EXAM

This exam consists out of 5 problems and 6 pages. ***Write your name and student number on every page containing answers.*** *It is not allowed to use your notes, books, mobile phone, etc. Read the questions carefully before you answer them. Answer the question precisely and clearly indicate how you got to the answer. When a justification is asked, it counts as least as many points as the answer itself. If your argumentation contains a lot of nonsense besides the correct answer points will be deducted. The number of points (total = 90) is indicative and may be re-evaluated.*

1) Many enzymes such as photosystem II, cytochrome c oxidase, and others are imbedded in membranes of e.g. mitochondria or chloroplasts in which they contribute to establishment of a trans membrane proton gradient. Explain how such enzymes can pump protons across a membrane in a unidirectional manner. What are the requirements for proton pumping? – *6 points*

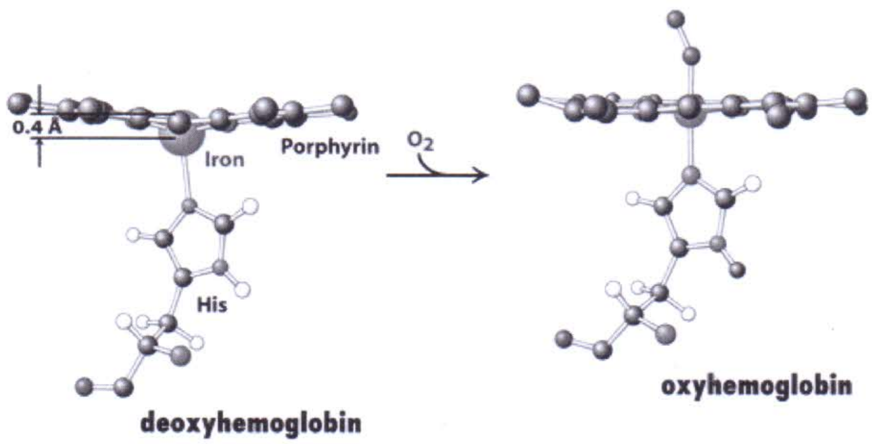
2) Hemoglobin is an enzyme that is responsible for the oxygen transport in vertebrates.

   a. Hemoglobin contains four heme subunits. Explain how the presence of four heme groups in the enzyme contributes to a more efficient delivery of dioxygen compared to the hypothetical case wherein hemoglobin would contain only one heme unit. – *5 points*

   b. The electronic structure of oxyhemoglobin has been a matter of debate for quite a long time. According to Pauling oxyhemoglobin is best described as an iron(III) center that coordinates a superoxide ligand (Pauling, L. *J. Am. Chem. Soc.* **1931**, *53*, 1367). The character of this interaction is rather covalent and the iron center and the superoxide moiety are antiferromagnetically coupled resulting in an S=0 ground state. Draw how the π* antibonding orbitals of the dioxygen fragment interact with the iron orbitals. – *6 points*

   c. Give the crystal field splitting of oxyhemoglobin according to Paulings theory. Make sure that you implement the interactions discussed in 2b and that you give the appropriate labels belonging to the orbitals. – *10 points*

   d. On basis of the diagram from question 2c, what orbital is the HOMO? And which one is the LUMO? Draw these orbitals. – *6 points*

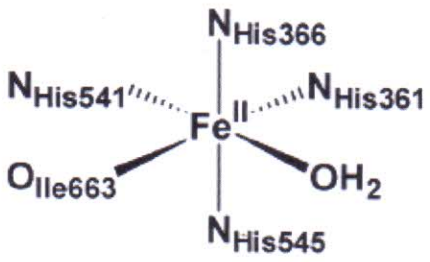


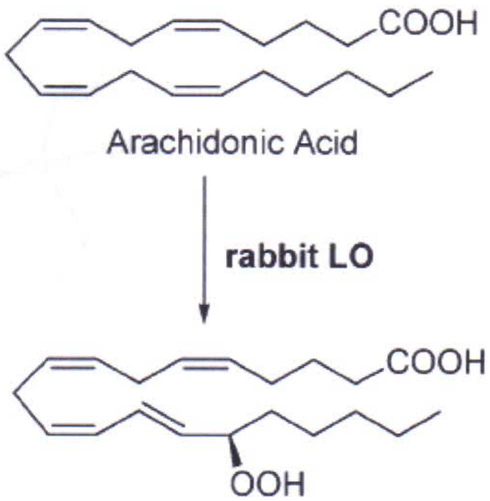
3) Lipoxygenases are capable of oxidizing 1,4-dienes with dioxygen to produce hydroperoxides. The observed kinetic isotope effect for this reaction was found to be $k_H/k_D \approx 50$.

