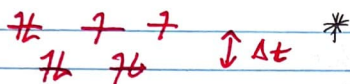
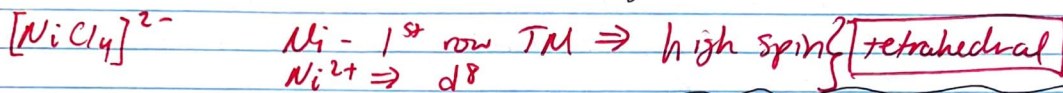


Week 8 Worksheet Answers

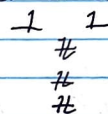
- 1) Nickel & Platinum belong to the same family, yet $[\text{NiCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$ differ greatly in physical properties. Give crystal field diagrams for each complex predicting the geometry, color, and magnetic properties.



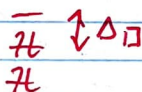
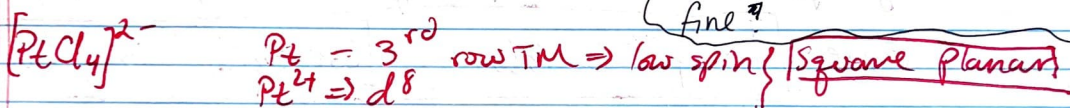
unpaired $e^- \Rightarrow$ **paramagnetic**

high spin \Rightarrow low field \Rightarrow small Δ_t
 So absorbs red, the color is **yellow/green**

* 2-out Jahn-Teller distortion is observed for this system so CF is actually:



But you never learned this so what is shown in red is fine.



No unpaired $e^- \Rightarrow$ **diamagnetic**

low spin \Rightarrow high field \Rightarrow large Δ_{sp} . So absorbs blue-violet
 Color is **yellow-orange**

- 2) Identify which complexes from the following list meet the criteria below.
- (complexes) with more than 4 unpaired electrons: **H**
 - (complexes) that are likely octahedral: **B, D, E, F, G, H**
 - (complex(es) that are likely square planar: **A**
 - (complex(es) that are ~~likely~~ colorless: **C, F**
 - (complex(es) that is/are chiral: **H**

- 3) What +3 ion is used as a MRI contrast agent since it has the greatest number of unpaired electrons of any naturally occurring element in the Periodic Table? What +2 ion has the greatest number of unpaired electrons?

Gd³⁺ is the MRI contrast agent (f^7)
Tb²⁺ is greatest # of unpaired electrons

- 4) Merhan is preparing solutions 14 & 15 for the qualitative analysis lab which contain $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{CoCl}_4]^{2-}$. Unfortunately, he confused himself and couldn't remember which was the blue colored solution and which was the yellow-colored solution. As the excellent chem 113 student you are, you quickly come to his rescue and know how to tell the difference! Please explain which is which so that you can save the lab.

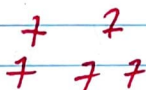
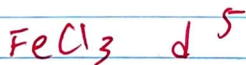
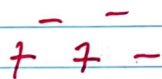
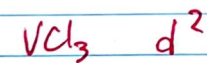
Blue \Rightarrow absorb orange light
 Yellow \Rightarrow absorb violet light

Yellow has greater Δ_o . So $[\text{Co}(\text{NH}_3)_6]^{2+}$ is octahedral with medium field ligand and $[\text{CoCl}_4]^{2-}$ is tetrahedral.

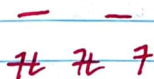
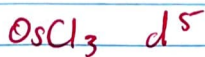
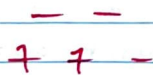
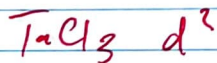
By spectroscopic series, $[\text{CoCl}_4]^{2-}$ is $\sim \frac{4}{9} \Delta_o$ of $[\text{Co}(\text{NH}_3)_6]^{2+}$

Hence, $[\text{CoCl}_4]^{2-}$ is blue : $[\text{Co}(\text{NH}_3)_6]^{2+}$ is yellow

- 5) The complexes VCl_3 , FeCl_3 , TaCl_3 , and OsCl_3 have been found to crystallize in the same lattice structure in which each of the metal cations is coordinated to 6 anions and each anion is coordinated to 2 metal cations. Experiments show that the lattice energy of VCl_3 is much greater than that of FeCl_3 . Further experiments have shown that the lattice energy of OsCl_3 is much greater than TaCl_3 . How can we explain these trends?



