MOLECULAR ORBITALS

Chapter 5

Expectations for MOs

- Draw correct MO diagrams for homonuclear diatomic molecules
- Know the definitions of bond order, HOMO, LUMO, paramagnetic, diamagnetic
- Derive SALCs for a given molecule, be able to match SALCs to central atom orbitals based on symmetry
- Predict an MO diagram for molecules with 3 atoms or more, based on interactions between central atom orbitals and SALCs.
  - We do not expect you to get the relative energy levels exactly right, however, you should properly indicate which orbitals and SALCS participate in bonding/antibonding interactions and which orbitals and SALCs are non bonding

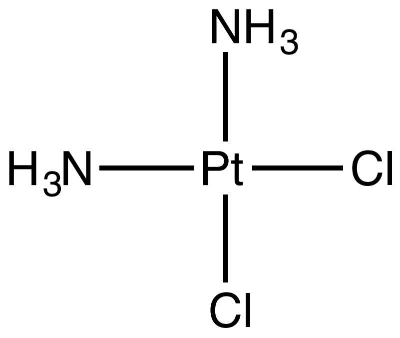
- Orbital energy levels will be provided on the exam, you do not have to memorize these.
- You do not need to know how to use the 'projection operator' (in MFT)

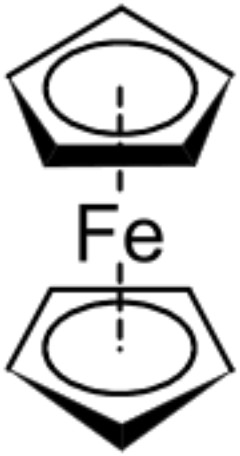
COORDINATION COMPLEXES

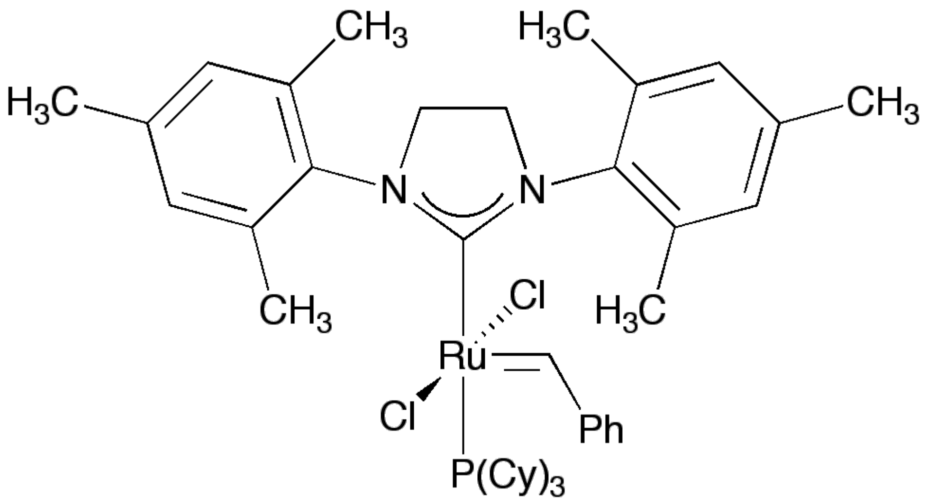
MFT Chapters 6,9,10

Coordination complexes

- Compounds that are composed of a metal atom or ion and one or more *ligands* (atoms, ions, or molecules) that donate electrons to the metal