a. What phenomena contribute to such a large difference in rate constants of deuterated and non-deuterated diene? Explain your answer in detail. – *6 points*

b. Enzymes such as cytochrome p_{450} and methane monooxygenase require the iron center to be in the +IV oxidation state to perform a hydrogen atom abstraction from the substrate. Why is the +III oxidation state of iron in case of lipoxygenase sufficient? – *3 points*

c. Give the mechanism wherein the 1,4-diene is converted to the hydroperoxide in the presence of the lipoxygenase enzyme illustrated below. – *6 points*

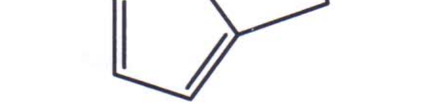




4) Given below is a cobalt catalyst for the reduction of dinitrogen to ammonia in the presence of the reductant KC_8 and the acid $[H(OEt)_2]BAr_F$, in which BAr_F is a large non-coordinating anion.

a. A key intermediate in a distal pathway for ammonia synthesis is a metal nitride species. Give the crystal field splitting of the corresponding neutral cobalt nitride species. What is the formal bond order of the M≡N bond? Is it likely that such a species is formed? – *10 points*

b. Based on your answer above, give a reasonable mechanism for the reduction of dinitrogen to ammonia in the presence of KC_8 and $[H(OEt)_2]^+$. Give the charge of all complexes involved and the oxidation states of both the metal <u>and</u> the nitrogen atoms derived from N_2 for all intermediates. You may move only one proton and/or one electron at a time. – *10 points*

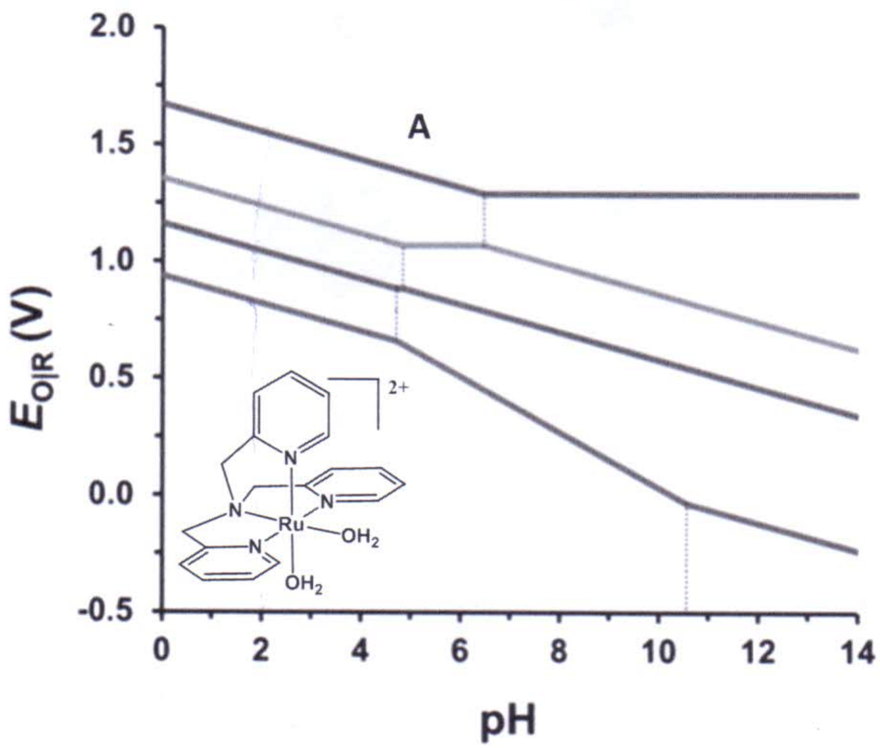


5) The complex $[Ru(OH_2)_2(tpa)]^{2+}$ is an active catalyst for the water oxidation reaction. Below is given the Pourbaix diagram of this species (see structure below).

