UNIVERSITY OF SWAZILAND

SUPPLEMENTARY EXAMINATION 2007

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) Suggest products of the following reactions:

(i) $MeBr + 2Li \rightarrow$

(ii) $Na + C_5H_6 \rightarrow$

(iii) $MgCl_2 + LiR \rightarrow$

(iv) $Me_3SiCl + Na[C_5H_5] \rightarrow$ [4]

(b) Sketch interactions of 1,3-butadiene, (CH_2=CH-CH=CH_2) with a metal atom via

(i) η^2 (ii) η^4 [4]

(c) Suggest products in the following reactions, and give likely structures for the products:

(i) $Fe(CO)_5$ irradiated with C_2H_4

(ii) $Re_2(CO)_{10}$ with Na/Hg

(iii) $Na[Mn(CO)_5]$ with ONCl

(iv) $Ni(CO)_4$ with PPh_3 [8]

(d) (i) Using a suitable explanation determine which of the two isoelectronic compounds $Cr(CO)_6$ and $[V(CO)_6]^-$ will have

(1) the higher CO stretching frequency?

(2) the shorter M—C bond?

(ii) Comment on the observation that on going from $Fe(CO)_5$ to $Fe(CO)_3(PPh_3)_2$, absorptions in the IR spectrum at 2025 and 2000 cm^{-1} are replaced by bands at 1944, 1886 and 1881 cm^{-1}. [9]

QUESTION TWO

(a) Use Wade's rules to suggest likely structures for

(i) B_5H_9 (ii) $[B_8H_8]^{2-}$ (iii) $[Os_8(CO)_{22}]^{2-}$ [9]

(b) Pick out pairs of isoelectronic species from the following list:

HF, $[NO_2]^+$, NH_3, $[H_3O]^+$, $[OH]^-$, CO_2 [3]

(c) Comment on the following observations:

(i) Imidazole derivatives are often used to model histidine-binding sites.

(ii) Thioneins bind, for example, Cd^{2+} in cysteine-rich pockets. [8]

(d) Which Ln^{3+} ion would you expect to show the same colour as

(i) Eu^{3+}. (ii) Pr^{3+} (iii) Dy^{3+} [3]

Explain. [2]

QUESTION THREE

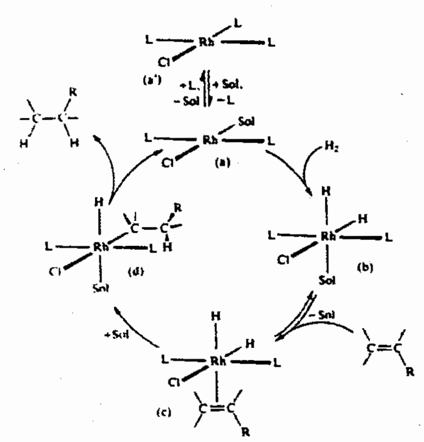
(a) (i) What type of reaction is the following, and by what mechanism does it occur?

$Mn(CO)_5Me + CO \rightarrow Mn(CO)_5(COMe)$

(ii) Write an equation to show β-hydrogen elimination from $L_nMCH_2CH_2R$.

[6]

(b) There is one oxidative addition reaction and one reductive elimination reaction in the figure below. Give balanced chemical equations for them both and assign oxidation numbers to all the rhodium complexes in the equations. [6]



The main catalytic cycle in the homogeneous hydrogenation of alkene by rhodium-phosphine complexes, $L = PPh_3$.

(c) Propose the main steps in the catalytic cycle for the conversion of pent-1-ene to hexanal using $HRh(CO)_4$ as the catalyst precursor. [8]

(d) $H_2Os_3(CO)_{10}$ catalyses the isomerization of alkenes:

$RCH_2CH{=}CH_2 \rightarrow E\text{-}RCH{=}CHMe + Z\text{-}RCH{=}CHMe$

By determining the cluster valence electron count for $H_2Os_3(CO)_{10}$ deduce what makes this cluster an effective catalyst. [5]

QUESTION FOUR

(a) Do (i) $[IrBr_2(CH_3)(CO)(PPh_3)_2]$ and (ii) $[Cr(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]$ obey the 18-electron rule? [2]

