

2024 FALL Semester Mid-term Examination
for General Chemistry II

Date: October 23 (Wed)

Exam Time: 19:00 ~ 21:00

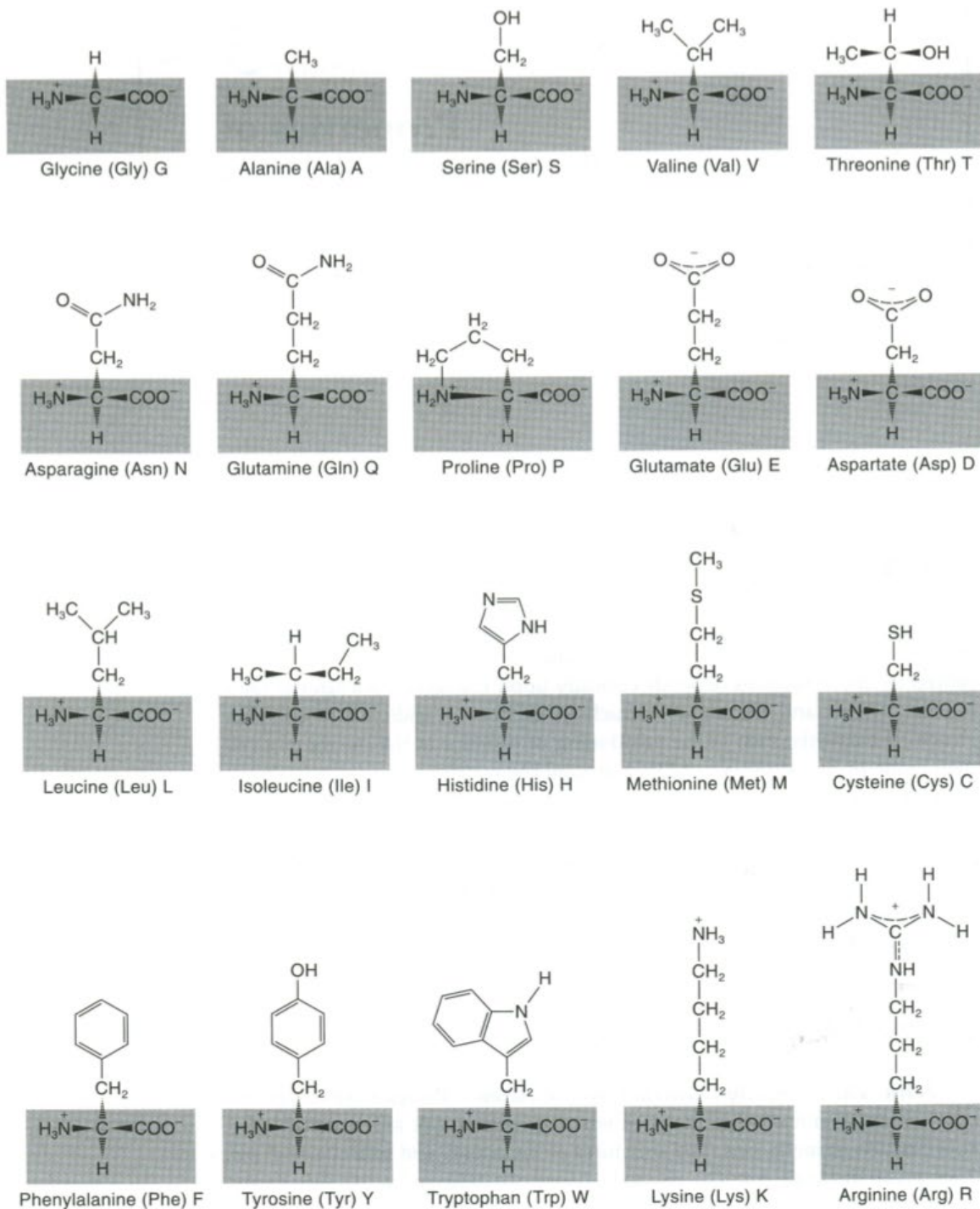
Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

