2024 FALL Semester Mid-term Examination

for General Chemistry II

Date: October 23 (Wed)

Exam Time: 19:00 ~ 21:00

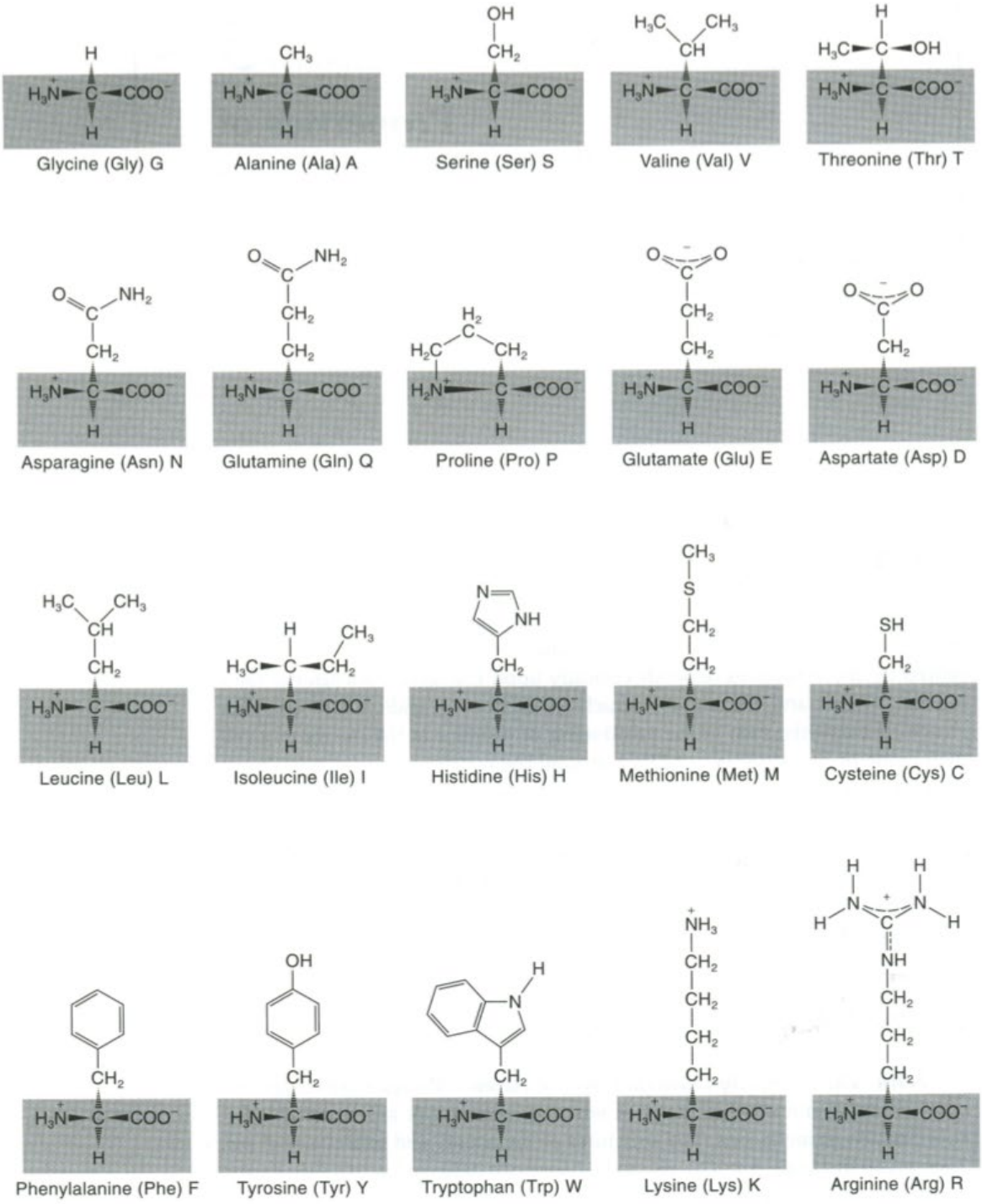
Write down your information neatly in the space provided below; print your Student ID in the upper right corner of every page.

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			

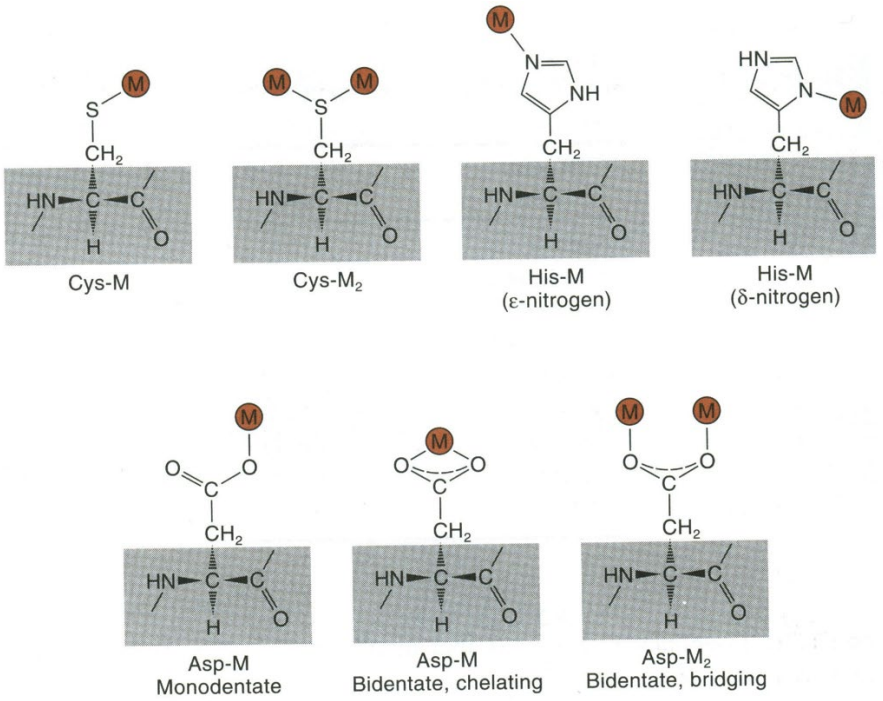
1. **(20 pts)** Draw the structures of 20 amino acids with full names and three & one characters.

