

AP Unit 7 Complex Ions, Isomers & Exceptions to the Octet Rule

I. Coordination Compounds

- are formed by transition metals. **They are often colored and paramagnetic.**

****Paramagnetic:** unpaired e^- (\uparrow), attracted to magnetic fields

Vs. ****Diamagnetic:** paired e^- ($\uparrow\downarrow$), not attracted to magnetic fields

Coordination compounds consist of:

A Complex Ion

- a **transition metal with its attached ligands.**

and a Counter Ion.

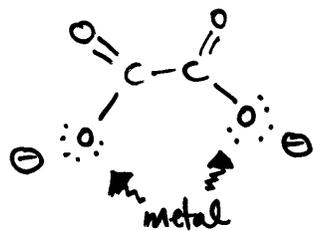
-**anion or cation** used to make the overall compound neutral.

Common Ligands:

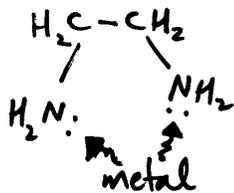
H_2O	aqua or aquo (neutral)
NH_3	ammine (neutral)
CH_3NH_2	methylamine (neutral)
CO	carbonyl (neutral)
NO	nitrosyl (neutral)

F^{-1}	fluoro
Cl^{-1}	chloro
Br^{-1}	bromo
I^{-1}	iodo
CO_3^{2-}	carbonato
CN^{-1}	cyano
OH^{-1}	hydroxo
SCN^{-1}	thiocyano
NO_2^{-1}	nitro

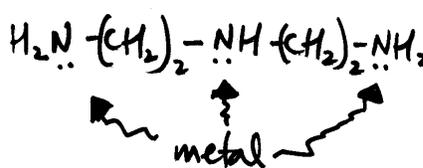
Ligands that attach in more than one position:



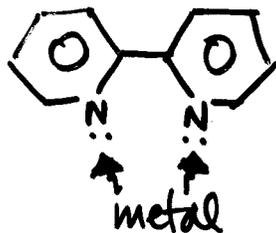
Oxalate



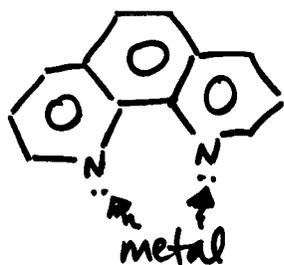
Ethylenediamine
(en)



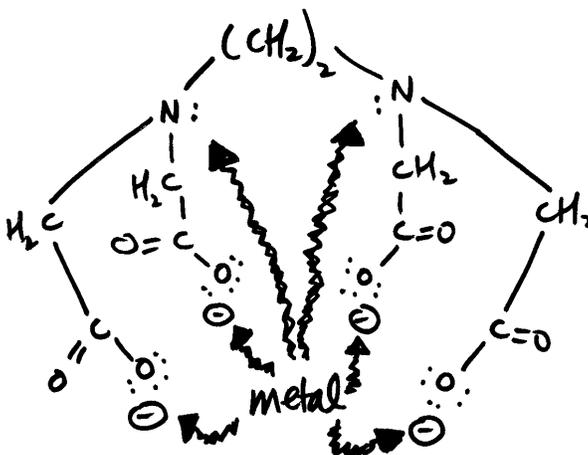
Diethylenetriamine
(dien)



Bipyridine
(bipy)



Ortho-phenanthroline
(o-phren)



Ethylenediaminetetraacetate
(EDTA)

The coordination number is the number of ligands.

The most common coordination numbers are 6, then 4, then 2.

****On the AP test the coordination number (# of ligands) is usually twice the charge on the cation. (1:2 ratio, charge of cation: # of ligands)**

{Not always so in real life.}

Common Coordination Numbers of Metals:

<u>+1 charge</u>	<u>+2 charge</u>	<u>+3 charge</u>
$\text{Cu}^{+1} = 2, 4$	$\text{Cu}^{2+} = 4, 6$	
$\text{Ag}^{+1} = 2$		
$\text{Au}^{+1} = 2, 4$		$\text{Au}^{3+} = 4$
	$\text{Co}^{2+} = 4, 6$	$\text{Co}^{3+} = 6$
	$\text{Fe}^{2+} = 6$	$\text{Fe}^{3+} = 4, 6$
	$\text{Mn}^{2+} = 4, 6$	
	$\text{Ni}^{2+} = 4, 6$	
	$\text{Pt}^{2+} = 4$	$\text{Cr}^{3+} = 6$
	$\text{Zn}^{2+} = 4, 6$	$\text{Sc}^{3+} = 6$