Student I.D. Number	Name

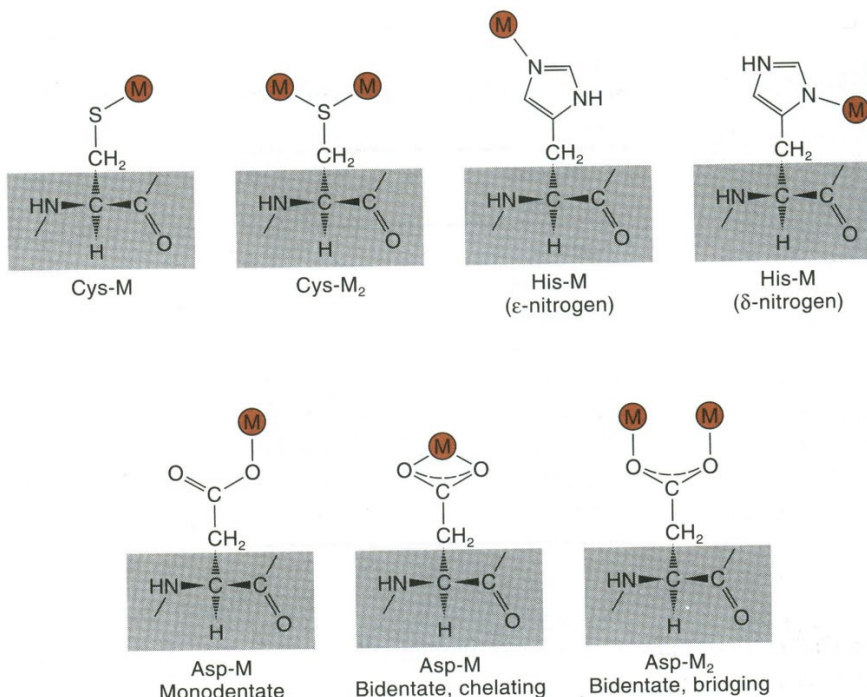
Problem	Points	Problem	Points	TOTAL (pts)
1	/ 20	8	/ 15	/ 107
2	/ 7	9	/ 6	
3	/ 8	10	/ 3	
4	/ 6	11	/ 10	
5	/ 5	12	/ 3	
6	/ 12	13	/ 3	
7	/ 9			

1. (20 pts) Draw the structures of 20 amino acids with full names and three & one characters.

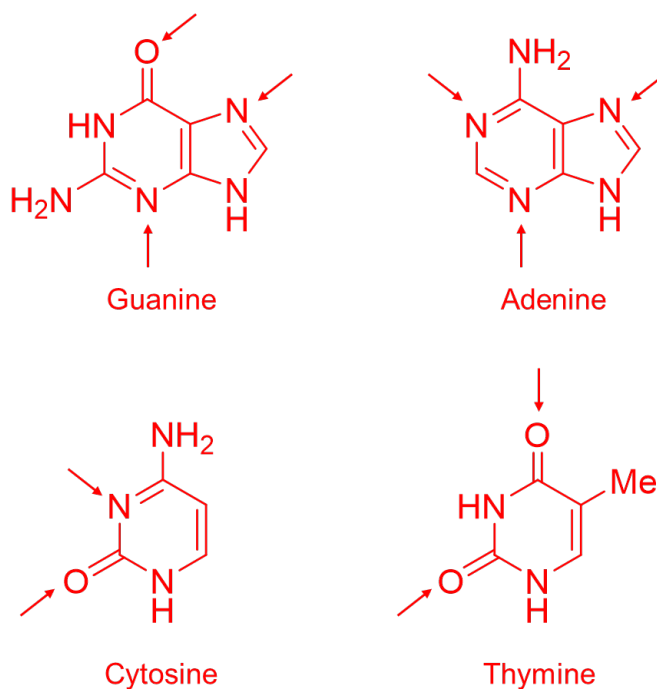
All (structures, full names, and three & one characters) should be right to get a full credit.



2. (7 pts) Indicate all possible metal-binding sites at the side chains of Cys, His, and Asp.
each (1 pt)



3. (8 pts) Draw the structures of DNA bases. Indicate metal-binding sites at DNA bases.
each structure (1 pt)
metal-binding sites / each base (1 pt)



4. (2 pts) (i) What do bacteria use for uptake of metal ions in the cells?
 (2 pts/each) What are human iron (Fe) (ii) transport and (iii) storage proteins?

(i) Siderophores

(ii) Transferrin

(iii) Ferritin, Hemosiderin

5. (5 pts) Explain the Fe uptake procedure for human (in the cells).

