

CHEM 321 — TEST
Inorganic and Structural Chemistry
Tuesday 14 July 2008, Room 431

Time: 7:00 pm to 9:00 pm

Time allowed: 120 minutes

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

Start each question on a new page.

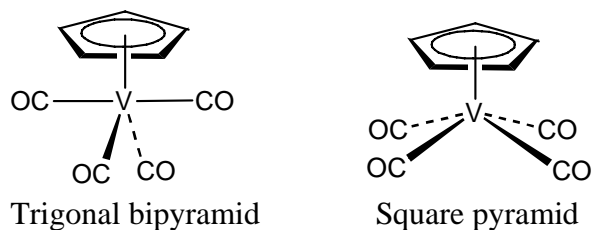
A periodic table and a chart to determine the point group is attached.

Question 1 (15 marks)

- (a) Write one symbol for each of the following combinations of operations:
- (i) C_2C_2
 - (ii) $C_6^2C_6^1$
 - (iii) $C_5\sigma_h$
 - (iv) $C_3^2C_3^2C_3^{-1}$
 - (v) $S_4\sigma_h$
- (b) How many operations are there in each of the following point groups?
- (i) C_4
 - (ii) D_{5h}
 - (iii) C_i
- (c) For each of the following point groups, sketch a molecule that exemplifies it:
- (i) C_{2v}
 - (ii) D_{3h}
 - (iii) $C_{\infty v}$
 - (iv) T_d

Question 2 (20 marks)

- (a) The transition metal carbonyl compound $(C_5H_5)V(CO)_4$ has two infra-red $\nu(CO)$ stretching bands (at 2030 and 1931 cm^{-1}). Consider the two possible geometries shown below (one is based on a trigonal bipyramid with the C_5H_5 ligand in an equatorial position; the other is based on a square pyramid). The C_5H_5 ligand can be considered as a point mass when determining the point group.



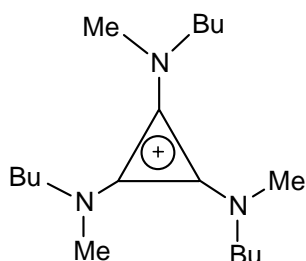
- (i) The trigonal bipyramidal geometry would have two A_1 , a B_1 and a B_2 symmetry species for the $\nu(CO)$ stretching vibrations. Using a character table provided below, which are infrared active?
- (ii) The square pyramidal geometry would have A_1 , B_1 and E symmetry species for the $\nu(CO)$ stretching vibrations. Using a character table provided below, which are infrared active?
- (iii) Based on the observed infrared bands, what is the actual geometry of $(C_5H_5)V(CO)_4$? Briefly justify your answer.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

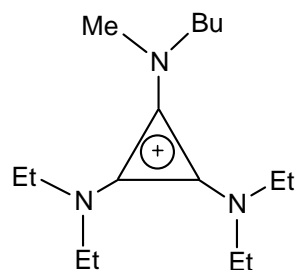
C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		$x^2 - y^2$
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x,y)(R_x, R_y)	(xz, yz)

(b) List all of the symmetry ELEMENTS for each of the following molecules:

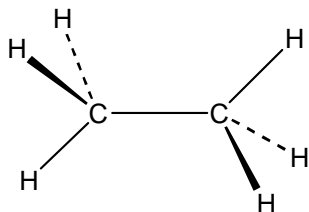
(i) The planar cyclopropenium:



(ii) The planar cyclopropenium:



(iii) Staggered ethane:



(c) Using the character tables given below, determine the symmetry species for the symmetric $\nu(\text{B}-\text{Cl})$ vibrational mode for planar BCl_3 and for pyramidal BCl_3 . Show your working. Which of these modes is/are IR active?

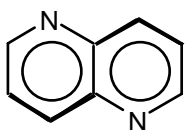
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(x,y)	$x^2 - y^2, xy$
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	(R_x, R_y)	(xz, yz)

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	$x^2 + y^2, z^2$
A_2	1	1	-1	R_z	
E	2	-1	0	(x,y)(R_x, R_y)	$(x^2 - y^2, xy)(xz, yz)$

Question 3 (15 marks)

(a) Using the flow chart provided on the last page (so that it can be detached for ease of use), determine the point group of each of the following molecules (you should show your working through the chart):

- (i) CO_2
- (ii) planar XeF_4
- (iii) $[\text{Co}(\text{en})_3]^{3+}$
- (iv) *trans*-1,3-dichlorocyclobutane
- (v)



- (b) Which of the molecules in part (a) is/are polar?
- (c) Which of the molecules in part (a) is/are chiral?
- (d) Which of the molecules in part (a) is/are centrosymmetric?

Question 4 (14 marks)

(a) Draw the structure of each of the following compounds:

- (i) $(\eta^5\text{-Cp})\text{CoCl}(\text{NO})$
- (ii) $\text{MnCo}(\text{CO})_9$
- (iii) $[\text{CpMo}(\text{CO})_2]_2$
- (iv) $\text{Cp}_2\text{W}(\text{CO})_2$

(b) For each of the following sets of compounds, list the compounds in order of increasing average $\nu(\text{CO})$ and explain your order.

- (i) $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$, $\text{Mo}(\text{CO})_6$ and $\text{Mo}(\text{PPh}_3)_3(\text{CO})_3$
- (ii) $\text{Fe}(\text{CO})_4(\text{CH}_3)\text{Br}$, $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4(\text{Br})_2$

Question 5 (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 $\text{Mo}(\text{CO})_5(\text{THF})$ ($\text{THF} =$ 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 $\text{Ru}(0)$ complex **C**.
- Suggest structures for **A**, **B** and **C**.
 - 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 6 (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:
- $\text{Ru}(\text{PMe}_3)_4(\eta^2\text{-C}_2\text{H}_4)$
 - $\text{Mo}(\eta^1\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_8)(\eta^5\text{-C}_5\text{H}_5)$
[$\text{C}_3\text{H}_5 =$ allyl; $\text{C}_4\text{H}_8 =$ butadiene; $\text{C}_5\text{H}_5 =$ cyclopentadienyl]
 - $\text{Mo}(\text{CO})_5$
 - $[\text{Au}(\text{CO})_2]^+$
- (b) Draw the expected transition metal product from each of the following reactions:
- $\text{Co}_2(\text{CO})_8 + \text{Br}_2$
 - $\text{Mo}(\text{CO})_6$ in refluxing acetonitrile (MeCN)
 - $\text{VCl}_3 + \text{Na} + \text{CO}$ (200 atm) at 160°C
 - $\text{Mo}(\text{CO})_6 + \text{Cp}^-$

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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