

**UNIVERSITY OF FORT HARE**

**CHE 522**

**DEGREE EXAMINATION**

**NOVEMBER 2018**

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**Time : 3 HOURS**

**Subject : INORGANIC CHEMISTRY**

**Marks : 100**

**This paper consists of 8 pages including cover page, periodic table of elements and Potentially Useful Information**

**Internal Examiner**

**Dr. JZ Mbese**

**External Examiner**

**Prof. W Purcell**

**Instructions**

- 1. Answer any four questions**
- 2. Each question carries 25 marks**

### QUESTION 1 [25 marks]

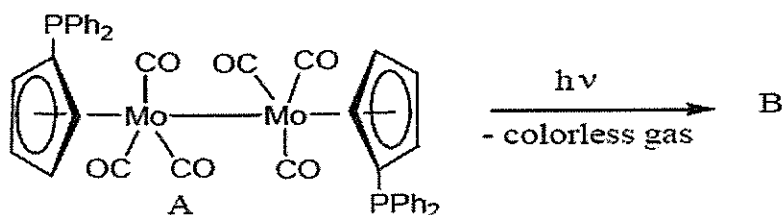
- 1.1 What do the terms low-spin (L.S.) and high-spin (H.S.) mean? [4 marks]
- 1.2 What is the Jahn-Teller Effect? How does one go about detecting it? [5 marks]
- 1.3 The complex  $[\text{NiCl}_4]^{2-}$  is paramagnetic with two unpaired electrons whereas the compound  $[\text{Ni}(\text{CN})_4]^{2-}$  is diamagnetic. Deduce the geometries of the two compounds and explain the observations in terms of ligand field theory. [8 marks]
- 1.4 Calculate the Crystal Field Stabilization Energy (CFSE) for a high spin  $d^7$  ion in an octahedral field. [3 marks]
- 1.5  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  both appear blue in solution because of the presence of copper ions. However, the two solutions are not identical. How would the appearance of these solutions differ? If given an unlabeled sample of each, how could the two solutions be distinguished without collecting any spectra? [5 marks]

### QUESTION 2 [25 marks]

- 2.1 You are supplied with  $\nu\text{CO}$  bands 1977, 2085, 2254, 2190, 1850, 1757 in no particular order, corresponding to carbonyl spectra for a series of complexes as shown in the Table below. Match the correct values of the given  $\nu\text{CO}$  bands to the third row (5d) transition metal carbonyls. [9 marks]

Compound	$\nu\text{CO}$ ( $\text{cm}^{-1}$ )
$[\text{Hf}(\text{CO})_6]^{2-}$	
$[\text{Ta}(\text{CO})_6]^-$	
$[\text{W}(\text{CO})_6]$	
$[\text{Re}(\text{CO})_6]^+$	
$[\text{Os}(\text{CO})_6]^{2+}$	
$[\text{Ir}(\text{CO})_6]^{3+}$	

- 2.2 The molybdenum compound A under UV irradiation liberates two moles of a gas giving a new compound B. The phosphorus NMR spectra of compound A gave a singlet at  $-17.0$  ppm while for B a singlet was observed at  $+68.2$  ppm. The  $\nu\text{CO}$  stretching bands of both A and B were found to be in the range of  $1896$  to  $1959$   $\text{cm}^{-1}$ . Given that both A and B obey the 18 electron rule and B has a symmetrical structure, provide the structure of compound B. [8 marks]



2.3 At 178 K, the  $^1\text{H}$  NMR spectrum of  $[(\mu\text{-H})_3\text{Ru}_4(\text{CO})_{12}]^-$  exhibits three signals due to two isomers:

A:  $\delta -15.9$ , d,  $J = 2.5$  Hz, relative integral 2

$\delta -19.1$ , t,  $J = 2.5$  Hz, relative integral 1

B:  $\delta -17.4$ , s, relative integral 3.7

At room T, the cluster exhibits a singlet at  $\delta -16.9$ . Draw the two isomers A and B and interpret these spectroscopic observations. [8 marks]