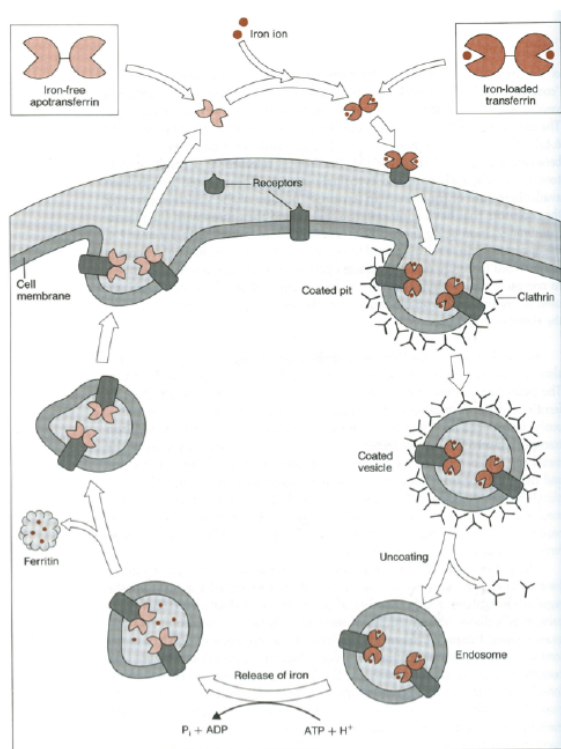


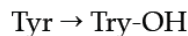
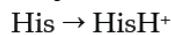
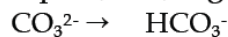
Figure 6.6 Scheme depicting the extracellular binding of iron to apotransferrin, receptor-mediated endocytosis, ATP-driven release of iron into the endosome, and loading of the metal ion into ferritin.

Through **endocytosis (1 pts)**

Receptor binds only **holotransferrin**

1. Fe binds Tf
2. Tf binds the receptor
3. Membrane pinches off to form coated vesicle (protein: clathrin)
4. In cells, coat is removed to form endosome
5. ATP-driven proton pumps (at the membrane of endosome)

at lower pH (5 - 6): ligand protonation



6. Fe is released/binds to Ferritin
7. Vesicle/ ApoTf fuses to plasma membrane

Total time: 15 min

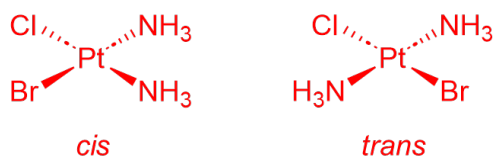
Explain all processes (5 pts)

6. **[each 3 pts]** For each inorganic compound below, write the name (2 pts) and the coordination number (1 pt) of the metal ion.

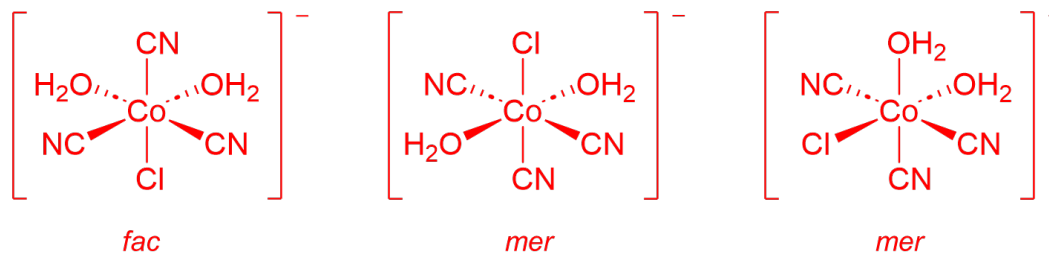
Formula	Name (2 pts)	Coordination Number (1 pt)
(a) $K_2[Cr(OH_2)_2(C_2O_4)_2]$	potassium diaquabis(oxalato)chromate(II)	6
(b) $[Cu(NH_3)_2Cl_2]$	diamminedichlorocopper(II) or diamminedichloridocopper(II)	4
(c) $[Pt(NH_3)_4BrCl]Cl_2$	tetraamminebromidochloridoplatinum(IV) chloride or tetramminebromochloroplatinum(IV) chloride	6
(d) $[Co(NH_3)_5(CO_3)]Br$	pentaamminecarbonatocobalt(III) bromide	6

7. **[each 3 pts]** Draw the structures of all possible isomers for the following complexes. Indicate which isomers are enantiomer pairs.

