UNIVERSITY OF SWAZILAND

FINAL EXAMINATION

ACADEMIC YEAR 2007/2008

TITLE OF PAPER:	**ADVANCED INORGANIC CHEMISTRY**
COURSE NUMBER:	**C401**
TIME ALLOWED:	**THREE (3) HOURS**
INSTRUCTIONS:	**THERE ARE SIX (6) QUESTIONS. ANSWER ANY FOUR (4) QUESTIONS. EACH QUESTION IS WORTH 25 MARKS.**

A PERIODIC TABLE AND OTHER USEFUL DATA HAVE BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

(a) Determine the specified quantity:

(i) The metal-metal bond order consistent with the 18-electron rule for $[(\eta^5\text{-}C_5H_5)Mo(CO)_2]_2^{2-}$. [1]

(ii) The identity of the first row-transition metal in $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (assume a single M-M bond), an 18-electron molecule. [1]

(iii) The expected charge on $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^z$ on the basis of the 18-electron rule. [1]

(b) (i) Is $[Mo(CO)_7]$ likely to be stable? [2]

(ii) What is the electron count for and oxidation number of platinum in the anion of Zeise's salt, $[PtCl_3(CH_2{=}CH_2)]^-$? [2]

(c) Identify the following reactions by type and predict the products:

(i) $Re_2(CO)_{10} + Na/Hg \rightarrow$ [2]

(ii) $Rh(PPh_3)_3Br + Cl_2 \rightarrow$ [2]

(d) (i) Suggest a sequence of reactions for the preparation of $Fe(CO)_3$(diphos), given iron metal, CO, diphos ($Ph_2P\text{-}CH_2\text{-}CH_2\text{-}PPh_2$), and other reagents of your choice. [4]

(ii) Propose a synthesis for $HMn(CO)_5$, starting with $Mn_2(CO)_{10}$ as the source of Mn and other reagents of your choice. [4]

(e) (i) Which of the two isoelectronic compounds $Cr(CO)_6$ and $[V(CO)_6]^-$ will have the higher CO stretching frequency? [2]

(ii) Which of the two chromium compounds $[Cr(CO)_5(PEt_3)]$ and $[Cr(CO)_5(PPh_3)]$ will have the lower CO frequency? Which will have the shorter M-C bond? [4]

QUESTION TWO

(a) The complex $[Cr(CO)_4(PPh_3)_2]$ has one very strong IR absorption band at 1889 cm^{-1} in the CO stretching region. What is the probable structure of the compound? [4]

(b) Give organic fragments isolobal with each of the following:
(i) $(\eta^5\text{-}C_5H_5)Ni$ (ii) $(\eta^6\text{-}C_6H_6)Cr(CO)_2$
(iii) $[Fe(CO)_2(PPh_3)]^-$ [3]

(c) Use Wade's rules to predict the structures of the following:
(i) $B_5H_8^-$ (ii) $Os_5(CO)_{16}$
(ii) $Os_6(CO)_{17}[P(OMe_3)]_3$ [6]

(d) (i) Give a definition of a metal cluster. [1]
(ii) What are the two broad classes of metal carbonyl clusters? [2]
(iii) $M_3(CO)_{12}$ clusters (M = Ru and Os) are unreactive. Give *three* ways by which they can be converted into more reactive derivatives. [6]

(e) If the highly substituted complex $[Mo(CO)_3L_3]$ is desired, which of the ligands $P(CH_3)_3$ or $P(^tBu)_3$ would be preferred? Give reasons for your choice. [3]

QUESTION THREE

(a) $Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$ reacts with 3-chloroprop-1-ene to give a solid, **A**, which has a molecular formula $(C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_3W$. Compound **A** loses carbon monoxide on exposure to light and forms compound **B**, which has the formula $(C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2W$. Treating compound **A** with hydrogen chloride and then potassium hexafluorophosphate, $K^+PF_6^-$, results in the formation of a salt, **C**. Compound **C** has the molecular formula $[(C_3H_6)(\eta^5\text{-}C_5H_5)(CO)_3W]PF_6$. Use this information and the 18-electron rule to identify the compounds **A**, **B**, and **C**. Sketch a structure for each, paying particular attention to the hapticity of the hydrocarbon. [9]