### QUESTION 3 [25 marks]

3.1 States Wades rule [4 marks]

3.2 Classify the following polyhedral boranes according to their valence electron count, show all your calculations: [12 marks]

(i)  $\text{B}_6\text{H}_6^{2-}$

(ii)  $\text{B}_5\text{H}_9$

(iii)  $\text{B}_4\text{H}_{10}$

(iv)  $\text{SB}_9\text{H}_{11}$

3.3 State Jemmis' mno rule [3 marks]

3.4 Apply Jemmis' mno rule to show the  $[(7,8\text{-C}_2\text{B}_9\text{H}_{11})\text{Fe}(\text{Cp})]^-$  is stable. [6 marks]

### QUESTION 4 [25 marks]

4.1 Construct the molecular orbital diagrams for (a) tetrahedral ( $\text{MH}_4$ ) and (b) octahedral ( $\text{MH}_6$ ) complexes. [10 marks]

4.2 Compare and contrast the differences between  $\pi$ -donor and  $\pi$ -acceptor ligands. Give an example of each ligand type. [5 marks]

4.3 Compare and contrast the differences between  $\sigma$ -donors and  $\pi$ -donor/acceptor ligands. Give appropriate examples of each ligand and use partial molecular orbital diagrams to support your argument. [10 marks]

### QUESTION 5 [25 marks]

5.1 Draw the following metal clusters  $\text{Os}_3(\text{CO})_{12}$ ,  $\text{Rh}_4(\text{CO})_{12}$ ,  $\text{Mn}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4$  [8 marks]

5.2 Compounds A and B in the given equation obey the 18 electron rule. Draw structures of compounds A and B clearly indicating hapticity of  $\text{Cp}^*$ .



Also indicate oxidation state of Zn in both A and B [The  $\eta^3$  hapticity can be ruled out as it is extremely rare]. [6 marks]

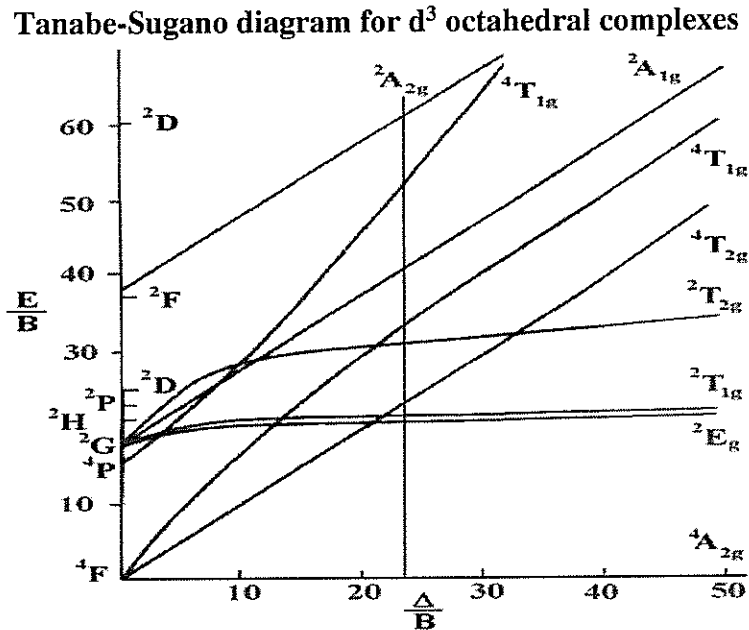
5.3 A metal complex having the empirical formula  $\text{FeC}_9\text{H}_7\text{O}_3\text{Cl}$ , has one ligand as a substituted cyclopentadienyl group. It is an ionic compound and has poor solubility in hydrocarbon solvents. The compound gives a white precipitate on treatment with  $\text{AgNO}_3$  solution. Assuming that it obeys the 18 electron rule, suggest its structure. [5 marks]