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.

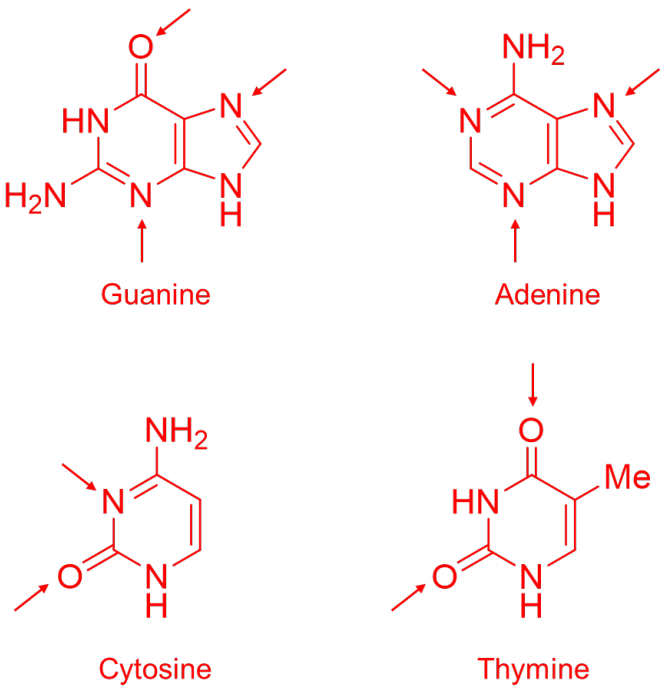
each (1 pt)



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).

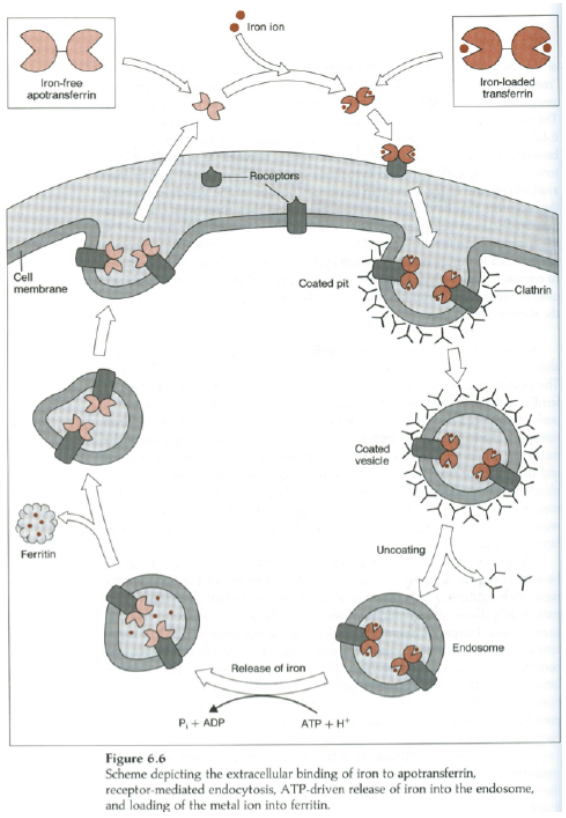


Figure 6.6
Scheme depicting the extracellular binding of iron to apotransferrin, receptor-mediated endocytosis, ATP-driven release of iron into the endosome, and loading of the metal ion into ferritin.

Through **endocytosis (1 pts)**

Receptor binds only halotransferrin

1. Fe binds Tf
2. Tf binds the receptor
3. Membrance 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

$CO_3^{2-} \rightarrow HCO_3^-$

$His \rightarrow HisH^+$

$Tyr \rightarrow Try\text{-}OH$

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

Total time: 15 min

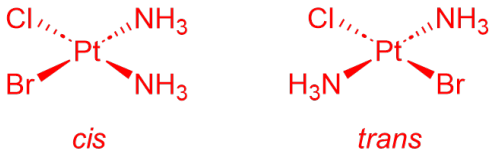
Explain all processes (5 pts)

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

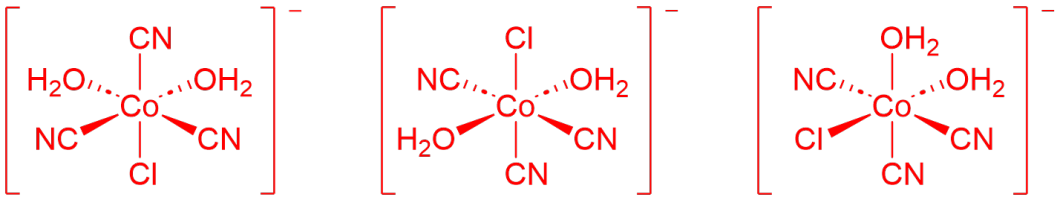
7. **[each 3 pts]** Draw the structures of all possible isomers for the following complexes. Indicate which isomers are enantiomer pairs.

(a) Diamminebromochloroplatinum(II)



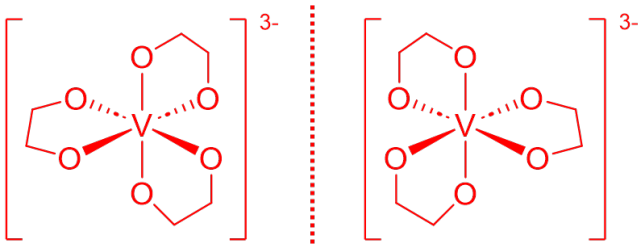
cis *trans*

(b) Diaquachlorotricyanocobalate(III) ion



fac *mer* *mer*

(c) Trioxalatovanadate(III) ion



enantiomeric pair

8. The octahedral complex ions $[FeF_6]^{3-}$, $[Fe(OH_2)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$ are all paramagnetic. But $[FeF_6]^{3-}$ and $[Fe(OH_2)_6]^{3+}$ are high spin and the $[Fe(CN)_6]^{3-}$ 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 $[FeF_6]^{3-}$, $[Fe(OH_2)_6]^{3+}$, and $[Fe(CN)_6]^{3-}$ molecules **(1 pt/each; 3 pts)**