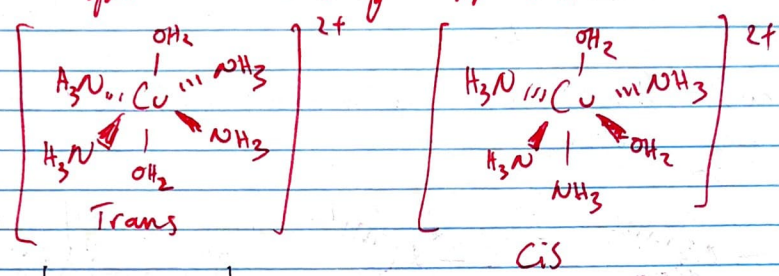
Lattice energy of VCl_3 is greater than FeCl_3 because CFSE of FeCl_3 is 0 ; VCl_3 is $= -\frac{4}{5} \Delta$



CFSE of OsCl_3 is greater than TaCl_3 which explains lattice energy.

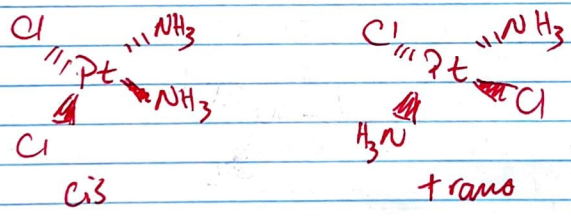
6) Name the compound and draw all possible isomers for each of the following complexes. Note the name of the molecular geometry is provided.

a) $[Cu(NH_3)_4(H_2O)_2]^{2+}$, octahedral
~~Tetraammine diaqua copper (II)~~
 Tetraammine diaqua copper (II)

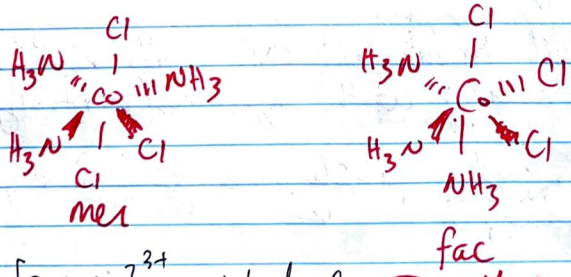


b) $[Pt(NH_3)_2Cl_2]$, square planar

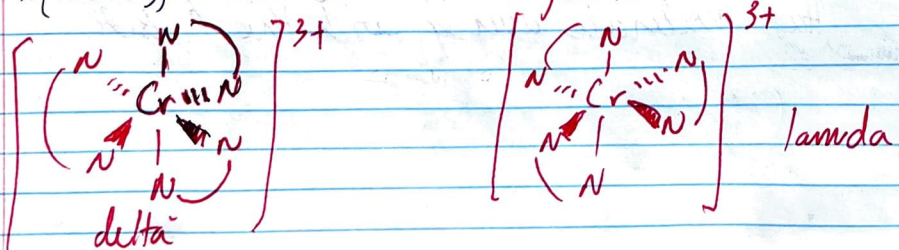
~~Diammine dichloro platinum (II)~~
 Diammine dichloro platinum (II)



c) $[Co(NH_3)_3Cl_3]$, octahedral
~~Triammine trichloro cobalt (III)~~
 Triammine trichloro cobalt (III)

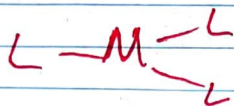


d) $[Cr(en)_3]^{3+}$, octahedral
 Trisethylenediamine chromium (III)

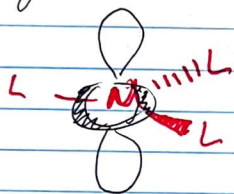


7) In this problem, we will construct the energy-level structure of the 3d orbitals in a trigonal planar crystal field.

a) Draw the generic ~~trigonal~~ trigonal planar structure. Use M for the metal ion and L for the ligands.



