

CHEM 361 — TEST
Inorganic and Structural Chemistry
Tuesday 14 July 2009, Room 431

Time: 7:00 pm to 9:00 pm

Time allowed: 120 minutes

Answer ALL FIVE questions. There are 100 marks available. Not all questions are of equal value.

Start each question on a new page.

A periodic table is attached.

Question 1 (20 marks)

- (a) The metal complex TiCl_4 prefers to bind to the following three ligands in the order $\text{NMe}_3 > \text{PMe}_3 > \text{CO}$, whereas the metal complex $\text{Mo}(\text{CO})_5(\text{THF})$ (THF = tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$) undergoes substitution reactions of the THF ligand with the following preference: $\text{CO} > \text{PMe}_3 > \text{NMe}_3$. Explain these observations in detail. Your answer should include a comparison of the metal complexes and a discussion of the mode of bonding of each of the ligands.
- (b) The reaction of $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ (**A**) with C_6Me_6 in the presence of $\text{Ag}[\text{BF}_4]$ gives $[(\text{C}_6\text{Me}_6)_2\text{Ru}][\text{BF}_4]_2$ containing cation **B**. Treatment of this compound with Na in liquid ammonia yields a neutral Ru(0) complex **C**.
- (i) Suggest structures for **A**, **B** and **C**.
- (ii) What is the other product in the reaction of **A** to give **B**?
- (c) Explain why $\text{CpNb}(\text{CO})_4$ obeys the 18-electron rule whereas CpNbCl_4 does not.

Question 2 (16 marks)

- (a) For each of the following compounds, give the d-electron count for the central metal and the 18-electron rule count for the transition metal complex:
- $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-O}_2)$
 - $\text{Mo}(\eta^1\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)$
[C_3H_5 = allyl; C_4H_8 = butadiene; C_5H_5 = cyclopentadienyl]
 - $\text{CrI}(\text{CO})_4(\text{CMe})$
 - $[\text{Au}(\text{CO})_2]^+$
- (b) Draw the expected transition metal product from each of the following reactions:
- $[(\text{C}_7\text{H}_7)\text{W}(\text{CO})_3]^+ + \text{MeCN}$ (hint: this is an addition reaction, not a substitution)
 - $\text{Fe}(\text{CO})_5 + 1,5\text{-C}_8\text{H}_{12}$ (1,5-cyclooctadiene)
 - $\text{VCl}_3 + \text{Na} + \text{CO}$ (200 atm) at $160\text{ }^\circ\text{C}$
 - $\text{Mo}(\text{CO})_6 + \text{C}_5\text{H}_6$

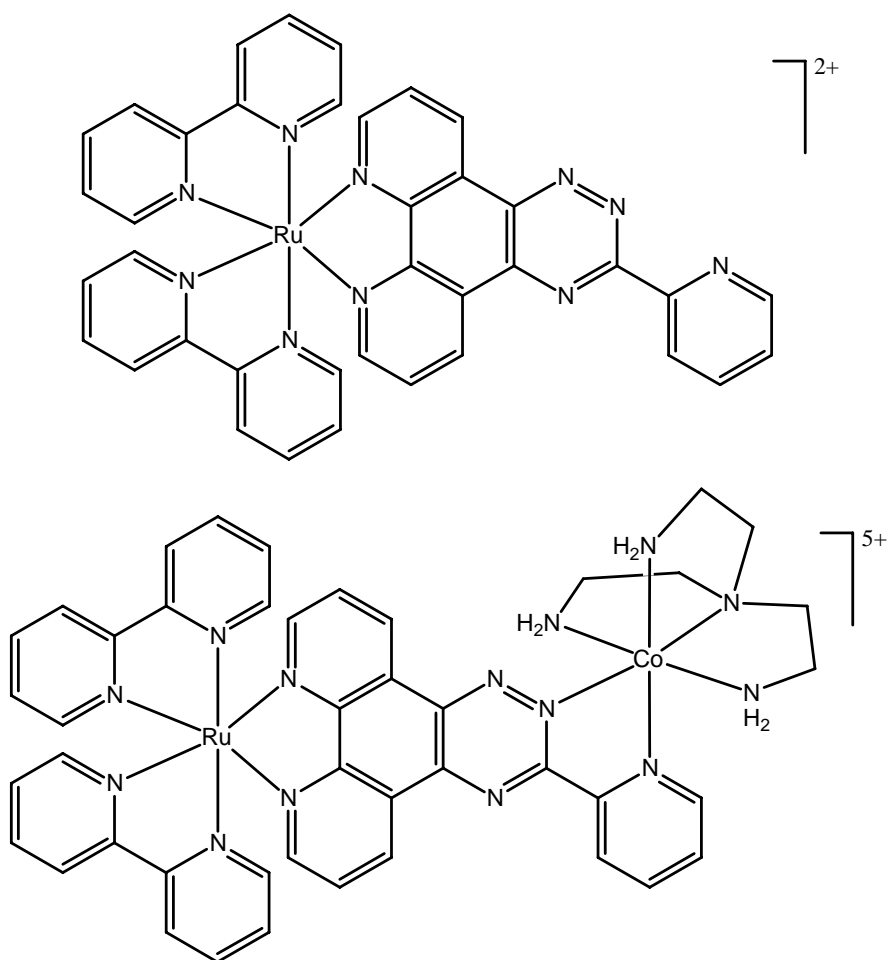
Question 3 (14 marks)

- (a) Draw the structure of each of the following compounds:
- The 18-electron complex $\text{RuCp}^*(\text{C}_6\text{F}_5\text{O})$ [$\text{C}_6\text{F}_5\text{O}$ is pentafluorophenoxide]
 - $\text{MnCo}(\text{CO})_9$
 - $\text{Cp}_2\text{Ni}_2(\mu\text{-PPh}_2)_2$
 - $\text{CpCo}(\text{SiMe}_3)(\text{NO})$
- (b) For each of the following sets of compounds, list the compounds in order of increasing average $\nu(\text{CO})$ and explain your order.
- $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$, $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{PPh}_3)_3(\text{CO})_3$
 - $\text{Fe}(\text{CO})_4(\text{CH}_3)\text{Br}$, $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4(\text{Br})_2$

Question 4 (30 marks)

The complexes shown below have been prepared recently in the Department of Chemistry.

- Use the first complex as a basis on which to discuss the different ways that metal complexes can interact with DNA. Provide additional examples if required.
- What forms of experimental evidence can be used to characterise the binding to DNA?
- How do you think the addition of the cobalt portion of the complex in the second example would affect DNA binding?



Question 5 (20 marks)

Describe the detailed mechanism by which cisplatin is believed to lead to anti-cancer activity and then use this as a basis to identify structural features that should be incorporated into a new anti-cancer drug.

Periodic Table

1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.8	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.0	10 Ne 20.2
11 Na 23.0	12 Mg 24.3											13 Al 27.0	14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.5	18 Ar 39.9
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.9	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.4	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc (99)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57-71 see below	72 Hf 178.5	73 Ta 181.0	74 W 183.9	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89-103 see below	104 Rf (257)	105 Db (260)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110	111	112						

57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
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89 Ac (227)	90 Th 232.0	91 Pa (231)	92 U 238.1	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (245)	98 Cf (251)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)
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