(b) The complex $[Rh(H)(CO)(PPh_3)_3]$ can be used in the catalytic synthesis of n-pentanal from an alkene having one less carbon atom.
(i) Outline the main steps in the mechanism of this process indicating the reaction type of each step (such as oxidative addition) and identifying the catalytic species. [10]
(ii) Predict the influence of added triphenylphosphine on the rate of hydroformylation catalysed by $[Rh(H)(CO)(PPh_3)_3]$. [4]

(c) Give the equation for a workable reaction that will convert $Fe(\eta^5\text{-}C_5H_5)_2$ into $Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4COCH_3)$. [2]

QUESTION FOUR

(a) (i) Give a balanced equation for the reaction of any of the lanthanide metals with aqueous acid. [1]

(ii) Explain why stable and readily isolable carbonyl complexes are unknown for the lanthanides. [3]

(iii) A mixture of lanthanide metal ions was prepared containing Ce^{3+}, Eu^{3+} and Yb^{3+}. To separate the ions, a portion of the solution of the ions was poured through a sulphonated polysterene ion-exchange resin. The column was then eluted with a dilute solution of H_4EDTA adjusted to pH 8 with ammonia.

(1) Which ion comes out first? Explain. [4]

(2) Suggest another buffer solution that could be used to elute the ions from the column. [1]

(b) An empty, a half-filled and a completely filled 4*f* electronic level is often said to confer stability on the oxidation state of a lanthanide ion. Cite examples which bear out this statement. [3]

(c) (i) Use Hund's rules to derive the ground state term of Nd^{3+}. [4]

(ii) Hence determine the magnetic moment, μ. [5]

(d) The compound $Ni_3(C_5H_5)_3(CO)_2$ has a single CO stretching absorption at 1761 cm^{-1}. The IR data indicate that all C_5H_5 ligands are pentahapto and probably in identical environments.

(i) On the basis of these data, propose a structure. [2]

(ii) Does the electron count for each metal in your structure agree with the 18-electron rule? [2]

QUESTION FIVE

(a) Describe the main types of interhalogen compounds giving examples of each. [6]

(b) Predict the products of the following reactions of interhalogens:

(i) $ClF + S \rightarrow$ [1]

(ii) $ClF_3 + SbF_5 \rightarrow$ [1]

(iii) $IF_5 + CsF \rightarrow$ [1]

(c) Given that 1.84 g of IF_3 reacts with 0.93 g of $[(CH_3)_4N]F$ to form a product **X**:

(i) identify **X** [2]

(ii) Use VSEPR model to predict the shapes of

(1) IF_3 [2]

(2) the cation in **X** [2]

(3) the anion in **X** [2]

(d) The interhalogen compound, I_2Cl_6 exists as a dimer in the solid state.

(i) Write a balanced equation for the preparation of this compound. [2]

(ii) I_2Cl_6 undergoes dissociation on warming to room temperature. Write the reaction for the dissociation process. [3]

(e) Ligand substitution reactions on metal clusters are often found to occur by associative mechanisms, and it is postulated that these occur by initial breaking of an M-M bond, thereby providing an open coordination site for the incoming ligand. If the proposed mechanism is applicable, which would you expect to undergo the fastest exchange with added ^{13}CO? $Co_4(CO)_{12}$ or $Ir_4(CO)_{12}$? Suggest an explanation. [3]

QUESTION SIX

(a) Identify <u>one</u> significant role in biological processes for the elements Fe, Mn, Mo, Cu, and Zn. [5]

(b) What role does the magnesium ion play in the functioning of chlorophyll? [2]

(c) (i) State the main components of cobalamin. [4]
(ii) How do B_{12}, B_{12r}, and B_{12s} differ? [1]

(d) Arrange $[Na(H_2O)_6]^+$, $[Sc(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$, and $[Ni(H_2O)_6]^{2+}$ in order of increasing acidity. [4]

(e) The molecule $(CH_3)_2N–PF_2$ has two basic atoms, P and N. One is bound to B in a complex with BH_3, the other to B in a complex with BF_3. Decide which is which and state your reason. [4]

(f) Consider each of the following solvents:
(i) ammonia, NH_3 (ii) acetic acid, CH_3COOH (iii) sulphuric acid, H_2SO_4
(1) Give equations for autoionization of the pure solvents. [3]
(2) Give appropriate equations to show what will happen if CH_3COOH is dissolved in (i) NH_3 and (ii) H_2SO_4. [2]

PERIODIC TABLE OF ELEMENTS

PERIODS	GROUPS 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 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											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								

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

TRANSITION ELEMENTS

***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.