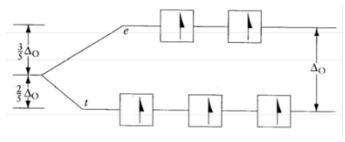
$[FeF_6]^{3-}$: $x + 6(-1) = -3$, $x = +3$

$[Fe(OH_2)_6]^{3+}$: $x + 6(0) = +3$, $x = +3$

$[Fe(CN)_6]^{3-}$: $x + 6(-1) = +3$, $x = +3$

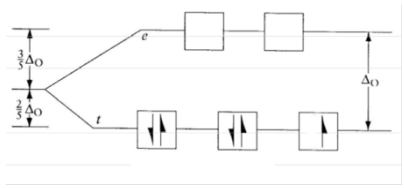
* Electron configuration of Fe^{3+}: $[Ar]3d^5$ → 5 *d* electrons

* The orbital energy-level diagrams of $[FeF_6]^{3-}$ and $[Fe(OH_2)_6]^{3+}$ * the configuration of *d*-electrons: $t_{2g}^3 e_g^2$



(3 pts)

* The orbital energy-level diagram of $[Fe(CN)_6]^{3-}$ * 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)

$[FeF_6]^{3-}$: 5 unpaired electrons → paramagnetic

$[Fe(OH_2)_6]^{3+}$: 5 unpaired electrons → paramagnetic

$[Fe(CN)_6]^{3-}$: 1 unpaired electron → paramagnetic

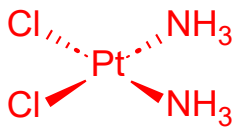
(c) [3 pts] Place which of the complexes has the shorter absorption λ_{max} in order and explain your answer.

λ_{max} : $[FeF_6]^{3-} > [Fe(OH_2)_6]^{3-} > [Fe(CN)_6]^{3-}$ **(1 pt)**

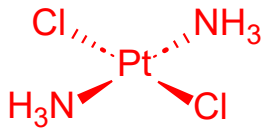
According to the spectrochemical series the ligand field strength is in order of $CN^- > OH_2 > F^-$, thus the crystal (or ligand) field splitting energy (Δ_o) becomes the largest for $[Fe(CN)_6]^{3-}$. **(1 pt)** Since the energy of the light absorbed is the greatest, the λ_{max} should be the shortest 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

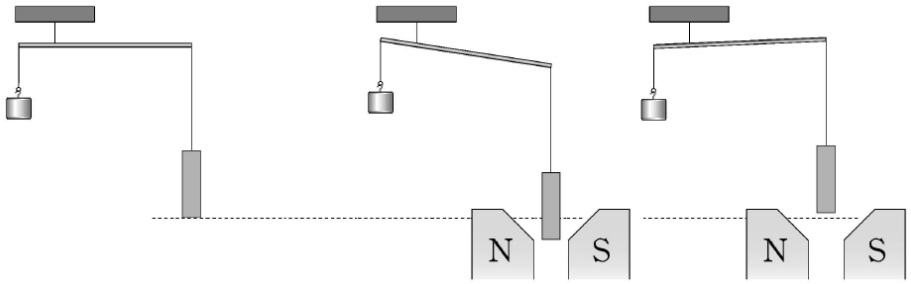


(ii) *trans* isomer (name: Transplatin)



(iii) d^8

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



<In equilibrium> <I> <II>

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**

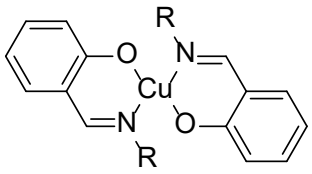
(b) **[1 pt]** What is the coordination structure of $[NiCl_4]^{2-}$ in $K_2[NiCl_4]$? **Tetrahedral**

(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.

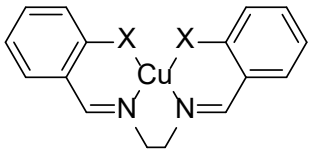
Compound Name	$E_{1/2}$ (V)*
Cu(*O*-sal)$_2$en	−1.21
Cu(Me-sal)$_2$	−0.90
Cu(Et-sal)$_2$	−0.86
Cu(*S*-sal)$_2$en	−0.83
Cu(*i*-Pr-sal)$_2$	−0.74
Cu(*t*-Bu-sal)$_2$	−0.66

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



Cu(*R*-sal)$_2$

R = Me (CH_3)
Et (C_2H_5)
i-Pr ($CH(CH_3)_2$)
t-Bu ($C(CH_3)_3$)



Cu(*X*-sal)$_2$en

X = *O* or *S*

(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 Cu(*O*-sal)$_2$en than Cu(*S*-sal)$_2$en in terms of the hard soft acid and base concept.

Cu(I) is softer acid than Cu(II), while *S* is softer base than *O* **(1 pt)**.

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

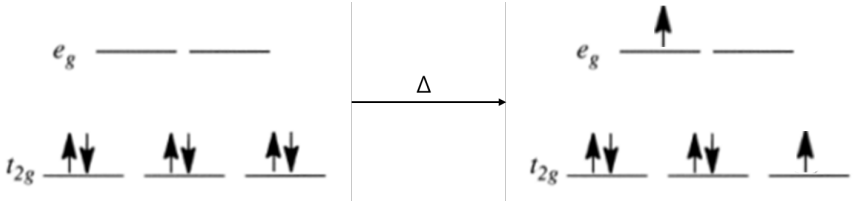
(d) **[3 pts]** Explain why the value of $E_{1/2}$ has trend of Cu(Me-sal)$_2$ < Cu(Et-sal)$_2$ < Cu(*i*-Pr-sal)$_2$ < Cu(*t*-Bu-sal)$_2$.

As the group goes Me < Et < *i*-Pr < *t*-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 –R group becomes larger **(1 pt)**.

