UNIVERSITY OF SWAZILAND

FINAL EXAMINATION 2011/2012

TITLE OF PAPER:	**BIO-INORGANIC CHEMISTRY**
COURSE NUMBER:	**C617**
TIME ALLOWED:	**THREE (3) HOURS**
INSTRUCTIONS:	**ANSWER ALL FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE IS PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

(a) Identify significant roles in biological processes for the elements Na, Co and Zn. [6]

(b) The structure of haemoglobin, Hb may be classified as 'relaxed' [R] or 'tense' [T] as alternative terms for oxygenated and deoxygenated. The R and T structures differ in both the relation among the four subunits (the quaternary structure) and the conformation within a subunit (the tertiary structure). Explain how these structural differences relate to the difference in the oxygen binding curve of Hb as compared to myoglobin, Mb. [6]

(c) For the hemocyanins, indicate
- (i) the number of metal atoms needed to bind one O_2 molecule. [1]
- (ii) the identity (i.e. Fe, Co, Cu, Zn, etc.) of the metal atoms. [1]
- (iii) the oxidation state of the metal in the deoxy form of the protein. [1]
- (iv) the oxidation state of the metal in the oxy form of the protein. [1]
- (v) whether the oxygen, when bound, is best considered to be a neutral O_2, superoxide (O_2^-), peroxide (O_2^{2-}), or a hydroperoxide (HO_2^-). [1]

(d)
- (i) What prevents simple porphyrins from functioning as O_2 carriers? [3]
- (ii) How has this problem been avoided in successful models of Fe–porphyrin O_2 carriers? [3]
- (iii) The complex [Co(salen)(py)] is a model complex for O_2 binding. How is the model related to Haemoglobin or Myoglobin. [2]

QUESTION TWO

(a) Oxygen coordinates to both haemoglobin and myoglobin. What is the advantage of employing these different dioxygen complexes? [6]

(b) The diameter of a high-spin Fe(II) ion is larger than that of the 'hole' at the centre of the porphyrin ring, whereas a low-spin Fe(II) ion is smaller than the hole.
- (i) Give the electron configurations for the two spin states in an octahedral environment. [2]
- (ii) Why is the high-spin ion larger? [4]

(c)
- (i) What electron transport systems are used in photosynthesis? [1]
- (ii) The conversion of carbonic acid, H_2CO_3 to CO_2 + H_2O is a natural process; why is carbonic anhydrase needed? [2]
- (iii) The direct reduction products of water, H_2O_2 (or HO_2^-) and O_2^-, are toxic. How are these handled in biological systems? [4]

(d) Discuss <u>three</u> factors that illustrate the difference in the roles between Ca^{2+} and Mg^{2+}. [6]

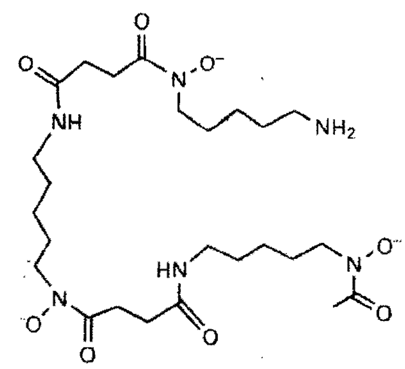
QUESTION THREE

(a) *Iron overload* is a medical condition where the body cannot cope with abnormally high levels of iron in the system. *Chelation therapy* by administering desferrioxamine shown below is used to treat the problem.

(i) Suggest the origin of the name chelation therapy. [1]

(ii) What form should the iron be in for the therapy to be most effective? [1]

(iii) Suggest how the therapy works using compound below. [3]



Desferrioxamine

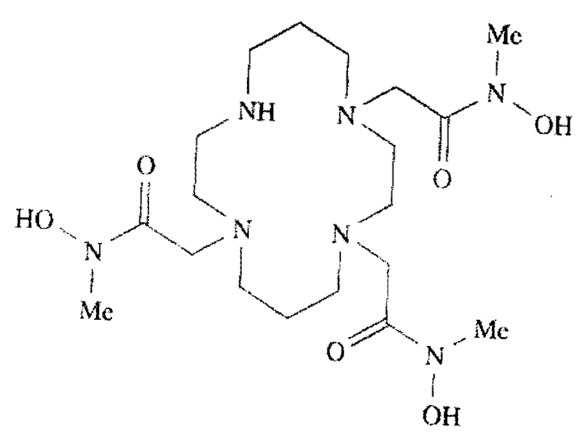
(b) Compound **A** below reacts with $Zn(ClO_4)_2{\cdot}6H_2O$ to give a complex $[Zn(A)(OH)]^+$ that is a model for the active site of carbonic anhydrase.