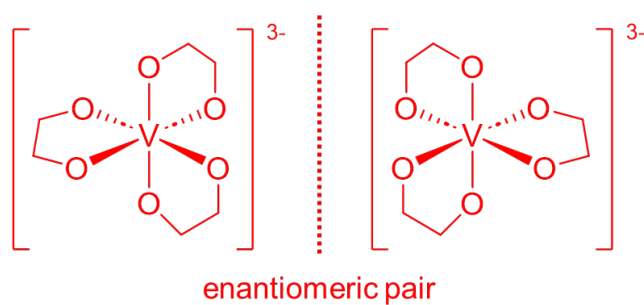
(a) Diamminebromochloroplatinum(II)



(b) Diaquachlorotricyanocobalate(III) ion



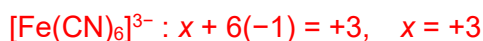
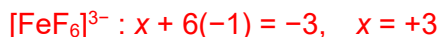
(c) Trioxalatovanadate(III) ion



8. The octahedral complex ions $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ are all paramagnetic. But $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{OH}_2)_6]^{3+}$ are high spin and the $[\text{Fe}(\text{CN})_6]^{3-}$ is low spin. Answer for each question below.

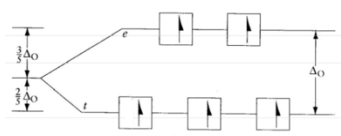
(a) [9 pts] Draw an orbital energy-level diagram for each octahedral complex ion (show how to get the oxidation numbers for Fe ions in each complex).

* The oxidation numbers of $[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{OH}_2)_6]^{3+}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ molecules (1 pt/each; 3 pts)



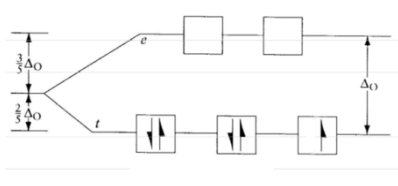
* Electron configuration of Fe^{3+} : $[\text{Ar}]3d^5 \rightarrow 5 d$ electrons

* The orbital energy-level diagrams of $[\text{FeF}_6]^{3-}$ and $[\text{Fe}(\text{OH}_2)_6]^{3+}$ * the configuration of d -electrons: $t_{2g}^3 e_g^2$



(3 pts)

* The orbital energy-level diagram of $[\text{Fe}(\text{CN})_6]^{3-}$ * the configuration of d -electrons: t_{2g}^5



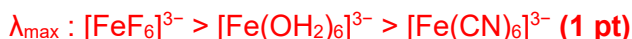
(3 pts)

(b) [3 pts] Predict the number of unpaired electrons for each complex.

(1 pt/each; 3 pts)



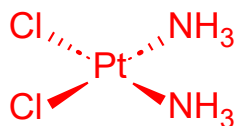
(c) [3 pts] Place which of the complexes has the shorter absorption λ_{max} in order and explain your answer.



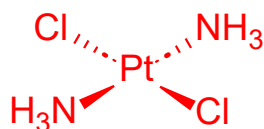
According to the spectrochemical series the ligand field strength is in order of $\text{CN}^- > \text{OH}_2 > \text{F}^-$, thus the crystal (or ligand) field splitting energy (Δ_o) becomes the largest for $[\text{Fe}(\text{CN})_6]^{3-}$. (1 pt) Since the energy of the light absorbed is the greatest, the λ_{max} should be the shortest from the relation $E = hc / \lambda$. (1 pt)

9. [each 2 pts] Draw (i) the structure of the first member platinum-containing anti-cancer drug and (ii) the structure of its geometric isomer that does not show any anti-cancer activity. (iii) Indicate the d-orbital electron configuration of the platinum-containing anti-cancer drug.