5.4 Give a scheme for the synthesis of  $\text{Mn}(\text{CO})_4(\text{PPh}_3)[\text{C}(\text{O})\text{CH}_3]$  starting from Manganese acetate,  $\text{Mn}(\text{OAc})_2$ . [6 marks]

**QUESTION 6 [25 marks]**

6.1 Calculate the value of  $B$  and  $\Delta$  for the  $\text{Cr}^{3+}$  ion in  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  if  $\nu_1=17000 \text{ cm}^{-1}$ ,  $\nu_2=24000 \text{ cm}^{-1}$  and  $\nu_3=37000 \text{ cm}^{-1}$ . Using Tanabe-Sugano diagram for a  $d^3$  system below.

[10 marks]

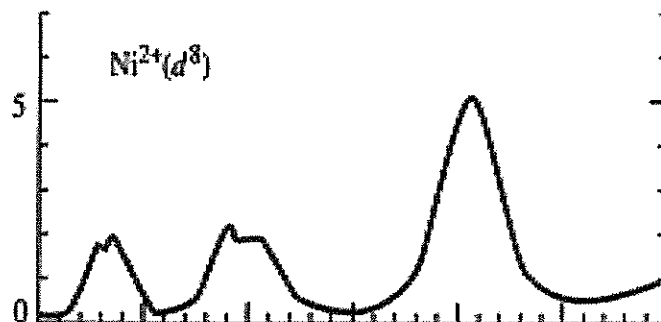


6.2 For the following complex ions (i)  $[\text{Co}(\text{NO}_2)_6]^{4+}$  (ii)  $[\text{Fe}(\text{OH}_2)_6]^{3+}$  (iii)  $[\text{RhF}_6]^{3-}$  (iv)  $[\text{Zn}(\text{en})_3]^{2+}$  determine the following:

- the number of unpaired electrons,
- the spin-only effective magnetic moment, and
- the ligand field stabilization energy.

[12 marks]

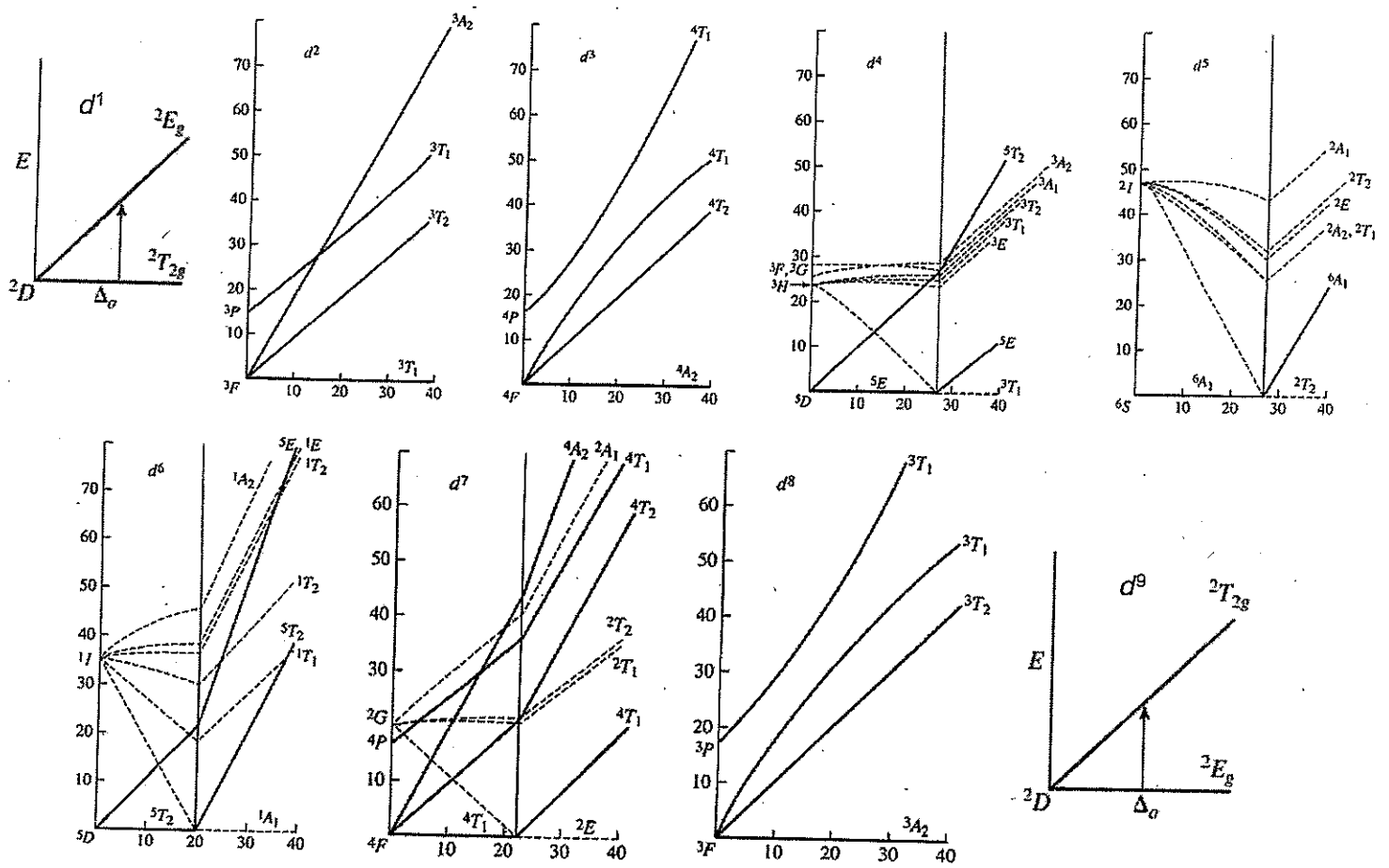
6.3 For a nickel(II) complex explain the following electronic spectrum with the help of the Tanabe-Sugano diagrams attached at the back of this questions paper. [3 marks]



