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 H₂O, CO, NH₃, H₂O as well as the main group anions I⁻, F⁻, Cl⁻, Br⁻, O²⁻, S²⁻, 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 (i.e., 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.

(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)$_2$NH$_3$$^-_1$: Octet rule requires the charges of the ligands to be Cl⁻, CN⁻ and neutral NH₃. 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).
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 valence 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)$\text{L}^4$
   ii. CoCl$^2$\text{L}$^2$
   iii. CoF$^3$\text{L}$^6$
   iv. MnBr$^2$(H$^2$O)$_2$
   v. Mn(CO)$^4$Cl
   vi. Cr(NH$^3$)$_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. Transition 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 $d_{x^2}$ and $d_{y^2}-y^2$. 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 $dsp^2$. $sq^3$ 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-orbital hybridization 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.