(i) **Square planar geometry**

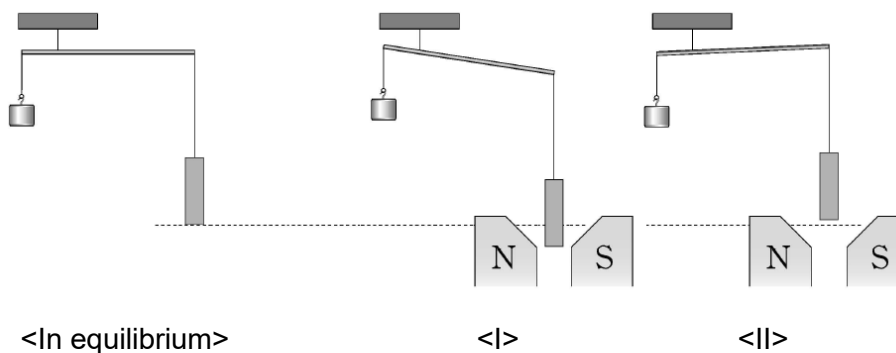


(ii) **trans isomer (name: Transplatin)**



(iii) **d^8**

10. [3 pts] The magnetic properties of the complexes are observed as follows.



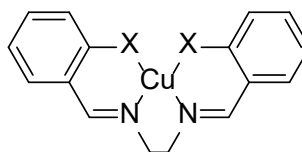
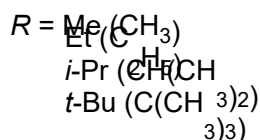
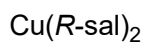
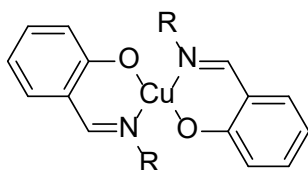
Complex	Observed
$K_3[CoF_6]$	<I>
$[Co(NH_3)_6]Cl_3$	<II>
$K_2[NiCl_4]$	<I>
$K_2[Ni(CN)_4]$	<II>

- (a) [1 pt] Which one has the stronger ligand field strength between NH_3 and F^- ? **NH_3**
- (b) [1 pt] What is the coordination structure of $[NiCl_4]^{2-}$ in $K_2[NiCl_4]$? **Tetrahedral**
- (c) [1 pt] How many electrons in $3d_z^2$ orbital of nickel in $K_2[Ni(CN)_4]$? **2**

11. [10 pts] The data in the table below summarize the half wave potential ($E_{1/2}$, the potential where the complex is half-oxidized and half-reduced) of Cu(II) chelates.

Compound Name	$E_{1/2}$ (V)*
Cu(O-sal) ₂ en	-1.21
Cu(Me-sal) ₂	-0.90
Cu(Et-sal) ₂	-0.86
Cu(S-sal) ₂ en	-0.83
Cu(<i>i</i> -Pr-sal) ₂	-0.74
Cu(<i>t</i> -Bu-sal) ₂	-0.66

* Measured in *N,N*-dimethylformamide (DMF)



- (a) [2 pts] Write down the *d* electron configurations of Cu(I) and Cu(II).

Cu(I): d^{10} configuration (1 pt), Cu(II): d^9 configuration (1 pt)

- (b) [3 pts] When it comes to coordination number of 4, Cu(I) prefers tetrahedral geometry, while Cu(II) complexes are typically square planar. Explain this tendency considering the electronic configurations and steric hindrances.

For d^{10} configuration, there is no differences in stabilization energy for both tetrahedral and octahedral geometry (1 pt).

In this case, the geometry favors the one that experiences less steric hindrance which is tetrahedral (1 pt).

On the other hand, the stabilization energy for square planar geometry is lower than that of tetrahedral geometry for d^9 configuration overwhelming the steric effect (1 pt).

Hence, Cu(I) prefers to have tetrahedral geometry, while Cu(II) prefers square planar.

- (c) **[2 pts]** Explain why the value of $E_{1/2}$ is lower in $\text{Cu}(\text{O-sal})_2\text{en}$ than $\text{Cu}(\text{S-sal})_2\text{en}$ in terms of the hard soft acid and base concept.

$\text{Cu}(\text{I})$ is softer acid than $\text{Cu}(\text{II})$, while S is softer base than O (1 pt).

Since soft acid prefers to bind with soft base, $\text{Cu}(\text{I})$ favors to bind with S rather than with O (1 pt). This alleviates the barrier for $\text{Cu}(\text{S-sal})_2\text{en}$ to be reduced.