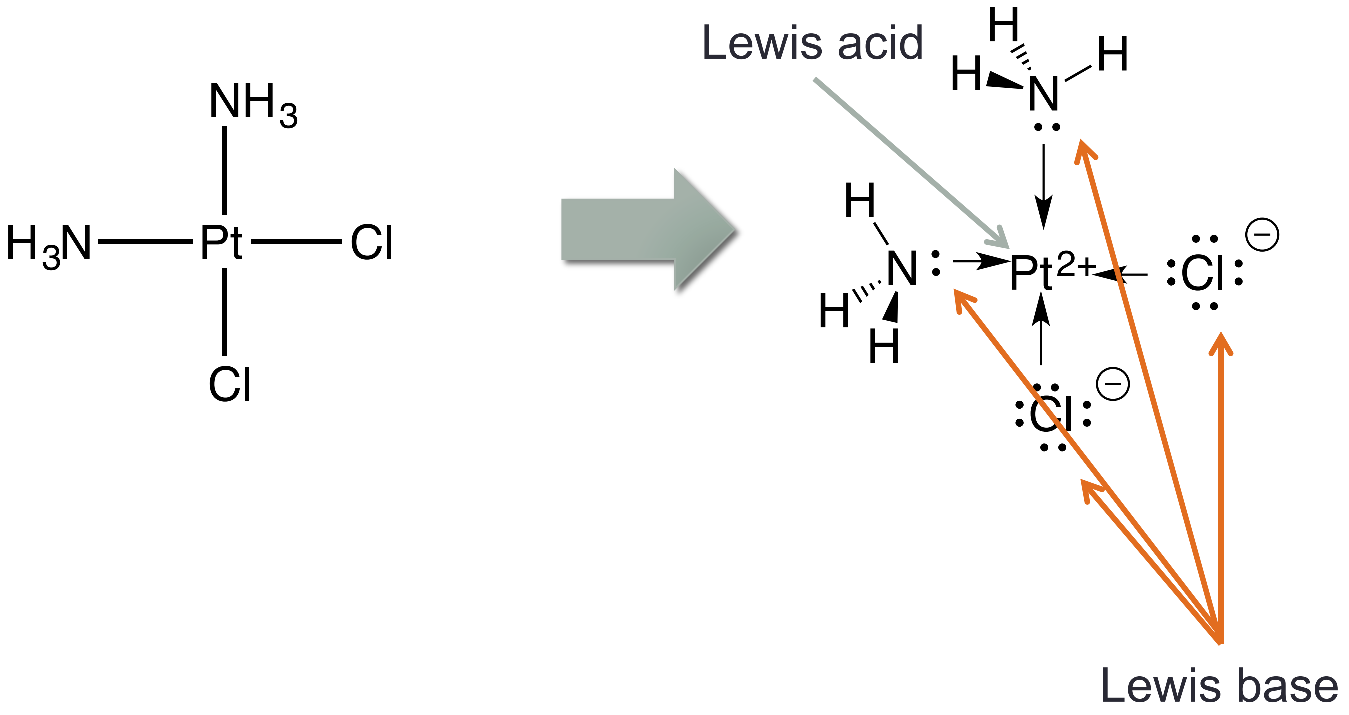




Acid-Base Donor-Acceptor Chemistry

- In a coordination compound, the metal center (M^{n+}) acts as a **Lewis acid** and the ligand (L) acts as a **Lewis base**

$$M^{n+} \longleftarrow :L$$



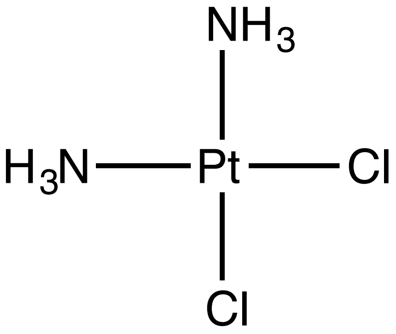
See Section 6.4 for more discussion

Bonding in coordination complexes

- You are familiar with covalent and ionic bonds
  - Covalent bond: electron pair in bond is shared between two atoms, typically one electron is donated from each atom
  - Ionic bond: electrostatic interaction between oppositely charge ions (electrons NOT shared)
- In transition metal complexes, the bonds are described as *coordinate covalent* or *dative* bonds
  - In the Lewis acid-Lewis base interactions in these compounds, the electron pair in the ligand (the ligand HOMO – highest occupied molecular orbital) is interacting with an empty orbital on the metal center (the LUMO – typically d orbitals)
  - In this bond, the electrons are shared by the metal and ligand, but both electrons come from the ligand