## Ligands Systems: Neutral and ionic methods

Ligand	Neutral atom	Oxidation state		Ligand	Neutral atom	Oxidation state	
		Electron contribution	Formal charge			Electron contribution	Formal charge
Carbonyl (M-CO)	2	2	0	Halogen (M-X)	1	2	-1
Phosphine (M-PR <sub>3</sub> )	2	2	0	Alkyl (M-R)	1	2	-1
Amine (M-NR <sub>2</sub> )	2	2	0	Aryl (M-Ar)	1	2	-1
Amide (M-NR <sub>2</sub> )	1	2	-1	acyl (M-C(O)-R)	1	2	-1
Hydrogen (M-H)	1	2	-1	η <sup>1</sup> -cyclopentadienyl	1	2	-1
Alkene (sidewise) η <sup>2</sup> -	2	2	0	η <sup>1</sup> -allyl	1	2	-1
Alkyne (sidewise) η <sup>2</sup> -	2	2	0	η <sup>3</sup> -allyl	3	4	-1
η <sup>2</sup> -C <sub>60</sub>	2	2	0	η <sup>5</sup> -cyclopentadienyl	5	6	-1
Nitrosyl bent	1	2	-1	η <sup>6</sup> -benzene	6	6	0
Nitrosyl linear	3	2	+1	η <sup>7</sup> -cycloheptatrienyl	7	6	+1
Carbene (M=CR <sub>2</sub> )	2	4	-2	Carbyne (M≡CR)	3	6	-3
Alkoxide (M-OR)	1	2	-1	Thiolate (M-SR)	1	2	-1
μ-CO (M-(CO)-M)	2	2	0	μ-H	1	2	-1
μ-alkyne	4	4	0	μ-X (M-X-M) X = halogen	3	4	-1
μ-alkyl	1	2	-1	μ-amido (M-(NR <sub>2</sub> )-M)	3	4	-1
μ-phosphido (M-(PR <sub>2</sub> )-M)	3	4	-1	μ-alkoxide (M-(OR)-M)	3	4	-1