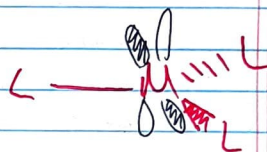
b) Draw & label the 5 3d orbitals, with the locations of the ligands shown.



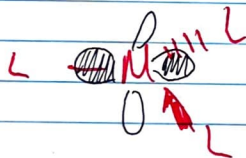
d_{z^2}



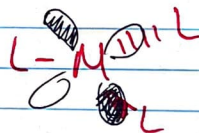
d_{xz}



d_{yz}



$d_{x^2-y^2}$



d_{xy}

c) Using your drawings, what orbitals do you think are isoeenergetic? Rationalize using repulsion/overlap concepts.

d_{xz} , d_{yz} likely isoeenergetic since node in equatorial plane; small overlap with ligands (virtually none).

~~d_{z^2}~~ $d_{x^2-y^2}$, d_{xy} likely isoeenergetic since good overlap with the ligands.

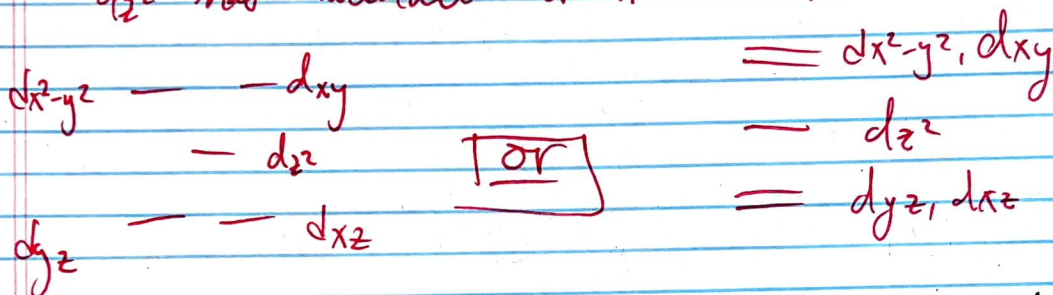
d_{z^2} likely not isoeenergetic with any ~~the~~ others. Has moderate overlap with the ligands.

d) Draw the energy level diagram for the trigonal planar crystal field, labeling each orbital. Give rationalizations for energy ordering.

$d_{x^2-y^2}$: d_{xy} have highest repulsive overlap \Rightarrow highest energy

d_{xz} : d_{yz} have least overlap \Rightarrow lowest energy

d_{z^2} has moderate : is in the middle



8) Name the complex in each set of octahedral complexes that will have the largest d-splitting (Δ). Give an explanation.

a) $\text{Na}_3[\text{CoCl}_6]$ vs. $\text{Na}_4[\text{CoCl}_6]$

$\text{Na}_3[\text{CoCl}_6]$: $\text{Co}^{2+} < \text{Co}^{3+}$ in spectrochemical series for metals. So Co^{3+} gives larger d-splitting.

b) $[\text{RhCl}_6]^{3-}$ vs. $[\text{RhI}_6]^{3-}$

$[\text{RhCl}_6]^{3-}$: $\text{I} < \text{Cl}$ in spectrochemical series.

c) $[\text{Fe}(\text{CO})_6]^{3+}$ vs. $[\text{Ru}(\text{CO})_6]^{3+}$

$[\text{Ru}(\text{CO})_6]^{3+}$: $\text{Fe} < \text{Ru}$ in spectrochemical series.

d) $\text{Co}(\text{OH})_6$ vs. $\text{Co}(\text{CN})_6^{1-}$

$\text{Co}(\text{CN})_6$: $\text{OH}_2 < \text{CN}^-$