(i) Suggest a structure for this complex. [2]

(ii) What properties does **A** possess that

(1) mimic the coordination site in carbonic anhydrase? [3]

(2) control the coordination geometry around the Zn^{2+} ion in the model complex? [3]



A

(c) (i) Oxygen, O_2 is a σ-donor and a π-acceptor. Carbon monoxide, CO is also an excellent example of this type of ligand. Can you use these facts to propose a mechanism for CO poisoning? [3]

(ii) Why are *d* metals such as manganese (Mn), iron (Fe), cobalt (Co), and Copper (Cu) used in redox enzymes in preference to zinc (Zn), gallium (Ga), and calcium (Ca)? [3]

(d) (i) What functional groups are found in all amino acids? [1]

(ii) Draw the structure of the amino acid leucine in acidic solution at a pH below the isoelectric point. [2]

(iii) Why might we expect some elements essential for life at low concentrations to be toxic at higher concentrations? [3]

QUESTION FOUR

(a) (i) Discuss the probable difference in the pockets present in carboxypeptidase and carbonic anhydrase. [4]

(ii) Describe the characteristics of the ligands that are adopted for binding Ca^{2+} to proteins and those used to bind Fe^{2+} in the oxygen-carrying protein haemoglobin. [3]

(b) For the hemerythrins, indicate

(i) the number of metal atoms needed to bind one O_2 molecule. [1]

(ii) the identity (i.e. Fe, Co, Cu, Zn, etc.) of the metal atoms. [1]

(iii) the oxidation state of the metal in the deoxy form of the protein. [1]

(iv) the oxidation state of the metal in the oxy form of the protein. [1]

(v) whether the oxygen, when bound, is best considered to be a neutral O_2, superoxide (O_2^-), peroxide (O_2^{2-}), or a hydroperoxide (HO_2^-). [1]

(c) (i) Give an example of each of the <u>two</u> types of reactions brought about by vitamin B_{12}. [4]

(ii) What are the prosthetic groups of cytochromes and haemoglobin? [1]

(iii) What are the <u>two</u> important systems for the biological electron-transfer processes? [2]

(d) Discuss the use of inorganic elements in the following fields of medicine:

(i) Cancer treatment. [3]

(ii) Anti-arthritis drugs. [3]

PERIODIC TABLE OF ELEMENTS

Atomic mass → 10.811
Symbol → B
Atomic No. → 5

GROUPS

PERIODS	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1.008 **H** 1																	4.003 **He** 2
2	6.941 **Li** 3	9.012 **Be** 4											10.811 **B** 5	12.011 **C** 6	14.007 **N** 7	15.999 **O** 8	18.998 **F** 9	20.180 **Ne** 10
3	22.990 **Na** 11	24.305 **Mg** 12					**TRANSITION ELEMENTS**						26.982 **Al** 13	28.086 **Si** 14	30.974 **P** 15	32.06 **S** 16	35.453 **Cl** 17	39.948 **Ar** 18
4	39.098 **K** 19	40.078 **Ca** 20	44.956 **Sc** 21	47.88 **Ti** 22	50.942 **V** 23	51.996 **Cr** 24	54.938 **Mn** 25	55.847 **Fe** 26	58.933 **Co** 27	58.69 **Ni** 28	63.546 **Cu** 29	65.39 **Zn** 30	69.723 **Ga** 31	72.61 **Ge** 32	74.922 **As** 33	78.96 **Se** 34	79.904 **Br** 35	83.80 **Kr** 36
5	85.468 **Rb** 37	87.62 **Sr** 38	88.906 **Y** 39	91.224 **Zr** 40	92.906 **Nb** 41	95.94 **Mo** 42	98.907 **Tc** 43	101.07 **Ru** 44	102.91 **Rh** 45	106.42 **Pd** 46	107.87 **Ag** 47	112.41 **Cd** 48	114.82 **In** 49	118.71 **Sn** 50	121.75 **Sb** 51	127.60 **Te** 52	126.90 **I** 53	131.29 **Xe** 54
6	132.91 **Cs** 55	137.33 **Ba** 56	138.91 ***La** 57	178.49 **Hf** 72	180.95 **Ta** 73	183.85 **W** 74	186.21 **Re** 75	190.2 **Os** 76	192.22 **Ir** 77	195.08 **Pt** 78	196.97 **Au** 79	200.59 **Hg** 80	204.38 **Tl** 81	207.2 **Pb** 82	208.98 **Bi** 83	(209) **Po** 84	(210) **At** 85	(222) **Rn** 86
7	223 **Fr** 87	226.03 **Ra** 88	(227) ****Ac** 89	(261) **Rf** 104	(262) **Ha** 105	(263) **Unh** 106	(262) **Uns** 107	(265) **Uno** 108	(266) **Une** 109	(267) **Uun** 110								

***Lanthanide Series**	140.12 **Ce** 58	140.91 **Pr** 59	144.24 **Nd** 60	(145) **Pm** 61	150.36 **Sm** 62	151.96 **Eu** 63	157.25 **Gd** 64	158.93 **Tb** 65	162.50 **Dy** 66	164.93 **Ho** 67	167.26 **Er** 68	168.93 **Tm** 69	173.04 **Yb** 70	174.97 **Lu** 71
****Actinide Series**	232.04 **Th** 90	231.04 **Pa** 91	238.03 **U** 92	237.05 **Np** 93	(244) **Pu** 94	(243) **Am** 95	(247) **Cm** 96	(247) **Bk** 97	(251) **Cf** 98	(252) **Es** 99	(257) **Fm** 100	(258) **Md** 101	(259) **No** 102	(260) **Lr** 103

( ) indicates the mass number of the isotope with the longest half-life.