Complex Ions:

$\text{Co}(\text{H}_2\text{O})_6^{3+}$	CoCl_4^{2-}	$\text{Ag}(\text{NH}_3)_2^{+1}$
	Co = +2, X2 = 4 ligands	
Co = +3, X2 = 6 ligands		Ag = +1, X2 = 2 ligands

A Coordination Compound will have ions attached to make the above complex ions neutral.

$\text{Co}(\text{H}_2\text{O})_6\text{Cl}_3$ now neutral, K_2CoCl_4 now neutral
Add 3 Cl^{-1} Add 2 K^{+1}

Ex. 1) Name the following compounds:

a) $[\text{Fe}(\text{NO})_5\text{Br}]\text{Cl}_2$ **Complex ion as cation (+)

complex ion: $[\text{Fe}(\text{NO})_5\text{Br}]$ counter ion: Cl_2
 $5\text{X} (\text{NO} = 0) + 1\text{X} (\text{Br} = -1) = -1$ $2\text{X} (\text{Cl} = -1) = -2$

To make a neutral compound **Fe must be +3**. (notice: since Fe = +3, then $2\text{X}3 = 6$ ligands)

To name it:

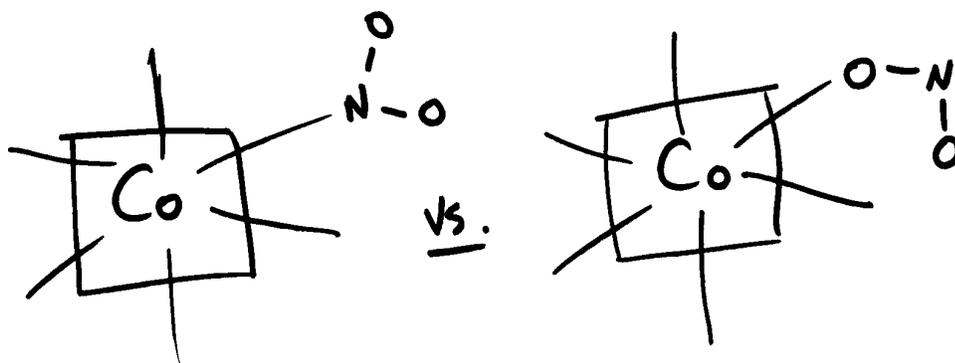
5 NO's 1 Br Iron +3 last Cl's never with a prefix, since added to make the
pentanitroso bromo iron III chloride compound neutral.

b) $\text{Na}_2\text{Cu}(\text{SCN})_4$ **Complex ion as anion (-)

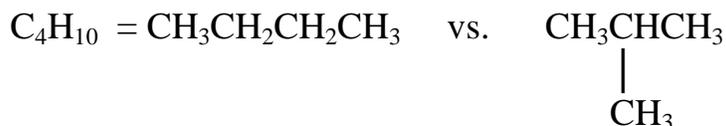
counter ion: Na_2 complex ion: $\text{Cu}(\text{SCN})_4$
 $2\text{X} (\text{Na} = +1) = +2$ $4\text{X} (\text{SCN} = -1) = -4$

To make a neutral compound **Cu must be +2**. (notice: since Cu = +2, then $2\text{X}2 = 4$ ligands.)

2) **Linkage isomers:** The ion is the same, but the attachment point is different.