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

12. **[3 pts]** The complex $[Fe(CN)_6]^{4-}$ 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 $[Fe(CN)_6]^{4-}$, and suggest which ligand can be used to create a lower temperature sensor.

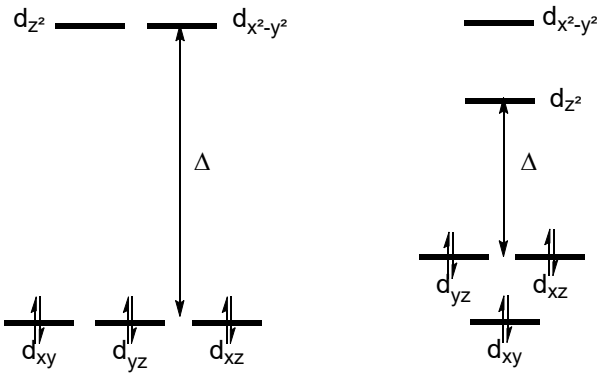


According to the CFT, the electron configuration of $[Fe(CN)_6]^{4-}$ is depicted in the diagram above. When heat is applied and a certain temperature is reached, electrons from the t_{2g} (d_{xy}, d_{yz}, and d_{xz}) orbitals gain energy and move to the e_g* (d_{z^2} and $d_{x^2-y^2}$) orbitals, leading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

To create a sensor that responses 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 $[Fe(phen)_3]^{2+}$ or $[Fe(bipy)_3]^{2+}$, 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 deceased 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)**



$W(CO)_6$ **(1 pt)**

$W(CO)_5$ **(1 pt)**

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

2024 Fall Semester Final Examination
for General Chemistry II

Date: December 18 (Wen)

Exam Time: 19:00 – 21:00 (2 hrs)

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	/ 65	**9**	/ 4	**/ 157**
2	/ 7	**10**	/ 18	
3	/ 2	**11**	/ 10	
4	/ 6	**12**	/ 8	
5	/ 5	**13**	/ 4	
6	/ 4	**14**	/ 6	
7	/ 3	**15**	/ 4	
8	/ 3	**16**	/ 8	

This paper consists of 10 sheets with 16 problems (page 13**: claim form). Please check all page numbers before taking the exam. All answers should be written in these exam sheets.

NOTICE: SCHEDULES on RETURN and CLAIM of the MARKED EXAM PAPER.

(채점 답안지 분배 및 이의신청 일정)

1. Period, Location and Procedure

○ Return and Claim Period: **December 20 (Friday, 12:00 ~ 14:00, 2 hrs)**
The claim is permitted only on this period. Keep that in mind!

○ Location: Each designated room of Creative Learning Bldg (E11)

Class	Room(E11)
A	409

○ Procedure

Rule 1: Students cannot bring their writing tools into the rooms (use a pen only provided by TA).

Rule 2: With or without claim, you must submit the paper back to TA (do not go out of the room with it).

If you have any claims on it, write them on the claim form and attach it to the top of the exam paper with a stapler. Give them to your TA.

WARNING!!

If you deliberately alter any original answers or insert something on your marked paper to achieve a better grade, you will get a F grade for this course. Or if you don't keep the rules above, we will regard it as a kind of cheating and give you 0 point. So please don't cheat.

2. Final Confirmation

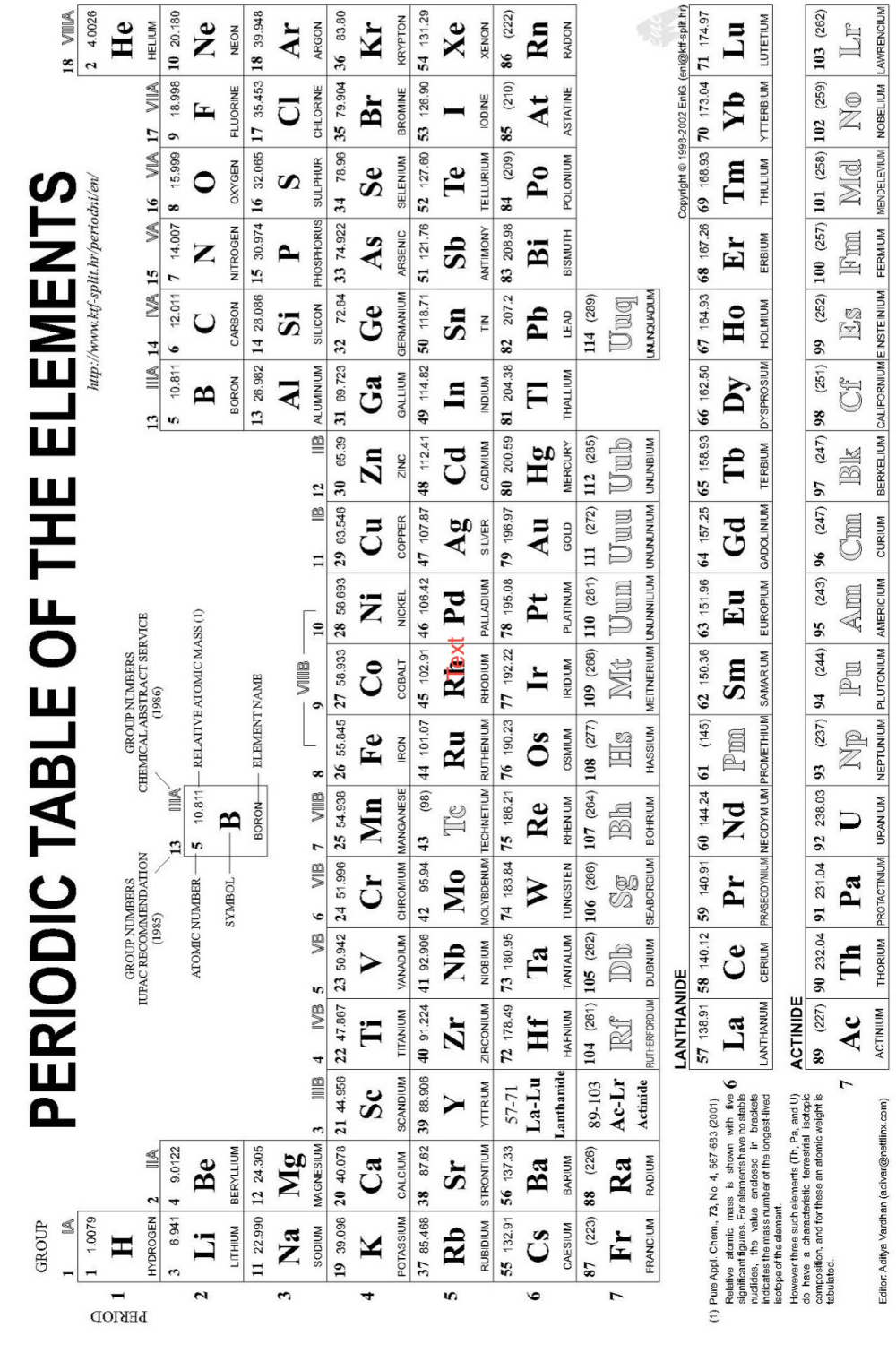
(1) Period: **December 21 (Sat) ~ 22 (Sun)**

