UNIVERSITY OF SWAZILAND

SUPPLEMENTARY 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 HAS BEEN PROVIDED WITH THIS EXAMINATION PAPER.

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QUESTION ONE

(a) Determine the specified quantity on the basis of the 18-electron rule:

(i) The number of CO ligands in $[(\eta^5\text{-}C_5H_5)W(CO)_x]_2$ having W-W single bond. [1]

(ii) The identity of the first-row transition metal in $(\eta^4\text{-}C_8H_8)M(CO)_3$. [1]

(iii) The expected charge on $[(CO)_3Ni\text{-}Co(CO)_3]^z$. [1]

(b) Sketch the structures of the following compounds, given that the central metal atoms obey the 18-electron rule.

(i) $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ [2]

(ii) *trans*-bis[tetracarbonyl(triphenylphosphine)manganese(0)] [2]

(c) Explain with necessary diagrams the bonding in CO to transitional metal atoms with emphasis on the σ-donor and π*-acceptor functions of the ligand. [4]

(d) Predict reasonable products for the following reactions:

(i) $(\eta^4\text{-}C_6H_6)Fe(CO)_3 + PPh_3 \rightarrow$ [2]

(ii) $Cr(CO)_6 + CH_2{=}CH\text{-}CH{=}CH_2 \rightarrow$ [2]

(iii) $Co(CO)_3(NO) + PPh_3 \rightarrow$ [2]

(iv) $Mo(CO)_6 + (CH_3)_2PCH_2CH_2P(Ph)CH_2CH_2P(CH_3)_2 \rightarrow$ [2]

(v) $H_3C\text{-}Mn(CO)_5 + SO_2 \rightarrow$ (no gases are evolved) [2]

(e) For each of the following sets, which complex would be expected to have the highest C-O stretching frequency? Explain.

(i) $Fe(CO)_4(PF_3)$, $Fe(CO)_4(PCl_3)$, $Fe(CO)_4(PMe_3)$ [2]

(ii) $[Re(CO)_6]^+$, $W(CO)_6$, $[Ta(CO)_6]^-$ [2]

QUESTION TWO

(a) On the basis of cluster valence electron count, predict the structures of the following species:

(i) $Fe_5C(CO)_{15}$ [2]

(ii) $Ni_5Os(CO)_{14}$ [2]

(b) Based on isolobal analogies, choose the organometallic fragments that might replace

(i) CH_2^+ — $Fe(CO)_4$, $Mn(CO)_5$, or $Re(CO)_4$ [1]

(ii) CH^- — $Ni(CO)_3$, $Co(CO)_3$, or $Mn(CO)_4$ [1]

(iii) CH_3 — $(\eta^5\text{-}C_5H_5)Co(CO)$, $Mn(CO)_5$, or $Cr(CO)_6$ [1]

(c) Use Wade's rules to predict the structures of the following:

(i) $Ru_6C(CO)_{17}$ [2]

(ii) $[Rh_7(CO)_{16}]^{3-}$ [2]

(iii) $Fe_4C(CO)_{13}$ [2]

(d) Consider the polynuclear carbonyl hydride complex, $H_2Os_3(CO)_{10}$

(i) Write down the equation for the formation of this species. [2]

(ii) From the application of the 18-electron rule, comment on the structure of this molecule. [2]

(iii) Compare the reactivity of this molecule with that of the complex $Os_3(CO)_{12}$. [2]

(e) Account for the observation that only a single carbonyl stretching band is observed for the ion $[Co(CO)_3(PPh_3)_2]^+$. [3]

(f) Consider the following species:

(i) NiNO (ii) $(\eta^5\text{-}C_5H_5)Ni$ (iii) BF

With which of these species are CO, $Co(CO)_2$ and $(\eta^6\text{-}C_6H_6)Co$ isoelectronic so far as valence electrons are concerned? [3]

QUESTION THREE

(a) (i) What is an "oxidative addition" reaction? Give an example. [2]

(ii) What are the requirement(s) for such a reaction to occur? [2]

(iii) What is the reverse reaction called? State three requirements on the complex that favour this reaction. [4]