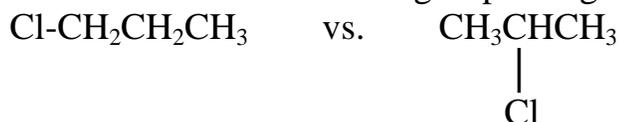


****3) Chain isomers:** The carbon chain is different.



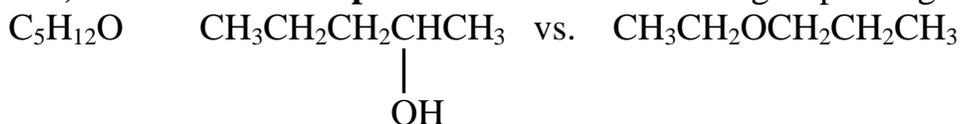
butane (4 carbon chain) vs. 2-methyl propane (3 carbon chain)

****4) Position isomers:** The substituent group changes position.



1-chloro propane vs. 2-chloro propane

****5) Functional Group isomers:** The functional group changes.



Alcohol

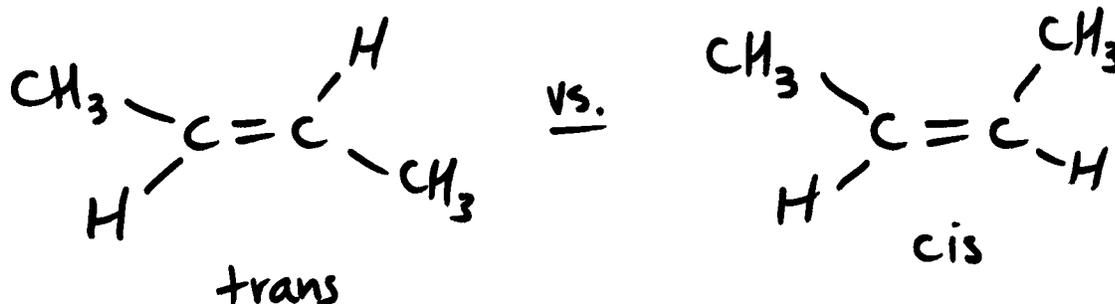
Ether

*********Position and Functional Group Isomers may be called the same in some references!

Stereoisomers (same atoms and bonds, just **spatially different**):

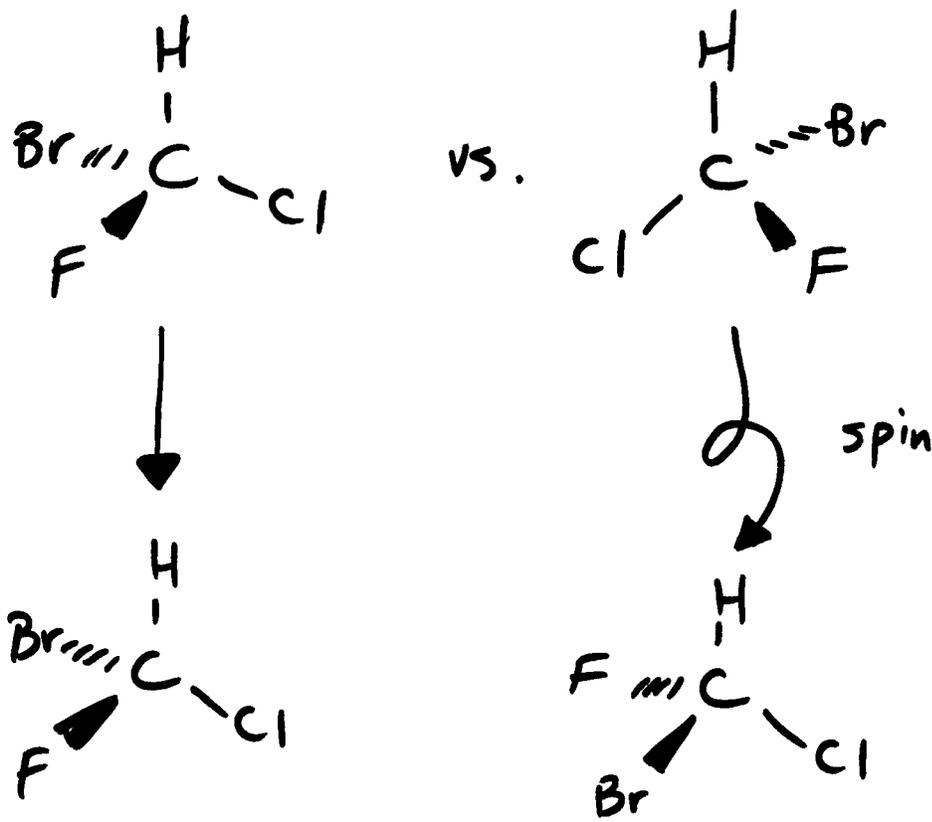
****1) Diastereomers:** are not mirror images of each other.