(2) Procedure: During this period, you can check final score of the examination *on the website* again (no additional corrections. If no change in your score after reasoning, the claims were not accepted).

****For further information, please visit General Chemistry website at**
www.gencheminkaist.pe.kr

1. **(65 pts)** Complete the periodic table (write the elements; 1 pt/element) in the periodic table.

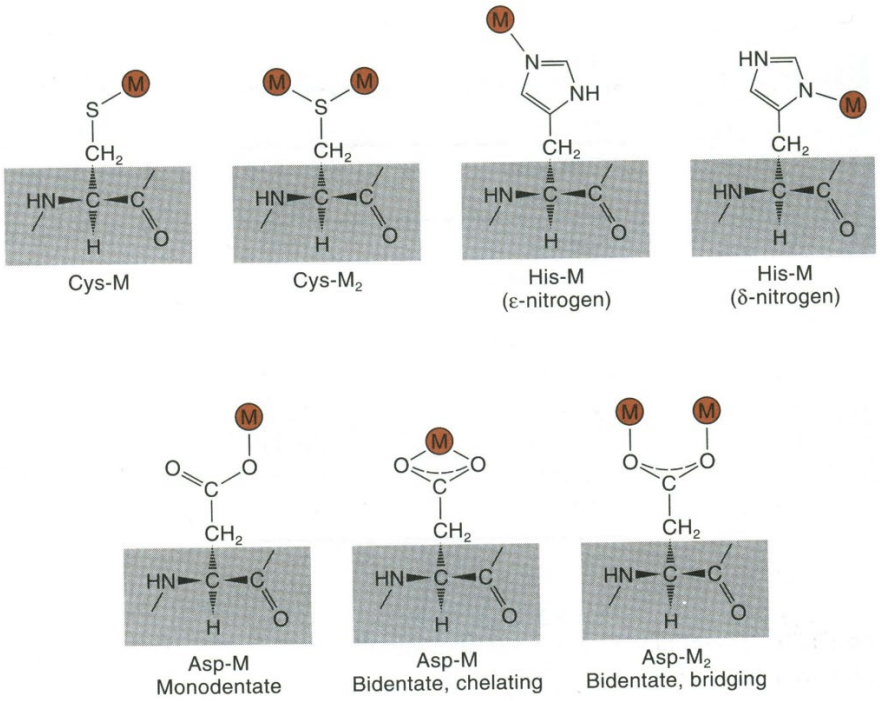
Ans)



(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

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

Ans)



3. **(2 pts)** How many Ca ions can bind to Calmodulin?

Ans) 4

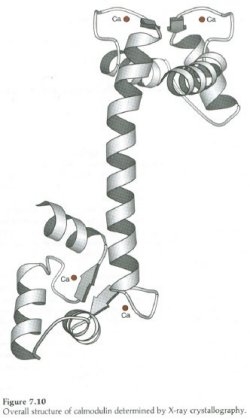


Figure 7.10
Overall structure of calmodulin determined by X-ray crystallography.

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?

Ans)

(i) **Siderophores**

(ii) **Transferrin**

(iii) **Ferritin, Hemosiderin**

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

Ans)

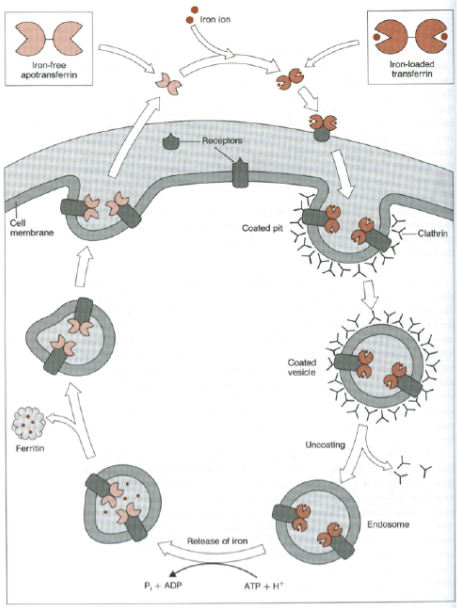


Figure 6.6
Scheme depicting the extracellular binding of iron to apotransferrin, receptor-mediated endocytosis, ATP-driven release of iron into the endosome, and loading of the metal ion into ferritin.