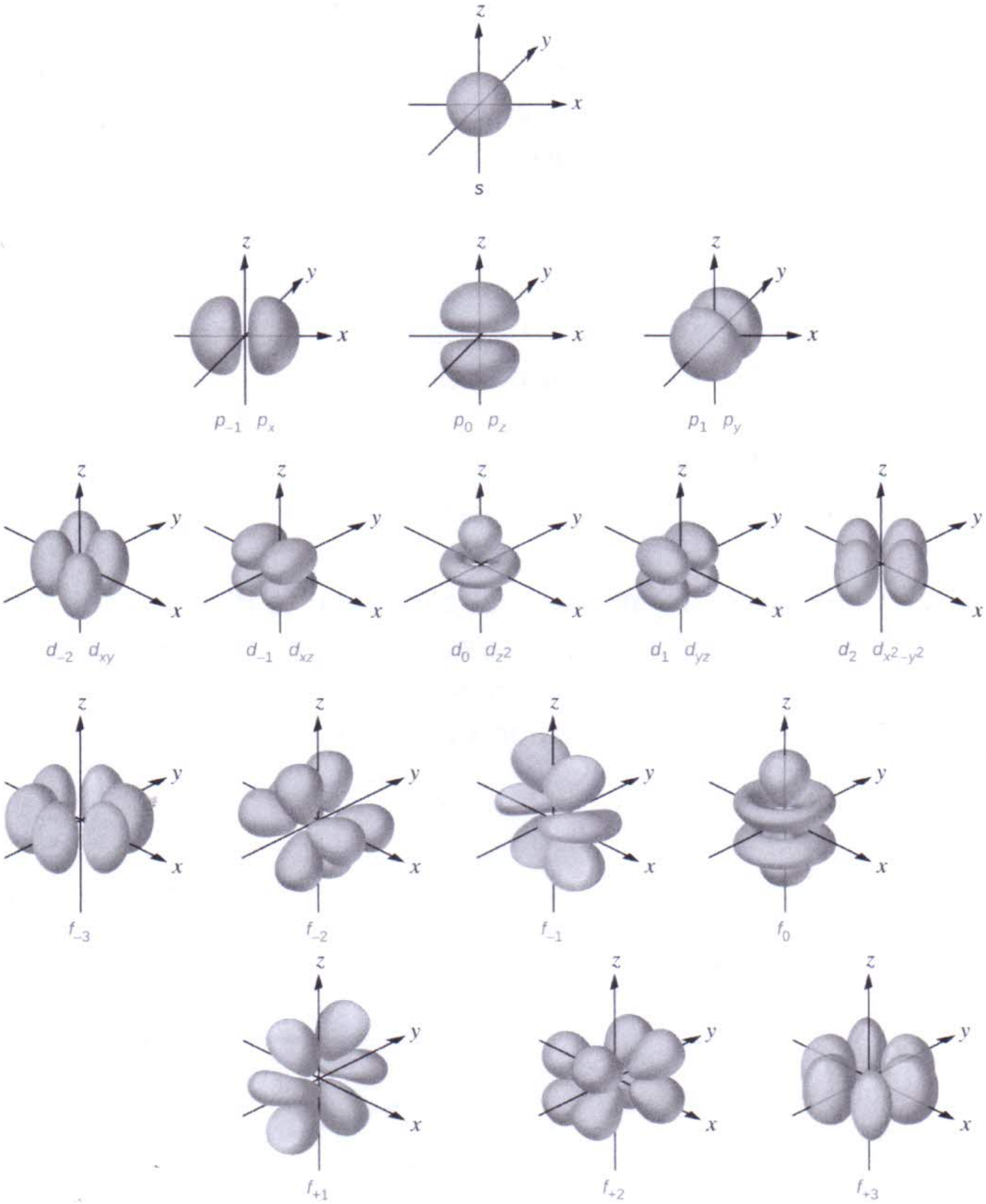
a. Give the structure of intermediate **A** and show how it is formed from the parent bisaqua complex (bottom left) in a stepwise manner at pH 2. How does the mechanism change at pH 6? And pH 8? – *10 points*

b. Give two possible reaction paths in which intermediate **A** can form the O-O bond. – *6 points*

c. Give two experiments that allow you to discriminate between both reaction paths that you have given at the previous question. Explain how these experiments can show via which path O-O bond formation takes place. – *6 points*



Appendix


s
p₋₁ pₓ
p₀ p_z
p₁ p_y
d₋₂ d_xy
d₋₁ d_xz
d₀ d_z2
d₁ d_yz
d₂ d_x2−y2
f₋₃
f₋₂
f₋₁
f₀
f₊₁
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f₊₃