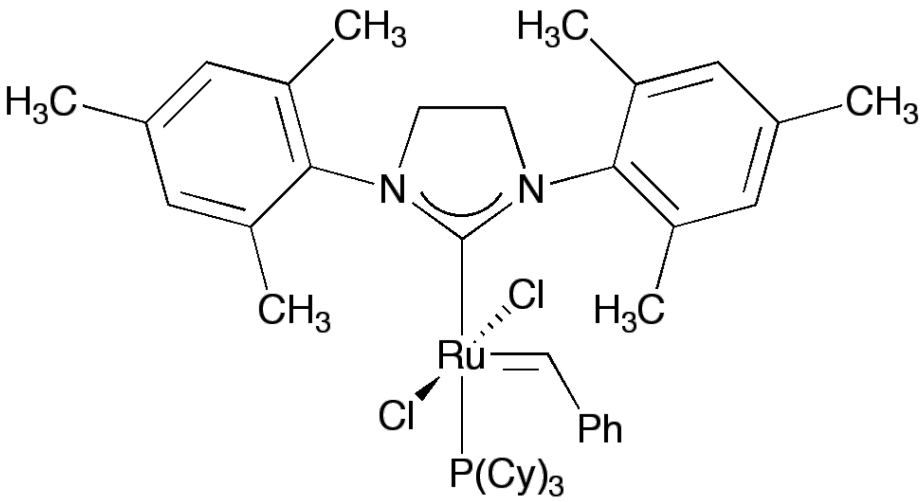
Coordination Complex Terminology:

- The following slides are the main terminology/nomenclature things I expect you to know, you do not need to memorize all the nomenclature rules in Ch 9
- Coordination number: how many ligands are attached to the metal center

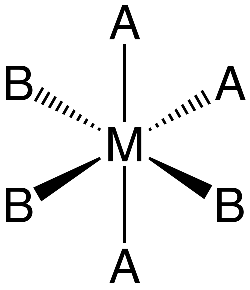


$$\begin{array}{ccc} & \mathrm{NH_3} & \\ & | & \\ \mathrm{H_3N} - & \mathrm{Pt} & - \mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}$$

4



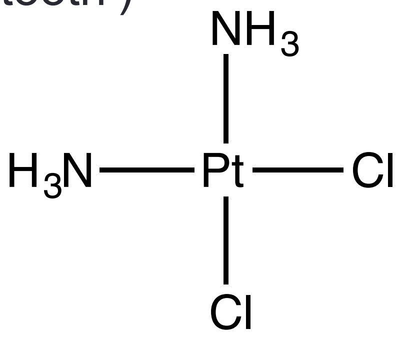
5



6

Ligand terminology

- Monodentate: ligand has only one point of attachment
  (‘one tooth’)

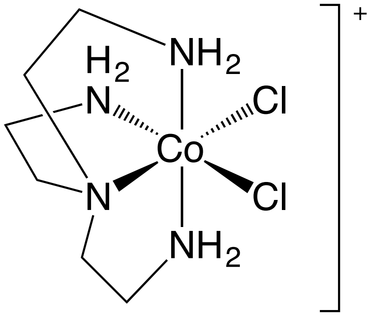


$$\begin{array}{ccc} & \mathrm{NH_3} & \\ & | & \\ \mathrm{H_3N} - & \mathrm{Pt} & - \mathrm{Cl} \\ & | & \\ & \mathrm{Cl} & \end{array}$$

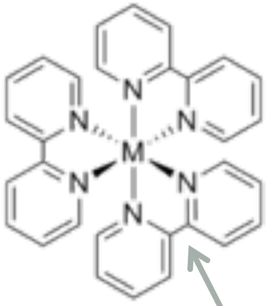
All ligands in cis platin are monodentate

Ligand terminology

- Polydentate or chelating ligands: ligand contains multiple points of attachment to metal ions



Tetradentate ligand/chelate



Bidentate ligand/chelate

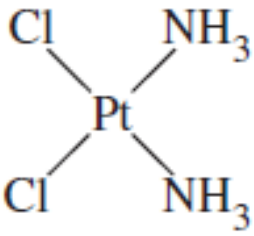
‘chelate’ comes from the Greek word *khele* for crab claw

- Chelate ring: how many atoms comprise a ligand-metal-ligand interaction in a chelating ligand

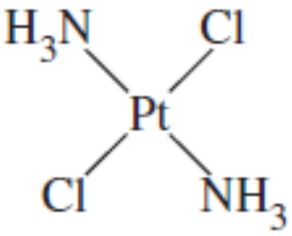
Isomerism in coordination complexes

- A certain ligand set may be able to arrange itself in different ways around a metal center
- For full set of isomer types, see MFT Section 9.3