Receptor binds only halotransferrin

1. Fe binds Tf
2. Tf binds the receptor
3. Membrance 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

$CO_3^{2-} \rightarrow HCO_3^-$

His → $HisH^+$

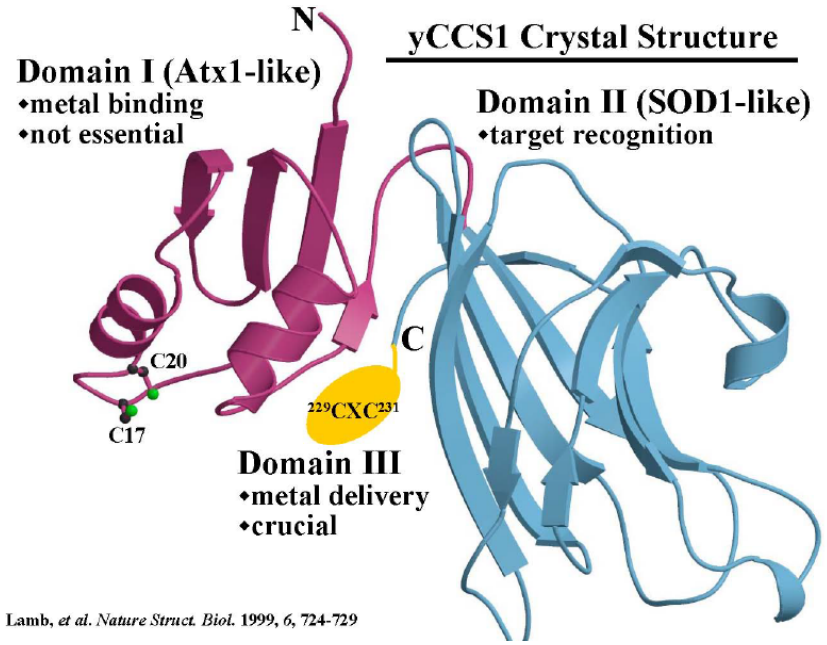
Tyr → Try-OH

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

Total time: 15 min

6. **(4 pts)** Indicate the name of the protein and the roles of three domains in the parentheses.

Ans)



Lamb, *et al. Nature Struct. Biol.* 1999, *6*, 724-729

No need to write "y" in front to "CCS1"

Also, please give a full credit for "CCS"

7. **(3 pts)** Why is the reaction of organic compounds with dioxygen unfavorable kinetically?

Ans)

Chemical reactions between dioxygen and typical organic compounds are spin-forbidden (dioxygen = triplet spin state; organic compounds = singlet spin state). To do spin-allowed chemical reaction, dioxygen needs to be excited to a singlet state, but it has high activation energy (lowest energy singlet excited state has 22.5 kcal/mol higher energy than ground state triplet dioxygen). So, the reaction is unfavorable kinetically.

8. **(3 pts)** What are three important factors related to electron transfer rates based on the "Marcus Theory"?

Ans)

Distance between donor and acceptor orbital, reorganization energy, and driving force

Distance and Driving Force Dependencies of ET Rates

$k_{ET} = (4\pi^2/h)T^2_{DA}(FC)$, where T_{DA} is the tunneling matrix element and measures the electronic coupling of donor and acceptor, FC is the Franck-Condon factor, and the other symbols have their usual meaning.

$T^2_{DA} = T^2_{0\,DA}\exp(-\beta(R - R_0))$; at $R = R_0$, van der Waals contact

β is a medium effect parameter: related to electron "pathway"

Marcus Theory:

$FC = (4\pi\lambda kT)^{-1/2}\exp[-(-\Delta G^0 - \lambda)^2/4\lambda kT]$

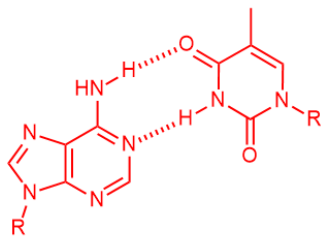
reorganization energy

standard free energy of the reaction

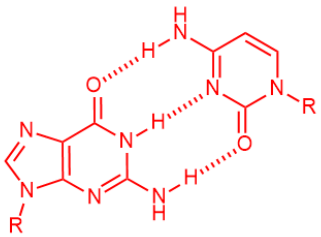
Predicts k_{ET} maximized when $\Delta G^0 = -\lambda$!!

9. **(4 pts; 2 pts / each)** Draw the "standard" base pairs (adenine-thymine and guanine-cytosine) and illustrate the hydrogen bonding interactions between them.

Ans)



A•T



G•C

10. **(18 pts)** Consider hemoglobin, which transports O_2 through the human body by forming a bond between O_2 and the iron ion at the center of the heme group.

a. **(9 pts; 1 pt / each)** In the deoxy form of heme, oxygen (O_2) or carbon monoxide (CO) can bind to the central iron atom, forming the oxy and carboxyl forms, respectively. Complete the table summarizing the chemical properties of the deoxy, oxy, and carboxyl forms of the heme.

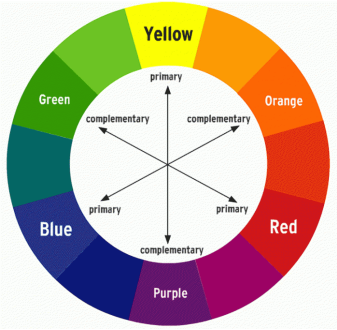
Form of heme	Deoxy-form	Oxy-form	Carboxyl-form
Oxidation state of Fe	**Fe(II)**	**Fe(III)**	**Fe(II)**
Number of unpaired electrons	**4**	**1**	**0**
Binding mode of O_2 and CO (linear *vs.* bent)	**–**	**Bent**	**Linear**

b. **(3 pts)** When comparing the affinity for CO, a heme has approximately 200 times greater affinity for CO than hemoglobin. This indicates that hemoglobin is structurally adapted to reduce susceptibility to CO poisoning, even in CO-rich environments. Explain how the structural properties of hemoglobin prevent the formation of carboxyhemoglobin.

Ans)

Hemoglobin contains a distal histidine near the heme binding site. (+1 pt.) This distal histidine prevents CO from binding in its preferred linear geometry by sterically blocking the space, resulting in less favorable binding to the iron atom. In contrast, the bent binding mode is optimal for O_2. (+1 pt.) Additionally, unlike O_2, CO cannot benefit from stabilization by the proton on the nitrogen of the histidine residue. Since free heme lacks this distal histidine, it cannot inhibit CO from binding in its most favorable bent configuration. (+1 pt.)

c. **(3 pts)** Oxyhemoglobin appears red, while deoxyhemoglobin has a bluish tint. Explain the reasons for the difference in color between these two forms of hemoglobin. Based on this information and the color wheel provided, predict the color of carboxyhemoglobin.