# Simplified Tanabe-Sugano Diagrams



# Periodic Table and Physical Constants

	1												18					
	1 <b>H</b> 1.008	2											13	14	15	16	17	2 <b>He</b> 4.003
	3 <b>Li</b> 6.941	4 <b>Be</b> 9.012											5 <b>B</b> 10.81	6 <b>C</b> 12.01	7 <b>N</b> 14.01	8 <b>O</b> 16.00	9 <b>F</b> 19.00	10 <b>Ne</b> 20.18
	11 <b>Na</b> 22.99	12 <b>Mg</b> 24.31	3	4	5	6	7	8	9	10	11	12	13 <b>Al</b> 26.98	14 <b>Si</b> 28.09	15 <b>P</b> 30.97	16 <b>S</b> 32.06	17 <b>Cl</b> 35.45	18 <b>Ar</b> 39.95
	19 <b>K</b> 39.10	20 <b>Ca</b> 40.08	21 <b>Sc</b> 44.96	22 <b>Ti</b> 47.88	23 <b>V</b> 50.94	24 <b>Cr</b> 52.00	25 <b>Mn</b> 54.94	26 <b>Fe</b> 55.85	27 <b>Co</b> 58.93	28 <b>Ni</b> 58.69	29 <b>Cu</b> 63.55	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.72	32 <b>Ge</b> 72.59	33 <b>As</b> 74.92	34 <b>Se</b> 78.96	35 <b>Br</b> 79.90	36 <b>Kr</b> 83.80
	37 <b>Rb</b> 85.47	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.91	40 <b>Zr</b> 91.22	41 <b>Nb</b> 92.91	42 <b>Mo</b> 95.94	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.1	45 <b>Rh</b> 102.9	46 <b>Pd</b> 106.4	47 <b>Ag</b> 107.9	48 <b>Cd</b> 112.4	49 <b>In</b> 114.8	50 <b>Sn</b> 118.7	51 <b>Sb</b> 121.8	52 <b>Te</b> 127.6	53 <b>I</b> 126.9	54 <b>Xe</b> 131.3
	55 <b>Cs</b> 132.9	56 <b>Ba</b> 137.3	57* <b>La</b> 138.9	72 <b>Hf</b> 178.5	73 <b>Ta</b> 181.0	74 <b>W</b> 183.9	75 <b>Re</b> 186.2	76 <b>Os</b> 190.2	77 <b>Ir</b> 192.2	78 <b>Pt</b> 195.1	79 <b>Au</b> 197.0	80 <b>Hg</b> 200.6	81 <b>Tl</b> 204.4	82 <b>Pb</b> 207.2	83 <b>Bi</b> 209.0	84 <b>Po</b> (209)	85 <b>At</b> (210)	86 <b>Rn</b> (222)
	87 <b>Fr</b> (223)	88 <b>Ra</b> 226.0	89** <b>Ac</b> 227.0	104 <b>Rf</b> (261)	105 <b>Db</b> (262)	106 <b>Sg</b> (263)	107 <b>Bh</b> (262)	108 <b>Hs</b> (269)	109 <b>Mt</b> (278)	110 <b>Ds</b> (281)	111 <b>Rg</b> (281)	112 <b>Cn</b> (285)	113 <b>Uut</b> (286)	114 <b>Uuq</b> (289)	115 <b>Uup</b> (289)	116 <b>Uuh</b> (293)	117 <b>Uus</b> (294)	118 <b>Uuo</b> (294)

*		58	59	60	61	62	63	64	65	66	67	68	69	70	71
Lanthanide Series	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>	
	140.1	140.9	144.2	(145)	150.4	151.9	157.3	158.9	162.5	164.9	167.3	168.9	173.0	175.0	
**	90	91	92	93	94	95	96	97	98	99	100	101	102	103	
Actinide Series	<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>	<b>Lr</b>	
	232.0	231.0	238.0	(237)	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)	