- **Stereoisomers**: *cis* and *trans*



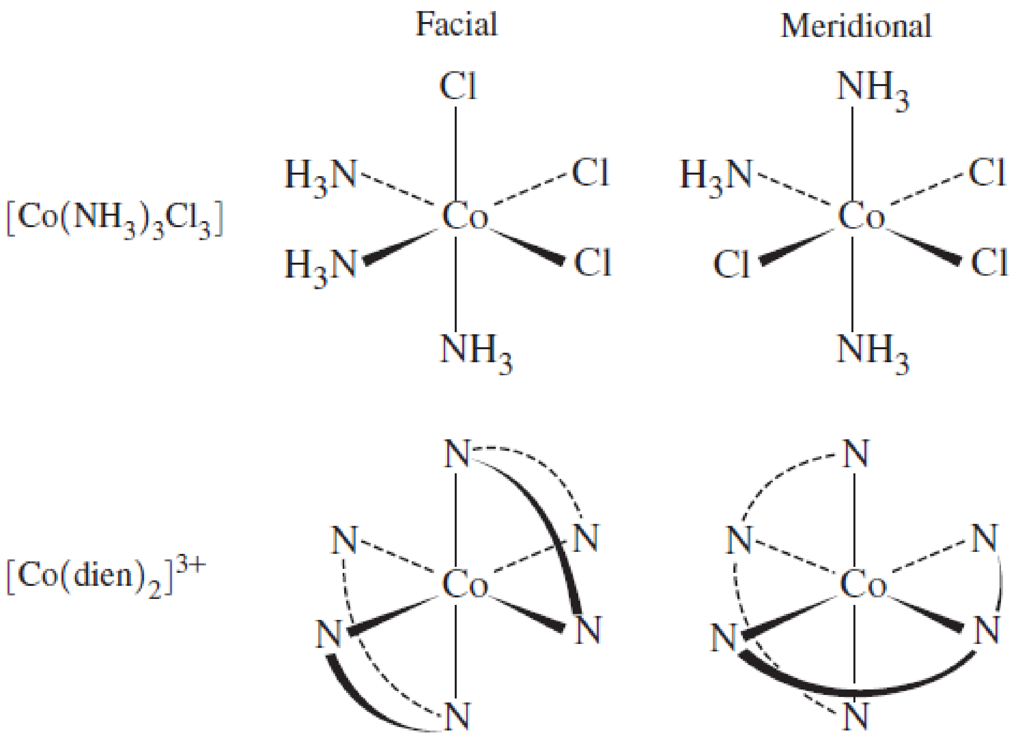
cis
(cisplatin)



trans

Isomerism in coordination complexes

- **Isomerism in 6-coordinate $ML_3L'_3$ complexes:** *mer* and *fac* isomers (meridional and facial)



Bonding in octahedral metal complexes

- We are going to focus our attention first on bonding in octahedral metal complexes and its effects on
  - d orbital energies of the metal centers
  - properties of these complexes (magnetic moment, electronic spectra)

- Simplified view: Crystal Field Theory

- Better description: Ligand Field Theory (uses molecular orbital theory!)

