Intro to Transition Metal Complexes (CH 21)

• Transition metal complexes exhibit properties quite at odds with those seen in other chemical compounds. Simply described as the combination of a metal cation and a group of Lewis base ligands (usually 4 or 6, though many other numbers are known), these compounds of formula ML₄⁺⁺ :
• Are often colored. Color is a rare phenomenon at the chemical compound level. Most compounds are colorless.
• The color will vary depending on the ligands and the metal and its oxidation state
• Variable valence and differing structures (octahedral, tetrahedral, and square planar) are seen
• Stable paramagnetism and, like color, variation in magnetic properties with variation in ligands is observed
• Given the nature of the possible ligands as well as other factors, metal ligand complexes are often quite labile. That is, ligands are added/removed/replaced relatively easily

Valence Bond Theory

• VBT descriptions of TM complexes are relatively straightforward, but one must keep in mind that they are not predictive, but rather constructed based upon known properties of the complex (its structure, magnetism, etc)
• In constructing the description there are two primary issues
  – The metal cation is stripped of its valence s electrons. It is of primary importance that the metal electron count be properly determined.
  – The ligand and metal electrons do not “mix” as the ligand is bringing in electron pairs in the formation of the Lewis acid-base adduct
• There are 14 orbitals available to the metal d s p d

Example

• A Co³⁺ complex is octahedral and has 3 unpaired electrons—what is its VBT description?
• Co³⁺ is d⁷
• The metal electrons are placed in the d orbitals in accordance with the stated spin information
  – 1 1 1 1 1 1 1 1 1 1 1 1 1 1
  – Next, the six electrons pairs from the ligands are added
  – 1 1 1 1 1 1 1 1 1 1 1 1 1 1
  – The complex is described as high spin, outer sphere, sp³d⁶
• An Fe^{2+} complex is octahedral and has no unpaired electrons-what is its VBT description
  • Fe^{2+} is d^9
  • The metal electrons are placed in the d orbitals in accordance with the stated spin information
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - Next, the six electrons pairs from the ligands are added
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - The complex is described as low spin, inner sphere, d^9sp^3

• An Ni^{2+} complex is tetrahedral and has 2 unpaired electrons-what is its VBT description
  • Ni^{2+} is d^8
  • The metal electrons are placed in the d orbitals in accordance with the stated spin information
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - Next, the four electrons pairs from the ligands are added
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - The complex is described as high spin, sp^3

• An Ni^{2+} complex is square planar and has no unpaired electrons-what is its VBT description
  • Ni^{2+} is d^8
  • The metal electrons are placed in the d orbitals in accordance with the stated spin information
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - Next, the four electrons pairs from the ligands are added
    - \[ \begin{array}{ccccccc}
    & & & & & & \\
    \text{metal} & \text{ligands} \\
    \end{array} \]
    - The complex is described as low spin, dsp^2

Since it seems to work well, what's wrong with VBT?
Metal Bonding VBT Summary

- The unique properties of TM complexes require a different bonding description than that used for other compounds
- VBT approaches the problem by dividing the electrons into two groups: the metal valence electrons and the electron pairs provided by the ligands
  - The metal electrons are distributed among the valence metal orbitals according to identified properties of the complex:
    - structure: octahedral, tetrahedral or square planar
    - high spin or low spin - or the number of unpaired electrons
    - inner or outer sphere
  - The ligand electron pairs are then placed in the next available orbitals
- Although this generally leads to a correct distribution, it is "after the fact" and not predictive. Further, it provides no real basis for why the complexes vary or the source of the color variation - a defining property of such compounds.

Why does something appear colored?

- The complex must be able to selectively absorb visible radiation
- There must, therefore, by some type of energy differential within the compound whose energy corresponds to such radiation: \( \Delta E = hf \)
- The only available processes with these characteristics are electronic transitions - remember the visible spectrum of hydrogen.
- Therefore, there must be a vacant electronic energy level (LUMO) whose "energetic distance" from the highest occupied level (HOL) corresponds to visible light
- TMs have vacancies in d orbitals. Also d^8 and d^10 complexes are colorless
- Crystal field theory removes the degeneracy of the d orbitals by placing two of them in different environments as a result of the charges due to the ligands. The next slide describes that process.

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Splitting the d orbitals - CFT

spherical field  __ __
Oct Field

gaseous ion

The issue of how the electrons are distributed becomes a matter of the relative sizes of the crystal field splitting ($\Delta$) and the pairing energy (PE).

If the PE > $\Delta$, splitting one gets a high spin complex. This is also called the weak field case.

If PE < $\Delta$, one gets the low spin complex. This is also called the strong field case.

- Two quick examples:
  - low spin Mn$^{2+}$ complex
    - the metal is $d^5$
    - $\uparrow\downarrow d_{x^2} \cdot d_{y^2}, d_{z^2}$
  - Weak field Co$^{3+}$ complex
    - metal is $d^4$
    - $\uparrow\downarrow d_{x^2} \cdot d_{y^2}, d_{z^2}$
    - $\uparrow\downarrow d_{x^2} \cdot d_{xy}$