1 Morning class week 6 day 4: transition metals and their orbitals

1. **Essential facts about transition metals**

   (a) Chem 2070 transition metal compounds have a transition metal atom at the center surrounded by *ligands*. Ligands are main-group molecules such as H_2O, CO, NH_3, H_2O as well as the main group anions I^-, F^-, Cl^-, Br^-, O^{2-}, S^{2-}, OH^-, SCN^-, and CN^-. The main group ligands obey the octet rule all by themselves.

   (b) The metal and the ligands are attached to one another through a combination of both the Coulombic ion-dipole interaction/ion-ion bonds *and* de Broglie wave length lengthening (ie., covalent) bonds. The more ionic of these attachments are called *coordination bonds*.

   (c) The six most common transition metal geometries are the octahedral, tetrahedral, trigonal-bipyramid, square planar, square, and linear geometries. The octahedral is the most common. Pictures of all six are shown below.

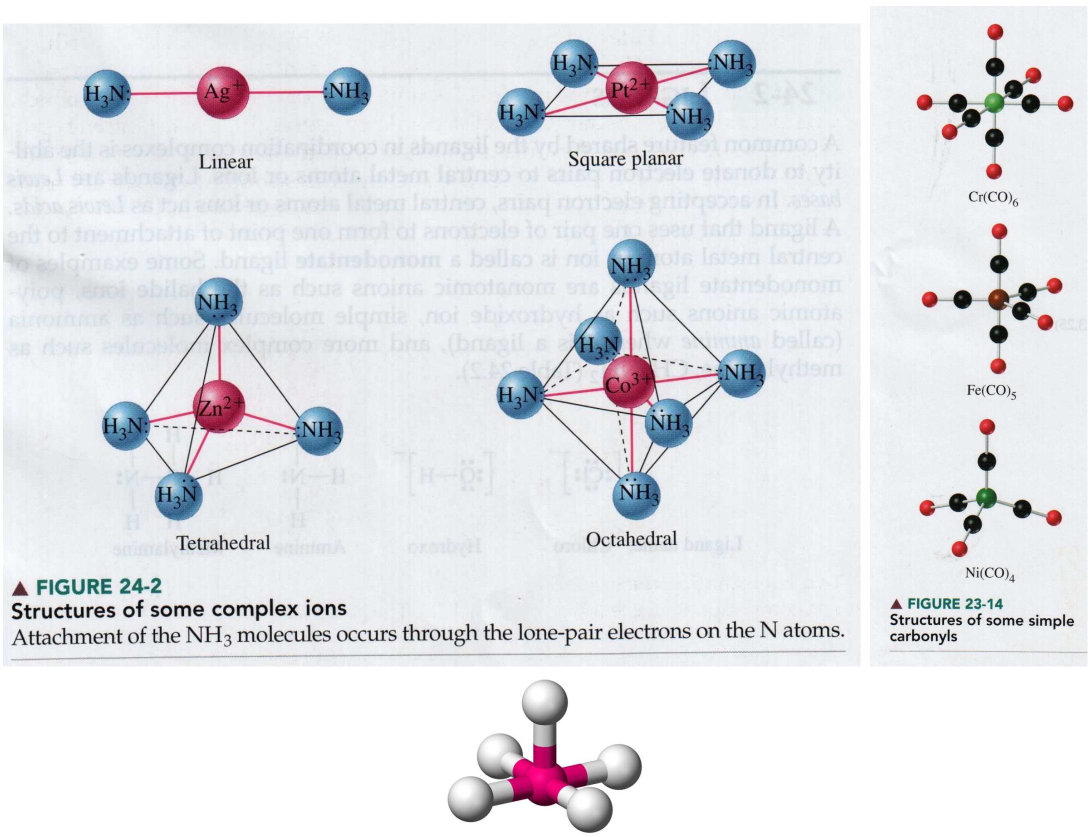

Figure 1: The six most common transition metal geometries, the square pyramidal geometry shown on the bottom.

   (d) Determining the transition metal ***d*-electron count** requires determination of the transition metal oxidations state. This in turn requires knowing the correct octet-rule-based charge to each of the main group ligands.

   Example: The compound $PtCl(CN)_2NH_3{}^{1-}$: Octet rule requires the charges of the ligands to be Cl^-, CN^- and neutral NH_3. The four ligands in the compound require together three additional electrons $(3 = 1 + (1 \times 2) + 0)$. One of these additional electrons derives from the overall charge of the ion, which in this case is -1. Two electrons need be taken from Pt. Pt is therefore Pt(II). **For**

transition metal atoms in transition metal compounds, all remaining transition metal valence electrons are ALWAYS assigned to the valence d-orbital.. Neutral platinum has ten valenece electrons. Pt(II) d-electron count is therefore d^8.

(e) Please find the d-electron count for the following transition metal species:

i. $Co(CO)_4^-$
ii. $CoCl_4^{2-}$
iii. CoF_6^{3-}
iv. $MnBr_2(H_2O)_2$
v. $Mn(CO)_5Cl$
vi. $Cr(NH_3)_6^{3+}$
vii. $K_4[Co(CN)_4]$. In this compound the K atoms are not bound to the Co atom. They are however oxidized.

(f) Please review the above information.

2. **Transtion metal compound hybridization** was discussed in yesterday's class. Chem 2070 may require for you to master two different transition metal electron bonding schemes: transition metal hybridization and d-orbital energy diagrams.

(a) *Octahedral complexes:* The hybridization scheme is d^2sp^3. The d-orbitals involved are d_{z^2} and $d_{x^2-y^2}$. Example: $Cr(CO)_6$. d^6 is the most stable octahedral d-electron count.

(b) *Trigonal bipyramidal complexes:* The hybridization scheme is dsp^3 or better yet $(dp)(sp^2)$. The d-orbital is the d_{z^2} orbital. Example: $Fe(CO)_5$.

(c) *Square planar complexes:* The hybridization scheme is dsp^2. sd^3 also plays a role. The d-orbital is $d_{x^2-y^2}$. Example: $IrClCO(PH_3)_2$. Square planar compounds are often d^8.

(d) *Tetrahedral complexes:* The leading term in the hybridization scheme is sp^3. Example: $Ni(CO)_4$.

(e) *Linear complexes:* The leading term in the hybridization scheme is *sp*. *dp* also plays a role. Example: $Hg(CH_3)_2$. $d^{10}$is the most stable linear d-electron count.

3. **d-orbital energy diagrams**

(a) The second type of transition metal electron bonding scheme is the *d-orbital energy diagram*. It can be thought to be based on a combination of both the electrostatic interactions *and* the orbital mixings between the d-orbitals and the ligand orbitals. In Chem 2070 you may be required to know the connection between transition metal hybridization schemes and d orbital energy diagrams.

(b) Please derive the d-orbital energy diagrams for the following geometries. State the connection to the d-orbtial hydridization schemes.

i. Octahedral geometry
ii. Square pyramidal geometry
iii. Square planar geometry
iv. Tetrahedral geometry
v. Linear geometry
vi. Trigonal bipyramidal geometry

(c) Please review the above information.