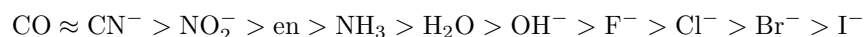


1 Morning class week 6 day 5: d -orbital energy diagrams

1. The octahedral d -orbital diagram with six identical ligands has three low-energy-lying d -orbitals, the t_{2g} orbitals. The two high-energy-lying orbitals are the e_g orbitals.

(a) Professor Johnson has told you about the spectrochemical series, the series which determines if the interaction between ligand and metal atom is strong. The spectrochemical series is



- Large splittings between t_{2g} and e_g orbitals are caused by ligands to the left of the *spectrochemical series*.
- Small splittings result from ligands to the right of the series.
- Large oxidation states on the metal atom increase the size of the t_{2g} to e_g splitting.
- Second and third row transition metals have large splittings.

(b) In Figure 1 we examine a small vs. a large Mn(III) t_{2g} to e_g splitting.

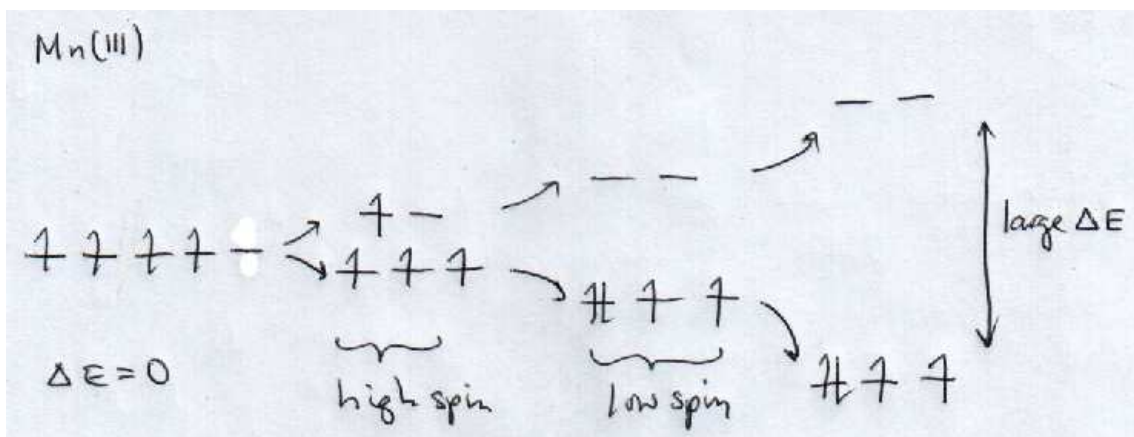


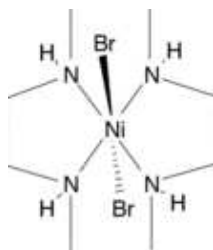
Figure 1: Mn(III), d^4 , in an octahedral complex for different energy splittings.

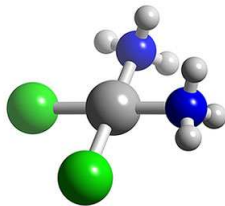
(c) On the left side of this figure, the t_{2g} -to- e_g splitting is still small enough that the Hund's rule forces still dominate. On the right side of the center of this figure, the energy splitting dominates over Hund's rule. The former case is called *high spin*, while the latter is *low spin*.

2. Please state the hybridization scheme and draw the d -orbital energy diagram for the following chemical species. Please fill in your diagrams with their correct electron filling.

(a) octahedral high spin $\text{Fe}(\text{H}_2\text{O})_6^{2+}$

(b) low spin $\text{NiBr}_2(\text{NH}_3)_4$, please place the Ni-Br bonds along the z -axis.





- (c) cisplatin, $\text{PtCl}_2(\text{NH}_3)_2$, shown above, please place all metal-ligand bonds along the x and y axes.
- (d) The two possible octahedral isomers of low spin $\text{Co}(\text{NH}_3)_3\text{I}_3$. Please draw two d -orbital energy diagrams for both isomers. (We make the simplifying assumption that the major d_{z^2} orbital lobes point to as many strong-field ligands as possible.)
- (e) In the last problem, what would be the principal differences in the two isomer's PES?
3. **Color and magnetism** The color of a compound is the color opposite to the color absorbed. An object which absorbs red light appears green, absorbs orange light appears blue, and so forth. The color wheel, shown below is helpful. The British color mnemonic "Richard of York gave battle (in) vain". The seventh color is indigo.



- (a) The absorption in kJ/mole for the following compounds are 218, 274, 278, and 401. The compounds are $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$, $\text{Co}(\text{CN})_6^{3-}$, and $\text{Co}(\text{H}_2\text{O})_6^{3+}$. What are the d -electron counts for the four compounds? Which compound absorbs which energy light?
- (b) Four vials each containing one of the three compounds $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$, and $\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2^+$ are blue-green, green and violet. Which compound is in which vial?
- (c) Three vials each containing one of the three compounds $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, $\text{Cr}(\text{NH}_3)_6^{3+}$, $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$, and $\text{Cr}(\text{NH}_3)_4\text{Cl}_2^+$ are blue-green, violet, green, yellow and violet. Which compound is in which vial (we can not sort between the two violet vials)?
- (d) Which compound is more likely to be high spin of the two $\text{Co}(\text{H}_2\text{O})_6^{2+}$ or $\text{Co}(\text{NH}_3)_6^{2+}$?
- (e) Which compound is more likely to be high spin of the two $\text{Co}(\text{H}_2\text{O})_6^{2+}$ or $\text{Co}(\text{H}_2\text{O})_6^{3+}$?
- (f) One of the two compounds, $\text{Co}(\text{NH}_3)_6^{3+}$ and CoF_6^{3-} is paramagnetic, the other diamagnetic. Which one is which?
- (g) Which of the following high spin compounds has the largest magnetic moment: $\text{Cr}(\text{H}_2\text{O})_6^{2+}$, $\text{Mn}(\text{H}_2\text{O})_6^{2+}$, or $\text{Fe}(\text{H}_2\text{O})_6^{2+}$?