Crystal Field Thoery

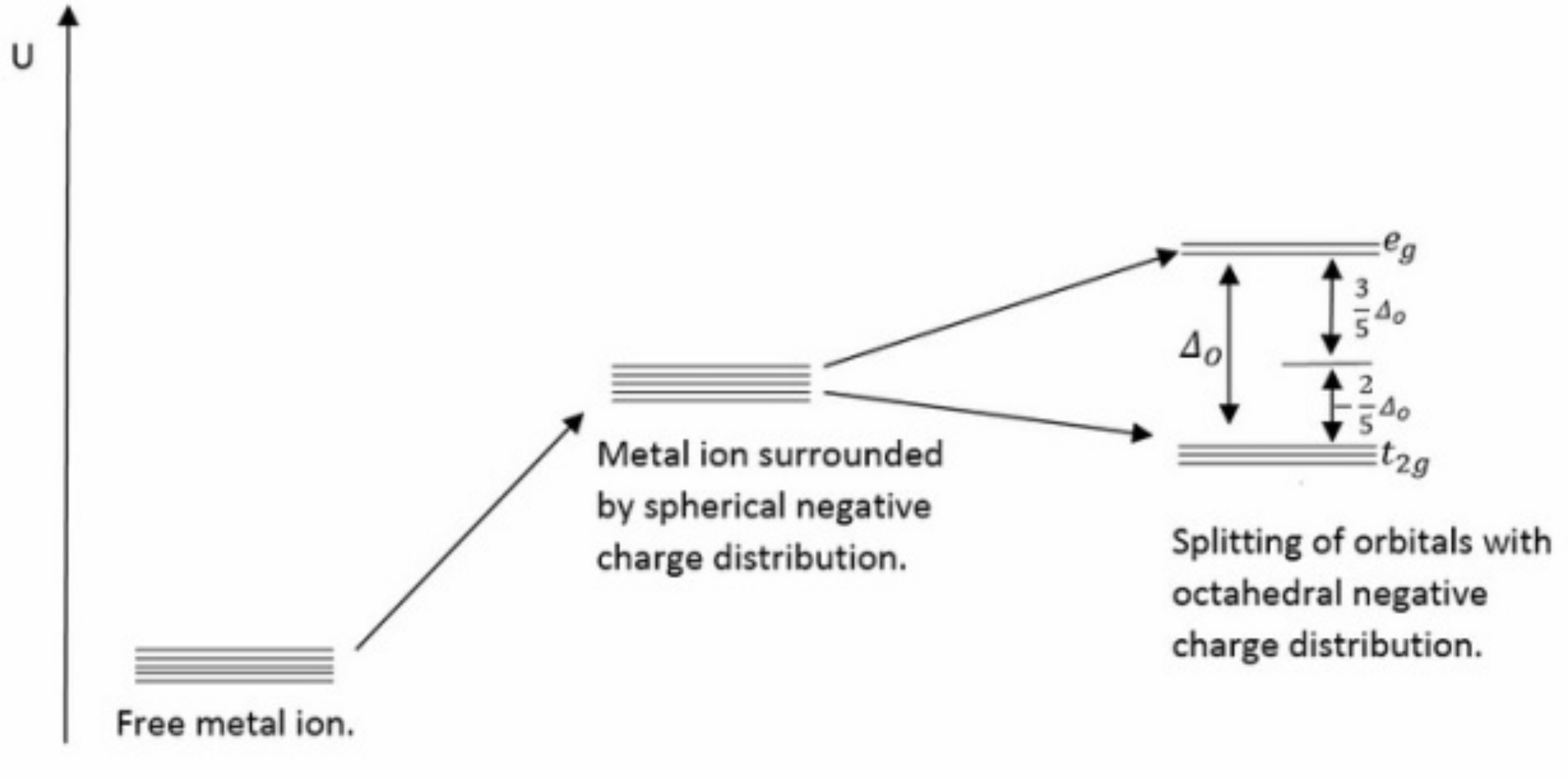
- A purely electrostatic approach that treats metal complexes in an oversimplified manner:
  - Ligands are treated as points of negative charge
  - Metal is treated as a positive charge
    - Overall attractive interaction between the +/- charges leads to complex formation and stability
    - Also a repulsive interaction between electrons from the ligands and electrons from d orbitals
- (Think of CFT as a metal complex analogue to Lewis dot structures-it can get you to the right answer but isn't a full view of the actual bonding in a complex)

Crystal Field Theory

- Repulsive Forces
- 1) d orbitals “feel” a repulsive interaction from ligands that change the energy levels of the d orbitals
- 2) Extent of the repulsive interaction for each d orbital depends on where the ligands are in space (geometry!!!)

- The result is that depending on the geometry, different d orbitals will have different relative energies

Octahedral crystal field splitting

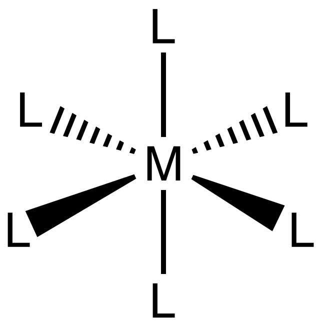


Crystal Field vs. Ligand Field Theory

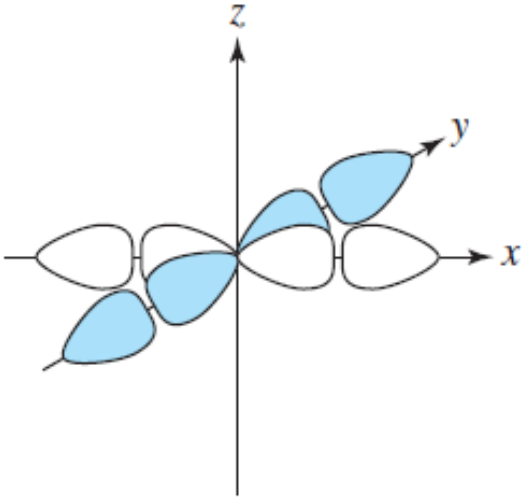
- Crystal Field Theory: oversimplified but useful approach, just uses electrostatics

