

BIRLA INSTITUTE OF TECHNOLOGY & SCIENCE – PILANI, K. K. BIRLA GOA CAMPUS
SECOND SEMESTER, 2022-23
CHEM F241, Inorganic Chemistry II
Comprehensive Examination (Closed Book)
Date: 11-05-2023, Duration: 3 hours, Max. Marks: 80

Instructions: Answer all the questions. Answer all parts of a question together. Do not use pencil.
Abbreviations used: *o*-phen: 1,10-phenanthroline, en = ethylenediamine, bpy = 2,2'-bipyridine

1. (a) Explain three differences between Fischer carbene and Schrock carbene. [3 marks]
- (b) In the ligand exchange reaction in square planar complexes, (i) what is the mechanism generally seen? (ii) what is the shape of the intermediate? (iii) comment on the position of good π -acceptor ligands (other than the incoming and outgoing ligands) in the intermediate, (iv) reason for the position occupied by the ligand mentioned in question (iii) above. [1+1+1+1 = 4 marks]
- (c) Write the shape of an octahedral complex of the form MX_6 (X = monodentate ligand) if it is (i) tetragonally distorted (ii) trigonally distorted. What is the point group of the resulting molecule in the above two cases? [4 marks]
- (d) Draw and explain the Tolman catalytic loop for Wilkinson catalysis for hydrogenation of alkene. [4 marks]
- (e) Explain the mechanism of inner-sphere electron transfer mechanism with suitable example. [5 marks]
2. (a) Explain the variations of Cr-P and Cr-C bond lengths (in pm) of the following carbonyl complexes $[\text{Cr}(\text{CO})_5\text{L}]$ utilizing the bonding model for metal carbonyl complexes: [4 marks]

L	Cr – P (pm)	Cr – C (trans to P) (pm)	Cr – C (trans to CO) (pm)
P(OPh) ₃	230.9	186.1	189.6
PPh ₃	242.2	184.4	188.0

- (b) Write the correct increasing order (**use only '<' sign**) of the infrared absorption frequencies associated with the C – O stretching vibration in the following complexes and explain your answer: [4 marks]
- $[\text{Ni}(\text{CO})_4], [\text{Fe}(\text{CO})_4]^{2-}, [\text{Co}(\text{CO})_4]^-$
3. (a) Oxygen is more electronegative than nitrogen and fluorine is more electronegative than the other halogens. However, fluoride is a stronger field ligand than the other halides, but ammonia is a stronger field ligand than water. Explain using suitable diagrams based on molecular orbital theory. [4 marks]
- (b) Solid CrF_3 contains a Cr(III) ion surrounded by six F^- ions in an octahedral geometry, all at distances of 190 pm. However, MnF_3 is in a distorted geometry, with Mn–F distances of 179, 191, and 209 pm (two of each). Explain. [2 marks]
4. (a) A first-row transition-metal complex, $[\text{M}(\text{H}_2\text{O})_6]^{2+}$, has a magnetic moment of 3.9 Bohr magnetons. Determine the most likely number of unpaired electrons and the possible metal-ions. [4 marks]
- (b) What are the magnetic moments of Co(II) in tetrahedral, weak-field octahedral, and square-planar complexes? Consider spin-only values. [4 marks]
5. (a) Determine the crystal field stabilization energies for each of the following complexes (in terms of Δ_{oct}): [6 marks]
- $[\text{Co}(\text{CO})_4]^-$, $[\text{Cr}(\text{CN})_6]^{4+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NO}_2)_6]^{4+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{MnO}_4]^-$
- (b) Although aqueous Co^{2+} forms the tetrahedral complex $[\text{CoCl}_4]^{2-}$ on treatment with concentrated HCl, aqueous Ni^{2+} does not form a similar complex. Explain [2 marks]
- (c) $[\text{NiBr}_4]^{2-}$ is paramagnetic, whereas $[\text{PdBr}_4]^{2-}$ is diamagnetic. Explain [2 marks]

6. Determine the ground terms for the following configurations:

- (a) Weak-field and Strong-field d^8 (O_h ligand field)
- (b) Weak-field and Strong-field d^3 (T_d ligand field)
- (c) Weak-field d^5 (O_h and T_d ligand fields)
- (d) Weak-field d^4 (O_h and T_d ligand fields)

[2 X 4 = 8 marks]