One type is **Geometric Isomers**. (cis/trans)



2) **Enantiomers: are mirror images of each other, but different molecules.

One type is **Optical Isomers**: These are Mirror Images of each other, but if one is rotated/spun to match the left one. You can see that they are different. (Make yourself models to see it.)



III. Exceptions to the Octet Rule

Remember:

For Lewis Diagrams: **include all electrons and don't be sloppy with them!!

**Double bond = 1 σ (sigma) and 1 π bond, remember sigma is directly between atoms and the pi bond has two lobes when the p-orbitals overlap. (like a hotdog (sigma bond) with a bun (2 pi lobes))

Triple bond = 1 σ (sigma) and 2 π bond, remember sigma is directly between atoms and the pi bond has two lobes when the p-orbitals overlap. (like a hotdog (sigma bond) with 2 buns (4 pi lobes all together)) Review the pictures in the book/old notes!!

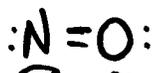
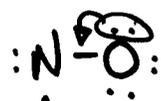
Exceptions:

Molecules and polyatomic ions can have:

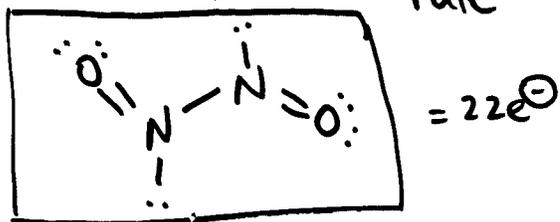
1) An odd number of electrons

A way to follow the octet rule is for the molecules to bond their extra (odd) electrons together making a double molecule, that follows the octet rule. These are called dimers.

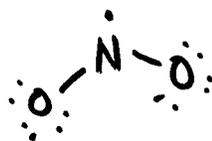
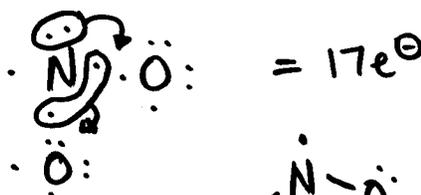
NO



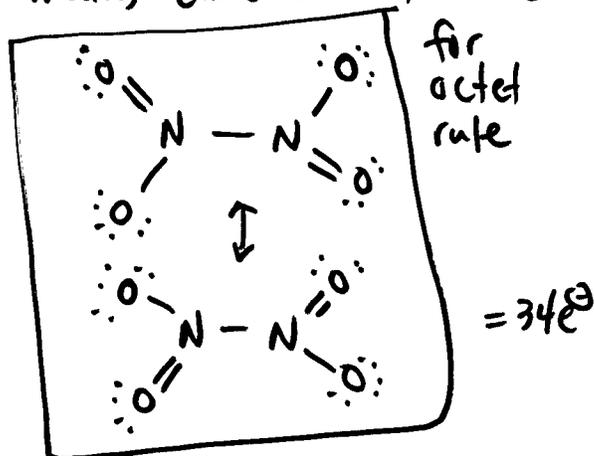
makes dimer with other NO for octet rule



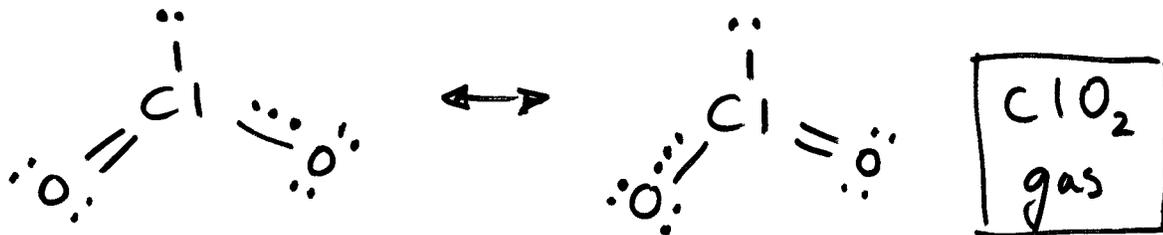
NO₂



makes dimer with other NO₂



But ClO_2 gas (not chlorite ion) does not make a dimer. It is proposed, that it has a double bond with a $3e^-$ single bond in it. This $3e^-$ plus $2e^-$ double bond is weaker, than a normal double bond.