- Ligand Field Theory: builds on CFT, but considers the shapes of both the metal and ligand orbitals, and their potential interactions, to further explain d orbital splitting (uses concepts from molecular orbital theory)

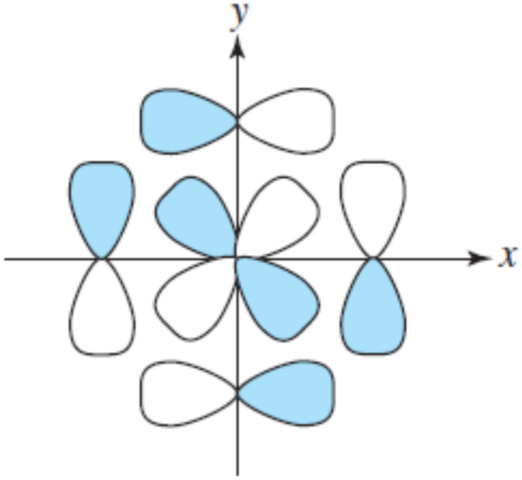
Sigma and pi interactions in octahedral complexes



Sigma bonding interaction between two ligand orbitals and metal d_{z^2} orbital



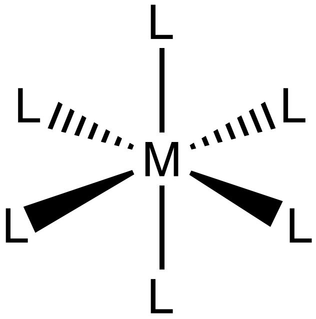
Sigma bonding interaction between four ligand orbitals and metal $d_{x^2-y^2}$ orbital

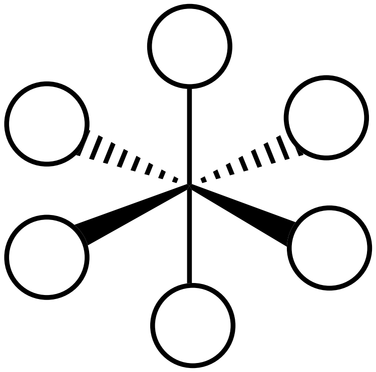


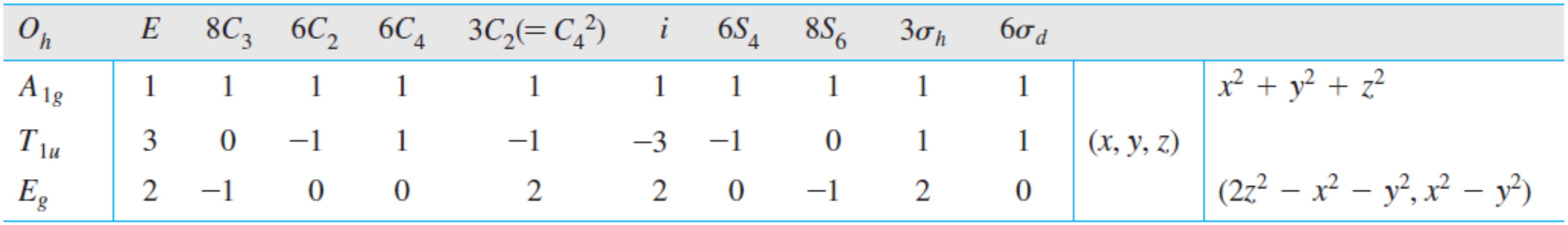
Pi bonding interaction between four ligand orbitals and metal d_{xy} orbital

LFT approach to octahedral metal complex bonding (MO approach)

- Time to derive SALCs for an ML_6 complex!
- For now, we will just consider σ interactions between ligand and metal. You can derive SALCs by finding Γ_s
- The end result after using reduction formula?
- $\Gamma_s = A_{1g} + T_{1u} + E_g$







O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$

MO diagram of octahedral metal complex, sigma interactions only