Simple Bonding Models – DMH Chap 2

Common Bonding Models

1. Lewis Dot Structures
2. VSEPR
3. Valence Bond Theory (VBT)
4. Molecular Orbital Theory (MOT)

↓ Increased Complexity
Ability to make predictions increases

} Make approximate molecular structure + make predictions + rationalizations about molecular props. + Reactivity

* A bonding model is only as good as the predictions it allows you to make

Experimental Data

Bond Lengths, Bond Angles } X-Ray Crystallography, Neutron Diffraction, Microwave, IR, Raman Spectroscopy

Bond Strengths – Calorimetry

1. Lewis Dot Structures – A highly oversimplified model of bonding

↳ Initially Developed by G. N. Lewis

↳ One of the first great American Chemists

"Valence + Structure of Atoms + Molecules" JACS 1916, 38, 762

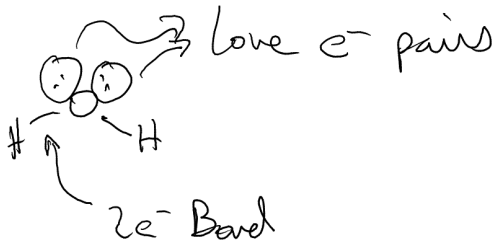
* Bonds exist where atoms share one or more pairs of electrons
* Some species have lone pairs which don't contribute to bonding
* Lone pairs can contribute to molecular shape + reactivity

"Octet Rule"

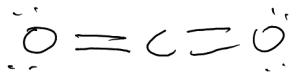
↳ Concept that says 8 valence (s^2p^6) electrons config is especially stable

↳ Exceptions exist!

H_2



H_2O

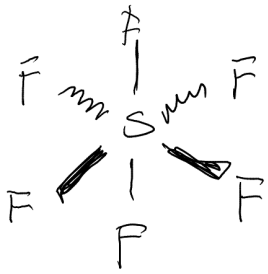


CO_2

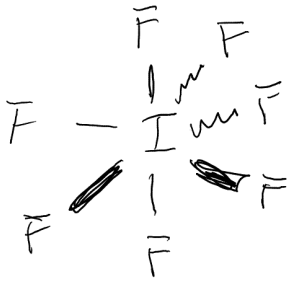
Expanded Octets also possible – d orbitals often invoked

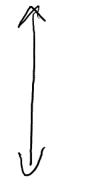
ClF_3 (10 e⁻)

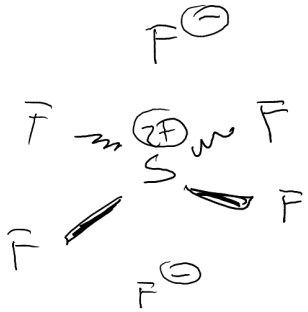
SF_4 (12 e⁻)



IF_7 (14 e⁻)



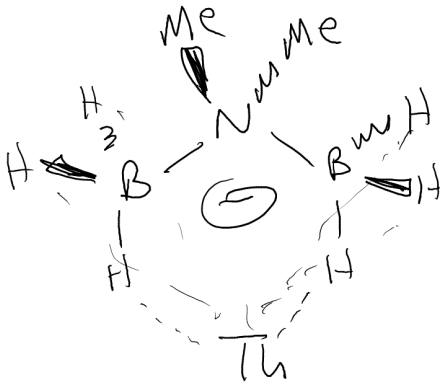




Theoretical limit for coordination about a central atom is 16

TM → limit is 9 bonding interactions

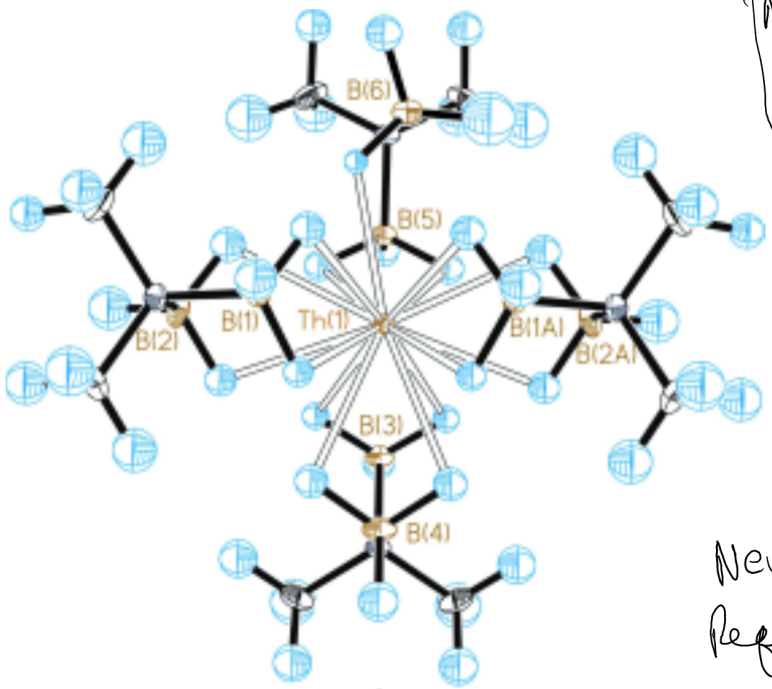
$[Th(H_3BN(Me)_2BH_3)_4]$



Synthesis and Properties of a Fifteen-Coordinate Complex: The Thorium Aminodiboranate $[Th(H_3BNMe_2BH_3)_4]$