(b) (i) Propose a mechanism for the following reaction: [8]

$$R\text{-}CH{=}CH_2 + CO + H_2 + Co_2(CO)_8 \rightarrow RCH_2CH_2CHO$$

(ii) Give electron counts for all the species postulated to be involved in the catalytic cycle for the reaction shown in (i) above. [4]

(iii) Kinetic studies indicate that the hydroformylation reaction rate is enhanced by an increase in H_2 pressure and inhibited by an increase in CO pressure. How is the mechanism in the above cycle consistent with these observations? [5]

QUESTION FOUR

(a) Discuss the steady decrease in ionic size of the Ln^{3+} ions across the period. [5]

(b) (i) Why are the colours of Ln^{3+} ions less intense than those of the first-row transition metal ions? [3]

(ii) Which Ln^{3+} ions would you expect to show the same colour as
(1) Eu^{3+} (2) Pr^{3+} (3) Dy^{3+} [3]
Explain. [2]

(iii) Why are Eu^{2+} and Yb^{2+} somewhat more stable with respect to oxidation than other Ln^{2+} cations? [3]

(c) (i) Determine the number of unpaired electrons in Er^{3+}. [1]

(ii) Derive the ground state term symbol for Er^{3+}, and calculate its magnetic moment. [6]

(iii) Write the symbols of <u>two</u> lanthanide metal ions whose magnetic moments can be calculated by the spin-only formula. [2]

QUESTION FIVE

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

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

(ii) $ClF_3 + H_2O \rightarrow$ [1]

(iii) $BrF_5 + F_2 \rightarrow$ [1]

(b) The structure of I_3^- is highly sensitive to the identity of the counter-ion. Describe the structure of I_3^- in combination with

(i) $[N(CH_3)_4]^+$ [2]

(ii) Cs^+ [2]

(c) Write the self-ionisation reaction for ICl and predict the structure for the <u>anionic</u> compound formed. [3]

(d) Suggest an <u>equation</u> for the preparation of each of the following species and predict the <u>structure</u> of each of them.

(i) $[ICl_4]^-$ (ii) $[BrICl]^-$ [6]

(e) (i) Give <u>two</u> ways used to prepare actinide metals from actinide salts. [4]

(ii) State the <u>two</u> factors on which the general methods for the preparation of synthetic actinides depend. [2]

(iii) Using the reactor irradiation method, write down a sequence of nuclear reactions that will produce $^{237}_{93}Np$ from $^{235}_{92}U$ [3]

QUESTION SIX

(a) (i) For each of the following elements, identify one significant role in biological processes:

(1) Mg [1]

(2) Co [1]

(3) K [1]

(ii) Why are *d* metals such as Mn, Fe, Co, and Cu used in redox enzymes in preference to Zn, Ga, and Ca? [1]

(iii) Metal ions in animals are often coordinated by nitrogen donor atoms. Give two examples of Nature's nitrogen ligands. [2]

(b) Briefly discuss CO poisoning. [3]

(c) Using the most appropriate acid-base theory, identify the acids and bases in the following reactions:

(i) $SiO_2 + Na_2O \rightarrow Na_2SiO_3$ [2]

(ii) $Cl_3PO + Cl^- \rightarrow Cl_4PO^-$ [2]

(iii) $BF_3 + 2ClF \rightarrow Cl_2F^+ + BF_4^-$ [2]

(d) (i) Name three properties that determine the utility of a solvent. [3]

(ii) Using hard-soft concepts, which of the following reactions are predicted to have an equilibrium constant greater than 1? Assume gas-phase or hydrocarbon solution and 25 °C.

(1) $R_3PBBr_3 + R_3NBF_3 \leftrightarrows R_3PBF_3 + R_3NBBr_3$ [2]

(2) $CH_3HgI + HCl \leftrightarrows CH_3HgCl + HI$ [2]

(iii) Account for the trend in acidity:

$[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$ [3]

PERIODIC TABLE OF ELEMENTS

GROUPS

Atomic mass → Symbol → Atomic No. (key shown on the element B)

TRANSITION ELEMENTS

PERIODS	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								

***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.