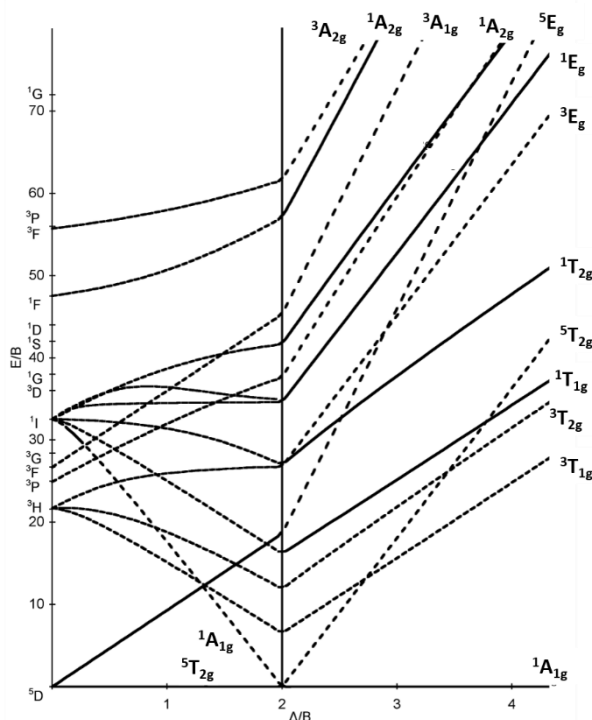
7. Explain the following observations:

(a) An aqueous solution of perrhenate is colorless, whereas an aqueous solution of permanganate is purple in color. [2 marks]

(b) The compound *trans*-Fe(*o*-phen)₂(NCS)₂ has a magnetic moment of 0.65 Bohr magneton at 80 K, which increases to 5.2 Bohr magnetons at 300 K. What are the number of unpaired electrons at the respective temperatures and how can the increase in magnetic moment with temperature be explained? [2 marks]

8. (a) The metal complex [Co(en)₃]³⁺ exhibits two bands in its UV-Visible spectrum. Using the Tanabe-Sugano diagram below, write down the electronic transitions that are responsible for the two bands. Are there any other electronic transitions possible apart from these two? If so, which one and why is it not observed in the UV-Visible spectrum? [4 marks]

(b) The metal complex *trans*-[Co(en)₂F₂]⁺ exhibits multiple bands in its UV-Visible spectrum as compared to just two bands in [Co(en)₃]³⁺ above. Utilizing the Tanabe-Sugano diagram and the correlation table below, write down all the predicted electronic transitions in *trans*-[Co(en)₂F₂]⁺. [4 marks]



O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	C_{2v}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2
E_g	E	E	$A_{1g} + B_{1g}$	$A_1 + B_1$	$A_1 + B_1$	$A_1 + A_2$
T_{1g}	T_1	T_1	$A_{2g} + E_g$	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$
T_{2g}	T_2	T_2	$B_{2g} + E_g$	$B_2 + E$	$B_2 + E$	$A_1 + B_1 + B_2$
A_{1u}	A_1	A_2	A_{1u}	B_1	A_2	A_2
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_1
E_u	E	E	$A_{1u} + B_{1u}$	$A_1 + B_1$	$A_2 + B_2$	$A_1 + A_2$
T_{1u}	T_1	T_2	$A_{2u} + E_u$	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$
T_{2u}	T_2	T_1	$B_{2u} + E_u$	$A_2 + E$	$B_1 + E$	$A_2 + B_1 + B_2$

9. Two bands at 11300 cm⁻¹ and 22000 cm⁻¹, respectively, are observed in the UV-Visible spectrum of [Co(bpy)₃]²⁺, whereas two bands at 9000 cm⁻¹ and 21100 cm⁻¹, respectively, are observed in the UV-Visible spectrum of [Co(NH₃)₆]²⁺.

(a) Using the Tanabe-Sugano diagram in the following page, find the values of Δ_o, Racah parameter B, and the crystal field stabilization energy for both the complexes (all in cm⁻¹)

(b) Write down the electronic transitions that are responsible for the two bands in each of the complexes above. Explain the difference if any.

(c) Calculate the nephelauxetic ratio β for both the complexes given that the B_{Co²⁺(free-ion)} = 971 cm⁻¹. What conclusion can be drawn from the values of β of the two complexes? [5 + 2 + 1 = 8]