Angewandte Chemie International Edition **2010**, *49*, 3379-81.

Not An X-Ray Structure!



1

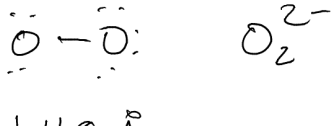
Neutron Diffraction Required to resolve M-H bonds

Molecular structure of $[Th(H_3BNMe_2BH_3)_4]$ from neutron diffraction data. Ellipsoids are drawn at the 20 % probability level. Th orange, B tan, N purple, C black, H blue.

Resonance Structures –

↳ A single Lewis structure is often a poor illustration of molecular structure

Ozone (O_3)



1.48 Å

O_2^{2-}

$O=O$ 1.21 Å

O_2

Ozone Microwave + IR Data

↳ 1 O–O bond of 1.34 Å

A

B

Ψ_A

Arrow denotes Resonance

Blending of 2 Structures

NOT an equilibrium or tautomerization process

C

D

$C_A = C_B >>>> C_C << C_D$

$\Psi(O_3) = C_A\Psi_A + C_B\Psi_B$

Coefficients that denote how important each structure is

The closer in value of C_x to each other the greater overall stabilization that's derived from resonance

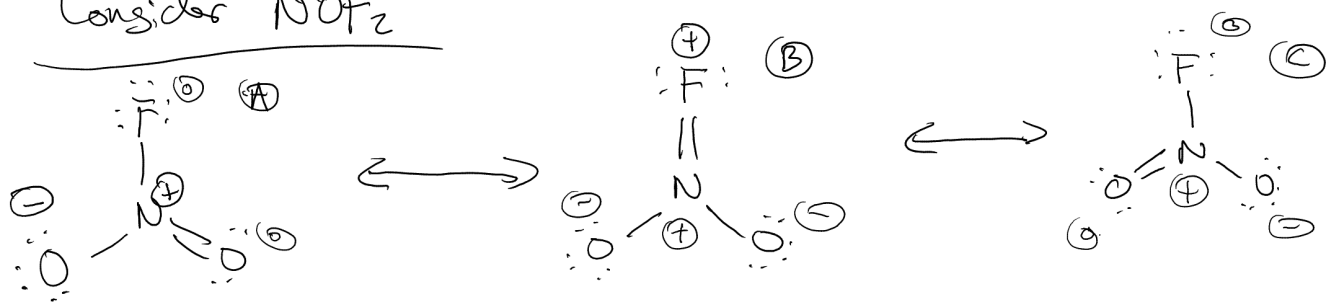
Formal Charge – Can help to assess relevance of resonance structures

↳ Charge of an atom in a molecule if bonding was perfectly covalent

↳ Atoms are considered to "own" half their bonding e^- + all non-bonding e^-

$$FC = \left[\begin{array}{l}\#\text{ of valence} \\ e^- \text{ in free atom} \\ \text{of element}\end{array}\right] - \left(\left[\begin{array}{l}\#\text{ of unshared} \\ e^-\end{array}\right] + \left[\begin{array}{l}\#\text{ of bonds} \\ \text{to that atom}\end{array}\right] \right)$$

Consider NO_2F



ΣFC = total charge of molecule

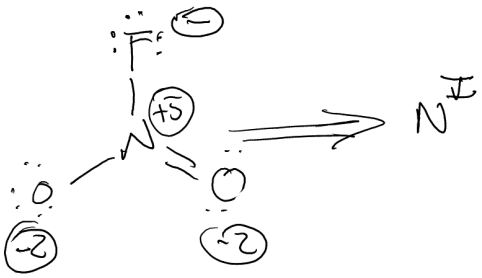
$\psi(NO_2F) = C_A \psi_A + C_C \psi_C \qquad C_A = C_C$

Oxidation Number (State) ω

↳ Over exaggerates rare bonding

↳ we that the most electronegative atom in a bonding pair holds all the bonding e⁻

NO_2F



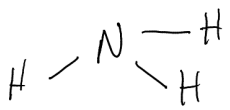
Even though O.S. is a formalism there are physical methods that we can use to inform on the O.S. of atoms in species.