Ans)

O_2 is a strong field ligand. When O_2 binds to hemoglobin, the d-orbital splitting in the iron atom increases, affecting absorption in the visible light region. (+1 pt.) As a result, deoxyhemoglobin absorbs light near the yellow-green region, giving it a bluish color, while oxyhemoglobin absorbs light at shorter wavelengths (in the green region), resulting in its red appearance. (+1 pt.) Since CO is an even stronger field ligand than O_2, the d-orbital splitting becomes even larger, causing the absorption wavelength to shift further toward shorter wavelengths. Consequently, carboxyhemoglobin is expected to exhibit a red-orange color. (+1 pt.)

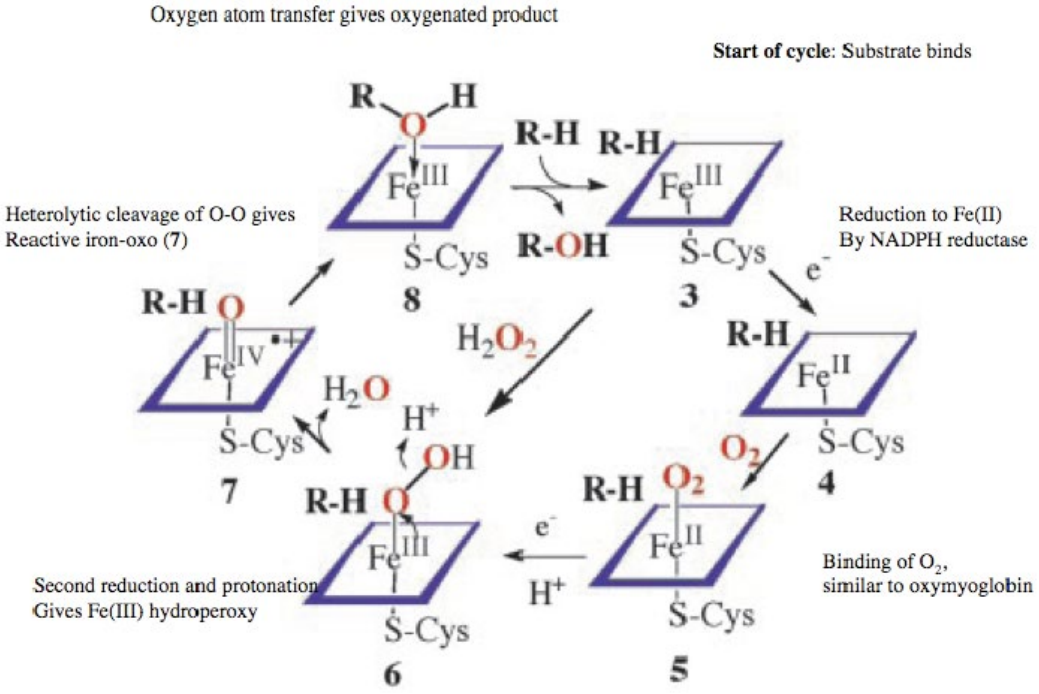
d. **(3 pts)** Compounds other than O_2 can bind to the iron atom in deoxyhemoglobin. Among the following species – CN^-, Cl^-, BF_3, and NO_2^- – identify which cannot bind to the iron in the heme group. Provide an explanation for your reasoning.

Ans)

CN^-, Cl^-, and NO_2^- can bind to the iron atom in deoxyhemoglobin because they all possess lone pairs of electrons that are available for dative bonding. In contrast, BF_3 (+1 pt.) lacks a lone pair (+1 pt.) and therefore cannot form a bond with the heme group. (+1 pt.)

11. **(10 pts)** This is the catalytic cycle of P450. Describe the full catalytic cycle (e^- & H^+ should be properly included in each step).

Ans) −1 pt. per wrong intermediate or oxidation state on iron



12. **(8 pts)** Classify each of the following statements as either 'True (T)' or 'False (F)'. If the statement is 'False', identify the incorrect part and provide the corrected version of the statement.

a. **(2 pts)** In some DNA binding proteins that regulate transcription, zinc fingers play an important role in maintaining the protein structure due to their preference for a square planar geometry.

F (+1 pt.); square planar → tetrahedral (+1 pt.)

b. **(2 pts)** Activated superoxide dismutase 1 (SOD1) has a tetrameric structure, with each monomeric protein unit containing both Cu(II)- and Zn(II)-binding sites.

F (+1 pt.); tetrameric → dimeric (+1 pt.)

c. **(2 pts)** The most favorable binding site for the activated form of cisplatin in the cytoplasm is the N7 moiety of adenine (the imine nitrogen on the five-membered ring of the purine base).

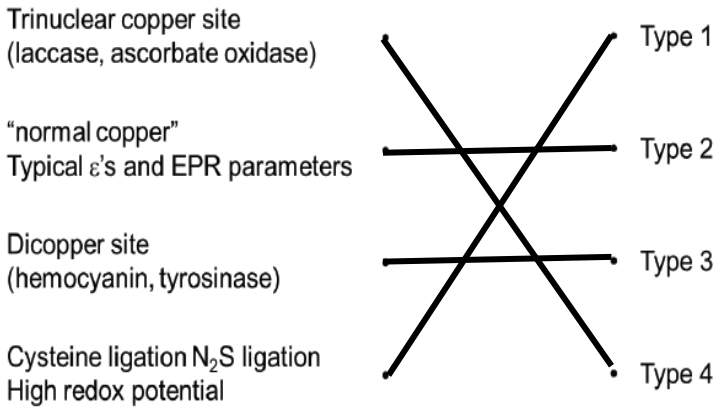
F (+1 pt.); adenine → guanine (+1 pt.)

d. **(2 pts)** In the first coordination sphere if the iron site in the free (deoxy-) form of hemoglobin and cytochrome P_{450}, there is no difference between the two proteins, despite their different functions involving dioxygen.

F (+1 pt.); there is a difference between the two proteins. Hemoglobin binds with an axial histidine (+0.5 pts.), while cytochrome P450 binds with an axial cysteine (+0.5 pts.).