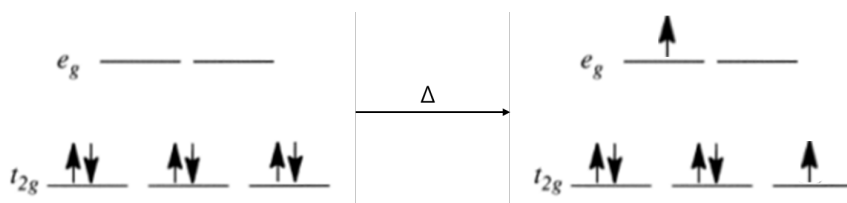
- (d) **[3 pts]** Explain why the value of $E_{1/2}$ has trend of $\text{Cu}(\text{Me-sal})_2 < \text{Cu}(\text{Et-sal})_2 < \text{Cu}(i\text{-Pr-sal})_2 < \text{Cu}(t\text{-Bu-sal})_2$.

As the group goes $\text{Me} < \text{Et} < i\text{-Pr} < t\text{-Bu}$, the size of the group becomes bulkier (1 pt).

Then due to the steric hindrance, the geometry of the central Cu becomes closer to tetrahedral as the $-\text{R}$ group becomes larger (1 pt).

Since $\text{Cu}(\text{I})$ species favors the tetrahedral geometry than square planar as in (b), the barrier for being reduced from $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$ gets lower (1 pt)

12. **[3 pts]** The complex $[\text{Fe}(\text{CN})_6]^{4-}$ is known to be diamagnetic at room temperature. However, when heated to a certain temperature, it becomes paramagnetic and is used as a temperature sensor. Explain this property using the orbital energy-level diagram of $[\text{Fe}(\text{CN})_6]^{4-}$, and suggest which ligand can be used to create a lower temperature sensor.

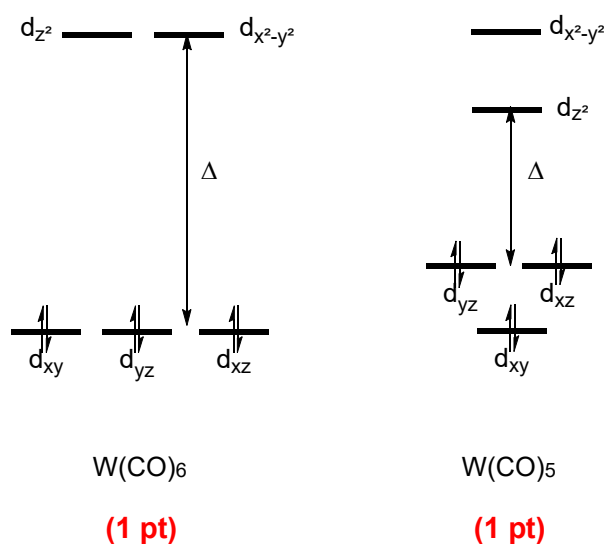


According to the CFT, the electron configuration of $[\text{Fe}(\text{CN})_6]^{4-}$ is depicted in the diagram above. When heat is applied and a certain temperature is reached, electrons from the t_{2g} (d_{xy} , d_{yz} , and d_{xz}) orbitals gain energy and move to the e_g^* (d_{z^2} and $d_{x^2-y^2}$) orbitals, leading to the presence of unpaired electrons. (2 pts)

To create a sensor that responds at lower temperatures, the Δ_o value must be decreased, making it easier to the electrons to be excited, but should still retain the low spin configuration. Therefore, using a strong-field ligand but lying at the lower position on spectrochemical series than CN^- , such as phen (1,10-phenanthroline) or bipy (2,2'-bipyridine) (to form $[\text{Fe}(\text{phen})_3]^{2+}$ or $[\text{Fe}(\text{bipy})_3]^{2+}$, respectively), would be a suitable approach (1 pt).

13. [3 pts] When light irradiates $W(CO)_6$, one of the carbonyl ligands can dissociate, generating the square-pyramidal complex $W(CO)_5$. Between these two complexes, which one has the smaller ligand-field splitting? Explain your answer using an orbital energy-level diagram.

CO ligand can participate in π -backbonding, which significantly lowers the energy level of t_{2g} (d_{xy} , d_{yz} , and d_{xz}) orbital in the octahedral complex. With the loss of a CO ligand along the z-axis from $W(CO)_6$, the energy levels of d_{yz} , and d_{xz} increase due to decreased π -backbonding along the z-axis. Additionally, the energy level of d_{z^2} decreases as the antibonding interaction is reduced. These changes in orbital levels bring them closer in energy compared to the octahedral complex, resulting in a lower transition energy. (1 pt)



- Points will not be awarded to the explanation based solely on the crystal field theory.