2) Less than 8 electrons

We have seen this for elements in columns #1-2 and the Al column.

**For this we need to look at the formal charge around the atom.

(The same goes for the last category.)

3) More than 8 electrons

We have seen this for all structures having more than a total of 4 bonding and/or lone pairs.

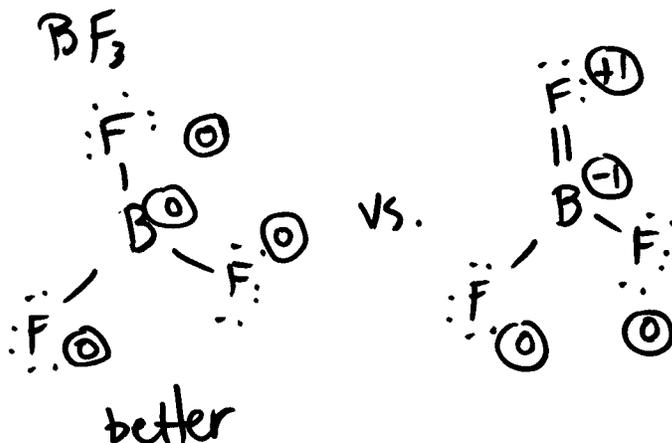
(These were the structures with more than 4 sticks.) But there are some molecules in this category, which could follow the octet rule, but don't.

The rules are thus:

- 1) **Atoms like to have formal charges as close to zero as possible.** (The more atoms with a formal charge of zero in the molecule, the better.)
- 2) **The negative formal charges should be on the most electronegative atoms** in the molecule or ion. Highest to Lowest Electronegativity Atoms (see electronegativity table):
F, O, N, Cl, Br, C, Se, S, I, As, P, Ge, B/Te same, At, Sb, Po, Si

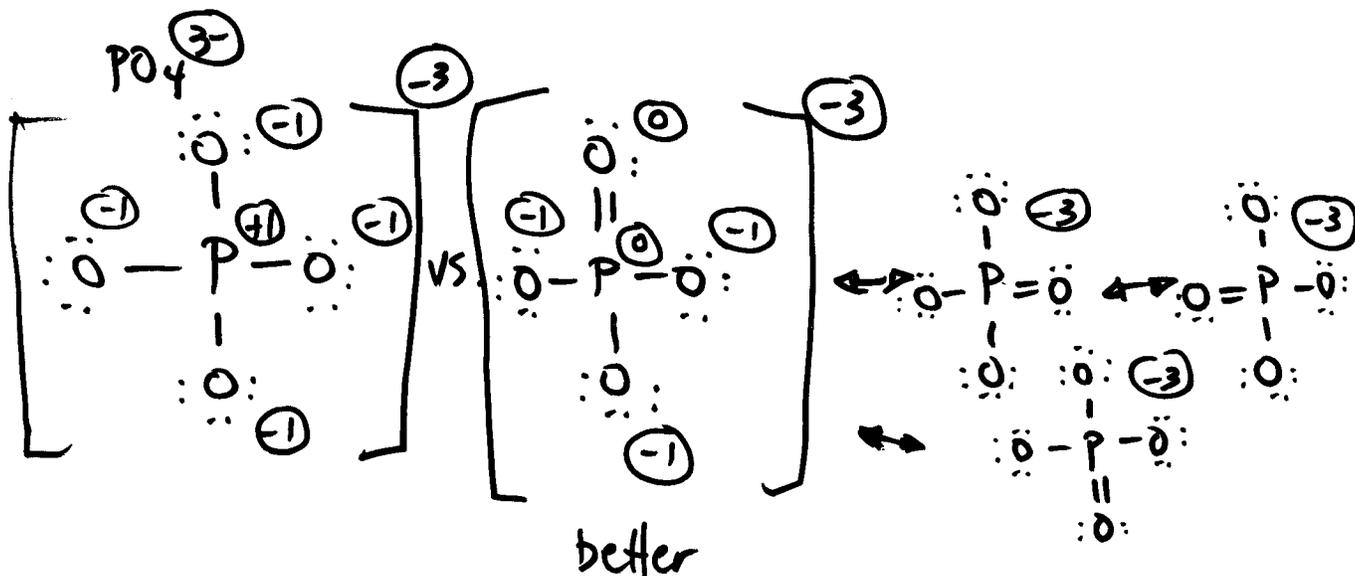
Less than 8 electrons:

Boron trifluoride can follow the octet rule (second picture) with a double bond. But this gives the boron a -1 charge. The more electronegative fluorines should have the negative charge, not the boron. Also the second picture has the least number of 0 formal charges, so the second picture is not favorable!