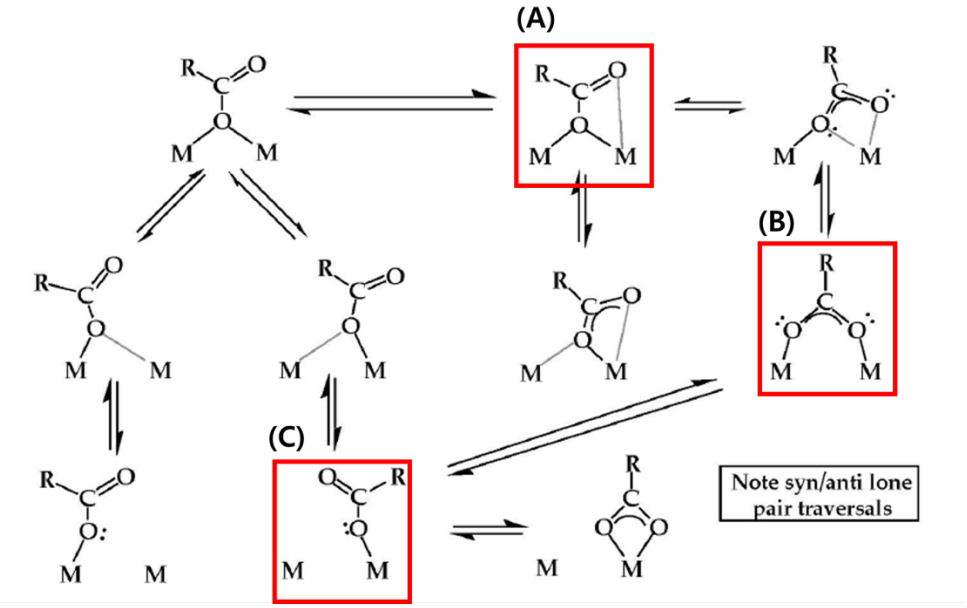
13. **(4 pts)** Connect the types of the Cu sites of metalloproteins.

Ans)



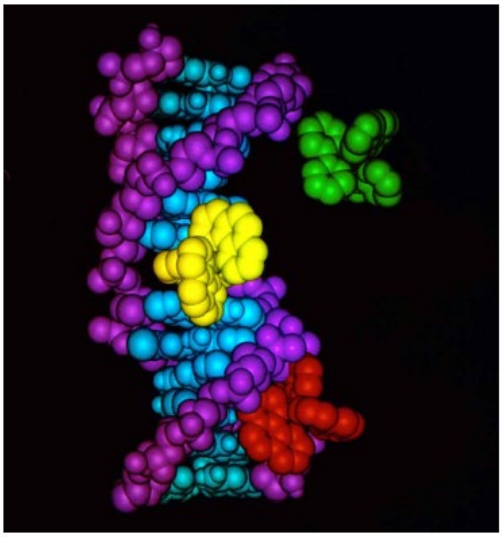
14. **(6 pts; 2 pts / each)** The schematic diagram illustrates the expanded carboxylate shift. Predict and draw the structures of (A), (B), and (C). Ensure that all lone pair electrons are explicitly indicated in your drawings.

Ans)



15. **(4 pts)** List the possible binding modes of transition metal complexes into DNA.

Ans) Electrostatic Interaction, Intercalation, Groove binding, Insertion



Three binding modes:

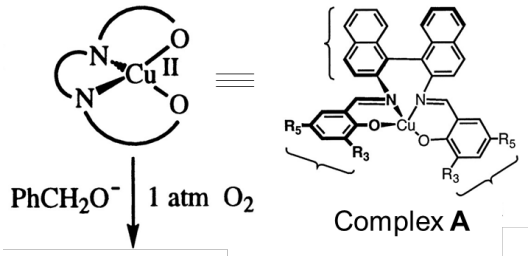
Electrostatic

Intercalation

Groove-Binding

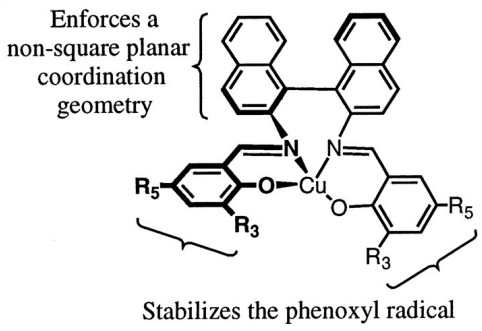
Insertion (NEW)

16. **(8 pts)** An important goal in bioinorganic chemistry is to design small inorganic complexes that replicate not only the structural and spectroscopic characteristics of their natural counterparts but also their functional behavior. As an example, Stack demonstrated biomimetic Cu(II)–phenoxyl radical reactivity to achieve alcohol oxidation to aldehyde using complex A. Answer the following questions:



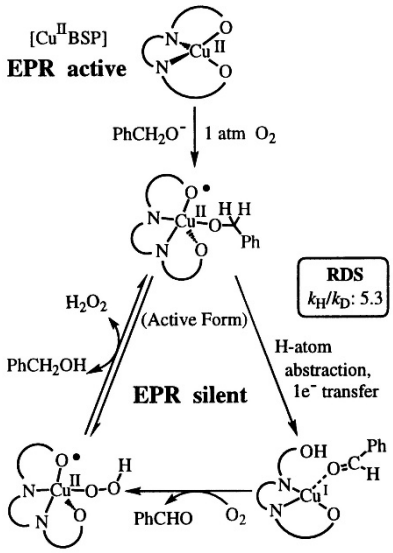
(a) **(2 pts)** Describe the role of the key structural feature, highlighted by braces, in enabling complex A to mimic the activity of galactose oxidase.

Ans)



(b) **(5 pts)** Draw and explain the complete catalytic cycle of this model complex, indicating the correct oxidation states of the metal at each step.

Ans)



(c) **(1 pt)** Determine the rate-limiting step in this catalytic cycle.

Ans)

The rate-determining step of this catalytic cycle is the “H-atom abstraction step”.

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