CHUKA  **UNIVERSITY**

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE

CHEM 812: ADVANCED COORDINATION CHEMISTRY

STREAMS: MSC CHEMISTRY **TIME: 3 HOURS**

DAY/DATE: WEDNESDAY 4/12/2019 **2.30 P.M – 5.30 P.M**

INSTRUCTIONS

Answer **All** Questions

QUESTION ONE [20 MARKS]

(a) Write the names of the following coordination compounds (2 ½ Marks)

(i) $[Co(NH_3)_5Cl]Cl_2$ (ii) $K_3[Fe(CN)_6]$ (iii) $[RhCl_3(PMe_3)_3]$ (iv) $K_2[CrCO(CN)_5]$ (v) $[Co(en)_3]3+$

(b) Write the formula for each of the following species (2 ½ Marks)

(i) tetrabromorhodate(II) (ii) ammonium diaquabis(oxalato)nickelate(II)

(iii) hexaammineiron(III) nitrate (iv) potassium hexafluorocobaltate(III)

(v) hexammineiron(III) hexacyanochromate(III)

(c) Compare, with the aid of energy-level splitting diagrams, the stability of a tetragonally elongated d^9 complex relative to that of an octahedral complex (3 Marks)

(d) A solution of $[Ni(H_2O)_6]^{2+}$ is green and paramagnetic (μ =2.90 BM), whereas a solution of $[Ni(CN)_4]^{2-}$ is colorless and diamagnetic. Give a qualitative explanation for these observations (2 Marks)

(e) Calculate the ligand field stability energy (LFSE) and the magnetic susceptibility of the following species (3 Marks)

(i) $[Fe(CN)_6]^{4-}$ (ii) $[CoCl_4]^{2-}$ (iii) $[IrBr_4]^{3-}$

(f) Set up a microstate table for a p^2 configuration, determine the free ion terms and organize the resultant terms in order of increasing energy (5 Marks)

(g) Explain the relative magnitudes of the crystal field splitting (Δ_o) in the following pair of compounds (2 Marks)

(i) $[CoF_6]^{3-}$ (Δ_o = 13, 100cm^{-1}) and $Co(NH_3)_6]^{3+}$ (Δ_o = 22, 900 cm^{-1})

(ii) $[Fe(H_2O)_6]^{3+}$ (Δ_o = 14, 000 cm^{-1}) and $[Fe(CN)_6]^{3-}$ (Δ_o = 32, 000 cm^{-1})

QUESTION TWO [20 MARKS]

(a) Construct an Orgel diagram for $[Ni(H_2O)_6]^{2+}$ and write the possible electronic transitions . (3 Marks)

(b) Estimate the values of Δ_o and the Racah parameter, B, for the $[Ni(H_2O)_6]^{2+}$ complex if it has absorption bands at 8,500, 15,400 and 26,000cm^{-1} (5 Marks)

(c) Draw a well labelled molecular orbital energy diagram for σ-bonding in $[Co(NH_3)_6]^{3+}$ complex and populate it with electrons (7 Marks)

(d) Explain, with the aid of relevant molecular orbital diagrams, the arrangement of ligands in the spectrochemical series (5 Marks)

QUESTION THREE [20 MARKS]

(a) Determine the ground state term for each of the following configurations (3 Marks)

(i) d^4 (low spin, O_h) (ii) d^6 (high-spin, O_h)

(b) Describe the four processes which can lead to the absorption of light by a transition metal complex (2 Marks)

(c) The electronic spectrum of a complex $[TiL_6]^{3+}$ (L= neutral monodentate ligand) shows a weak (ε = 7 dm^3 mol^{-1} cm^{-1}) absorption with a shoulder at λ_{max} =19, 200 cm^{-1}. Explain the origin of this absorption and the shoulder (3 Marks)

(d) Discuss the charge transfer transitions of coordination compounds (4 Marks)

(e) Determine the atomic orbitals that nickel can use for σ-bonding in the $[Ni(CN)_4]^{2-}$ complex and sketch the molecular orbital diagram (8 Marks)