(b) Propose two syntheses for $MeMn(CO)_5$ both starting with $Mn_2(CO)_{10}$, with one using Na and one using Br_2. You may use other reagents of your choice. [8]

(c) Discuss the uptake of O_2 by myoglobin and hemoglobin and the effect of partial pressure of O_2. [5]

(d) Using the concept of isolobality, give
- (i) the hydrogen-nitrogen molecule or molecular fragment that is isolobal with CH_3^-.
- (ii) the hydrogen-boron molecule or molecular fragment that is isolobal with the O atom.
- (iii) a nitrogen-containing species that is isolobal with $[Mn(CO)_5]^-$. [3]

(e) (i) Predict whether the equilibrium constants for the following reactions should be greater than 1 (reaction lies to the right) or less than 1 (reaction lies to the left):

(1) $CdI_2 + CaF_2 \leftrightarrows CdF_2 + CaI_2$ [2]

(2) $[CuI_4]^{2-} + [CuCl_4]^{3-} \leftrightarrows [CuCl_4]^{2-} + [CuI_4]^{3-}$ [2]

(ii) Account for the trend in acidity:
$[Fe(OH_2)_6]^{2+} < [Fe(OH_2)_6]^{3+}$ [3]

QUESTION FIVE

(a) Whereas the stability constant, *K*, for the equilibrium:

Haemoglobin + $O_2 \leftrightarrows$ (Haemoglobin)(O_2)

is of the order of 10, that for the equilibrium:

(Haemoglobin)$(O_2)_3$ + $O_2 \leftrightarrows$ (haemoglobin)$(O_2)_4$

is of the order of 3000. Rationalise this observation. [5]

(b) Metal-Metal bonding in multinuclear species is not always clear-cut. *Solely on the basis of the 18-electron rule,* suggest whether $(\eta^5\text{-}C_5H_5)Ni(\mu\text{-}PPh_2)_2Ni(\eta^5\text{-}C_5H_5)$ might be expected to contain a metal-metal bond. [3]

(c) Suggest what change in cluster structure might accompany the reaction:

$[Co_6(CO)_{15}N]^- \rightarrow [Co_6(CO)_{13}N]^- + 2CO$ [6]

(d) (i) Confirm that $H_2Os_3(CO)_{11}$ has sufficient valence electrons to adopt a triangular metal framework..

(ii) Do the modes of bonding of the CO and H ligands in (i) above affect the total valence electron count? [5]

(iii) Comment on the fact that $H_2Os_3(CO)_{10}$ also has a triangular Os_3-core.

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

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

QUESTION SIX

(a) Suggest products for the following reactions.

(i) $ClF + BF_3 \rightarrow$

(ii) $CsF + IF_5 \rightarrow$

(iii) $SbF_5 + ClF_5 \rightarrow$

(iv) $Me_4NF + IF_7 \rightarrow$ [4]

(b) Predict the structures of

(i) $[ICl_4]^-$ (ii) $[BrF_2]^+$ [6]

(c) (i) Use Hund's rules to derive the term symbol for the ground state of Ce^{3+} ion.

(ii) Hence calculate the value for the effective magnetic moment, μ_{eff}, of Ce^{3+}.

[5]

(d) Identify the starting isotopes **A** and **B** in each of the following syntheses of transactinoid elements:

(i) **A** + ${}^{4}_{2}He \rightarrow {}^{256}_{101}Md + {}^{1}_{0}n$

(ii) **B** + ${}^{16}_{8}O \rightarrow {}^{255}_{102}No + 5({}^{1}_{0}n)$ [4]

(e) Identify isotopes **C** – **H** in the following sequence of nuclear reactions:

(i) $^{238}U \xrightarrow{(n,\gamma)} \mathbf{C} \xrightarrow{-\beta^-} \mathbf{D} \xrightarrow{-\beta^-} \mathbf{E}$

(ii) $\mathbf{F} \xrightarrow{-\beta^-} \mathbf{G} \xrightarrow{(n,\gamma)} {}^{242}Am \xrightarrow{-\beta^-} \mathbf{H}$ [6]

PERIODIC TABLE OF ELEMENTS

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										Atomic mass → **Symbol** → Atomic No. →	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.