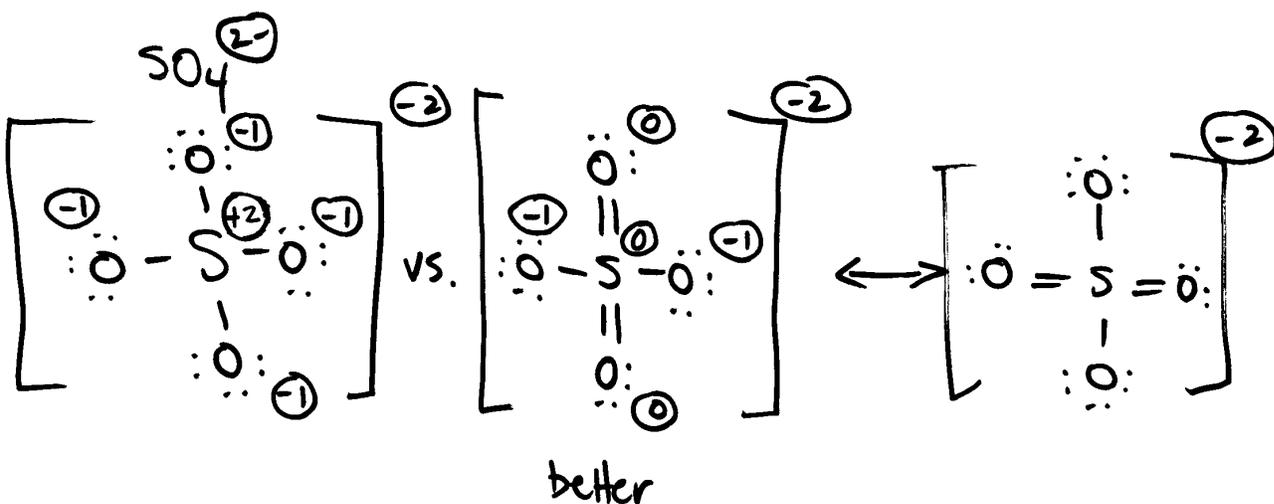


More than 8 electrons:

For phosphate, it can follow the octet rule, if it has all single bonds. The oxygens are more electronegative and have the negative charges, which is correct. But if a double bond is drawn, then there are more atoms with a 0 formal charge. Adding more double bonds would start giving P negative formal charges, which it should not have, since it is not the most electronegative atom. d-orbitals will need to contribute into making the sp^3 hybridized structure's double bond.



For sulfate, it can also follow the octet rule with single bonds. By adding two double bonds, the maximum number of 0 formal charges can be achieved. More double bonds would give sulfur a negative charge, which it should not have. Also remember, 6 bonds/sticks is the maximum. d-orbitals will need to contribute into making the sp^3 hybridized structure's double bond. **But with oxygen, the 6 bond maximum rule can be broken, as you will see later on.** (More d-orbitals will be used to make the extra bonds.)



Shortcut for drawing these structures:

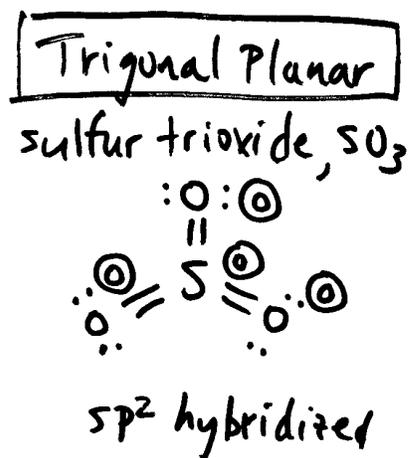
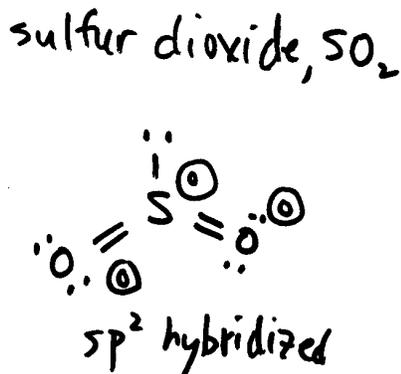
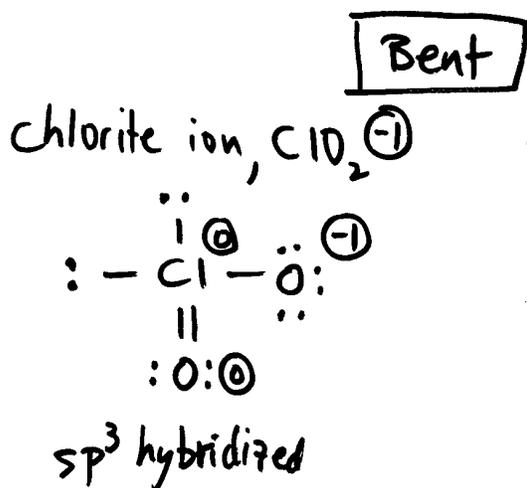
1) Oxygen is greedy and wants two e^- to make its bonds. Have each oxygen use two e^- from the central atom to make single bonds.

2) Then calculate the formal charges. Make enough double bonds, so that the central atom has a formal charge of zero.

**Notice in phosphate P was +1, so make 1 double bond. In sulfate S was +2, so make two double bonds. If the central atom was +3, make 3 double bonds.

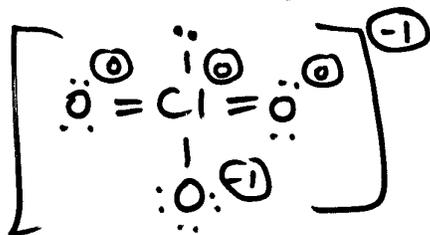
3) All structures with single and double bonds need resonance structures.

Other Exceptions to the Octet Rule:

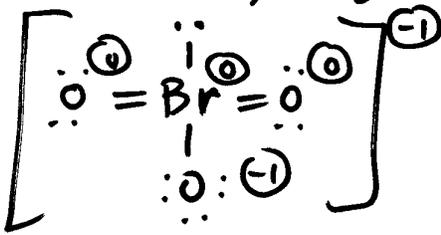


Trigonal Pyramidal, sp^3 hybridized

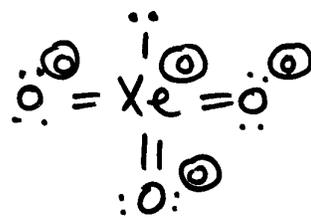
chlorate ion, ClO_3^{-1}



Bromate ion, BrO_3^{-1}



Xenon trioxide, XeO_3

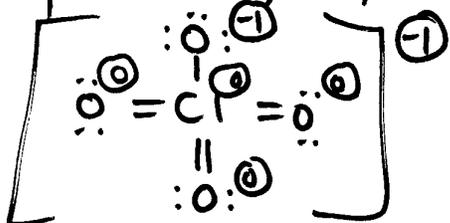


all oxyanions

Tetrahedral, sp^3 hybridized

covalent compounds

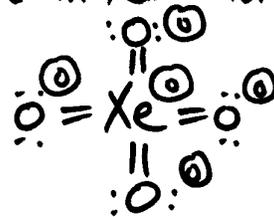
perchlorate ClO_4^{-1}



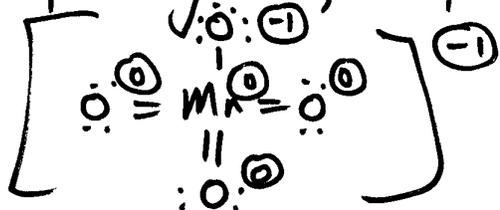
perbromate BrO_4^{-1}



Xenon tetroxide, XeO_4



permanganate, MnO_4^{-1}



End of Notes