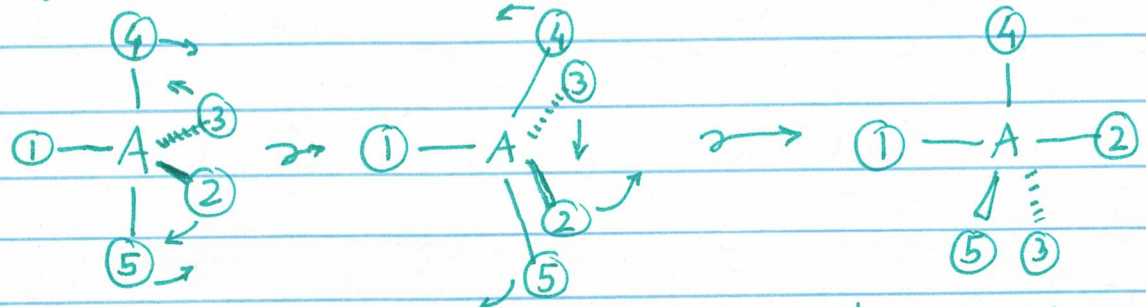


(B) - equatorial @ 120°
[B] - axial @ 90°

not all five ligands are equivalent

Common example for this geometry is PF_6.

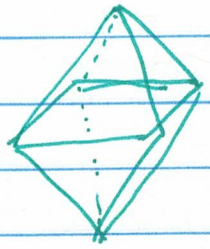
Trigonal bipyramidal complexes are often fluxional:

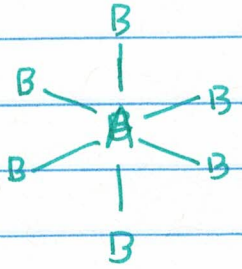


trigonal bipyramid → tetragonal pyramid (square ") → trigonal bipyramid

E) Hexavalent AB_6 and $A(BB)_3$ Systems

Octahedral geometry is very common:





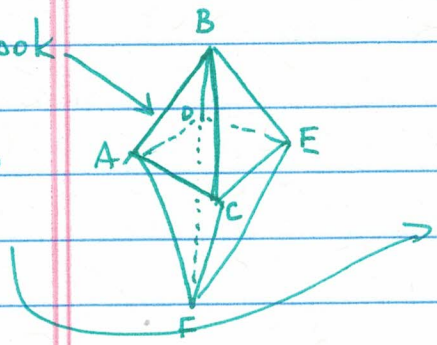
regular, all B ligands are equivalent

Examples: SF_6, $AlF_6^{\ominus}$, $PF_6^{\ominus}$

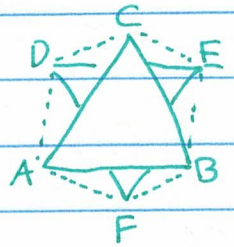
extremely common for transition metals

In some cases, especially with bidentate ligands, the octahedron transforms into trigonal prism. Let's see how that happens:

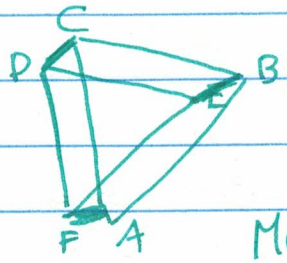
if we look at the triangle ABC



we will see this



Staggered arrangement of two triangles

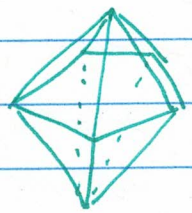


let's make them eclipsed

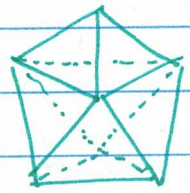
$Mo(carboxylates)_3$ are an example

F) Heptavalent Systems

Three main arrangements are possible



pentagonal bipyramid



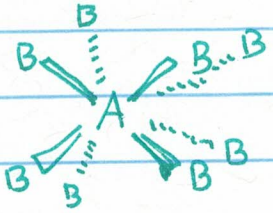
Capped octahedron

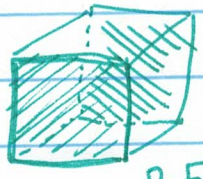
capped trigonal prism

$ZrF_7^{3\ominus}$ seems to act like a capped Octahedron, but all of these geometries are highly fluxional.

G) Octavalent Systems

Cubic:





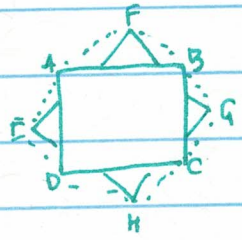
two squares are eclipsed

$PaF_8^{2\ominus}$

make them Staggered

these geometries are generally not available to smaller metals, but actinides routinely adopt them

$U(NCS)_8^{4\ominus}$



square antiprism

H) Nonavalent and Above

CN=9: tricapped trigonal prism: grow a tetrahedron at each side of a trigonal prism

~~ReH9~~ $ReH_9^{2\ominus}$

CN=10: only known for bidentate ligands (eg $K_2[Er(NO_3)_5]$) pentagonal antiprism and other fluxional geometries

CN=12: only known for bidentate ligands (eg $[Mg(H_2O)_6]_3[Ce(NO_3)_6]$) variants of distorted icosahedral geometries

Icosahedron: regular polyhedron with 12 triangular faces