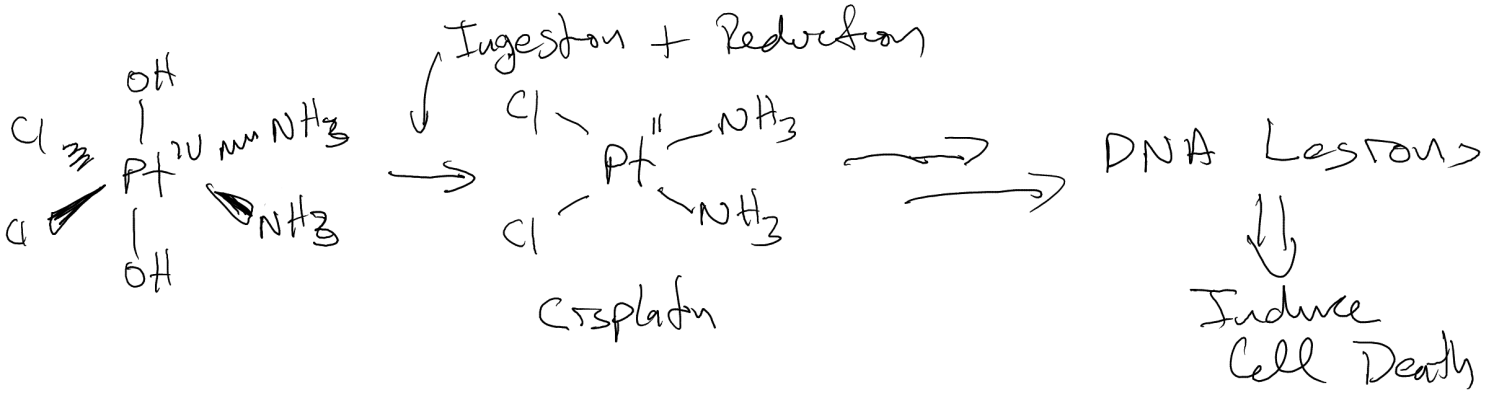
↳ X-Ray Abs Experiments

XAFS – X-Ray Abs. Fine Structure

XANES – X-Ray Abs. Near Edge Structure

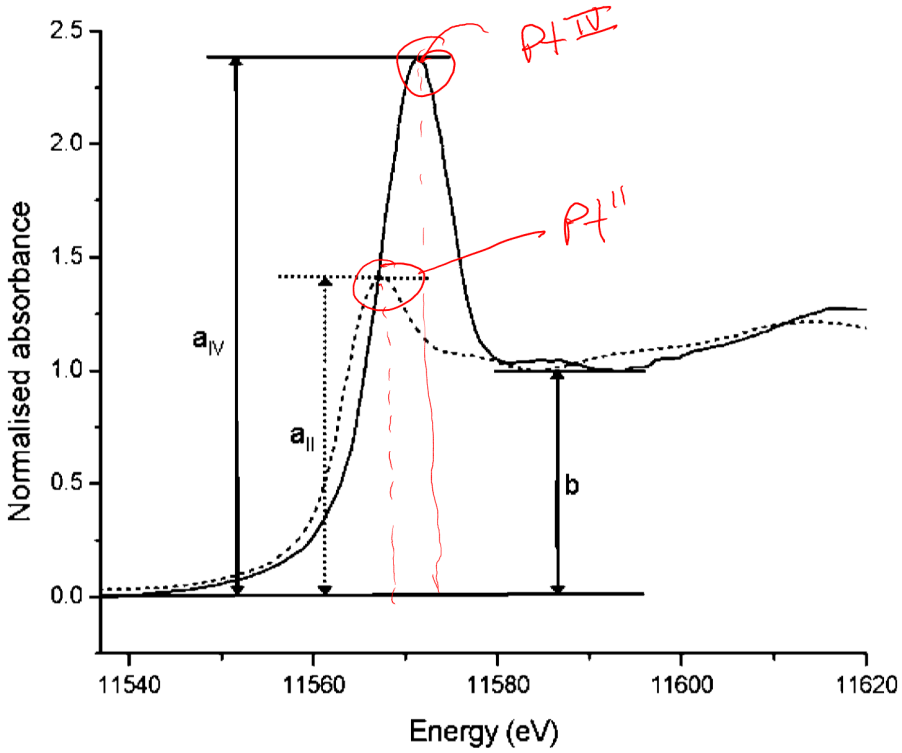
vs.





XANES Determination of the Platinum Oxidation State Distribution in Cancer Cells Treated with Platinum(IV) Anticancer Agents

J. Am. Chem. Soc., **2003**, *125*, 7524–7525.



XANES spectra of Pt(II) (···) and Pt(IV) (—) complexes, showing the difference in peak heights for the two oxidation states, and the parameters a and b used in determining the ratio a/b.