BENGAL ENGINEERING AND SCIENCE UNIVERSITY, SHIBPUR
M. Sc. (APPLIED CHEMISTRY) 3rd SEMESTER EXAMINATIONS, 2011

Inorganic Chemistry – III (PGC- 302)

Full Marks: 100 **Time: 4 hrs**

Use separate answer script for each group.

Group A

*Answer any **six** questions*

1. (a) Explain the very slow electron transfer reaction rate between $[Fe(H_2O)_6]^{+2}$ and $[Fe(H_2O)_6]^{+3}$ using Franck-Condon Principle.
(b) How the Marcus cross-relation helps to explain the mechanisms of outer-sphere electron transfer processes?

[5+5]

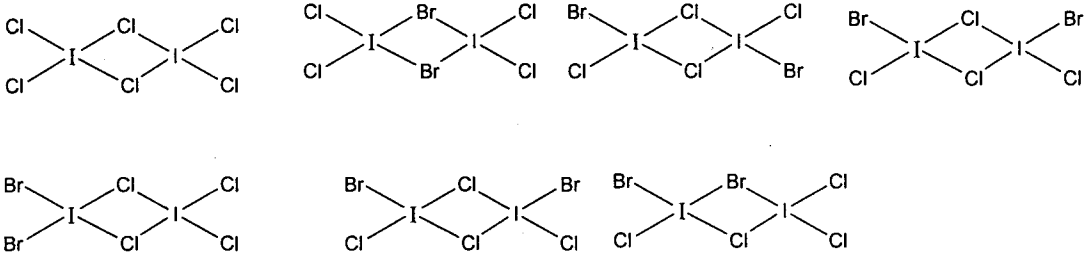
2. (a)The rate constants for the reduction of $[Co(NH_3)_6]^{3+}$ and $[Co(NH_3)_5H_2O]^{+3}$ by $[Cr(H_2O)_6]^{+2}$ are 8×10^{-5} $M^{-1}s^{-1}$ and 1×10^{-1} $M^{-1}s^{-1}$ respectively at 25 °C- Explain
(b) How solar excitation to the MLCT state in $[Ru(bpy)_3]^{2+}$ complex initiates the splitting of water to give clean burning fuel H_2?

[5+5]

3. (a) What are the effects of enthalpy of activation and entropy of activation in the kinetic study of substitution reaction?
(b) The LFER plot for the aquation of $[Co(NH_3)_5NCS]^{+2}$ gives a unit slope, while the same for $[Cr(H_2O)_5NCS]^{+2}$ has a slope of 0.56 –explain the mechanistic significance of the above slope values

[5+5]

4. (a) Predict the actual structure of $I_2Br_2Cl_4$, with explanation, from structural and spectroscopic information given below



7. (a) Assuming H.D.V.V. Hamiltonian for the description of magnetic interaction for a binuclear complex, where each metal ion contains one unpaired electron, derive an expression for the magnetic susceptibility of the system.
(b) Considering spin-orbit coupling predict qualitatively the nature of the temperature dependence of magnetic susceptibility for a metal complex with metal ion having d^1 configuration.

[6+4]

Group B

*Answer any **four** questions*

8. (a) In what way magnetic properties of 4*f* elements are different from 3*d* elements?
(b) How can you separate Ce(III) and Eu(III) ions from all other lanthanide ions? Give chemical equations.

[6+4]

9. (a) Compare the trend of variation of atomic radii of lanthanides and actinides.
(b) The electronic spectra of Eu(II) and Gd(III) are completely different although they have same number of electrons in the *f* orbitals. [5+5]

10. (a) Europium complexes show luminescence property – explain.
(b) Actinides show variety of structure – explain.
(c) Name two lanthanides that have greatest tendency to deviate from usual positive oxidation state and correlate this deviation with electronic structure.

[3+3+4]

11.(a) What are the reactions that are catalyzed by cytochrome P450 *in vivo*? Draw the catalytic cycle of cytochrome P450 and comment on 'complex-1' and 'peroxide shunt' in the catalytic cycle.
(b) Write a short note on $[Fe_2S_2]^{n+}$ proteins and Rieske centers.

[6+4]

12. (a) Using electronic and e.p.r. spectroscopy what inferences can be drawn about the coordination environment of metal ions in copper-zinc superoxide dismutase.
(b) Comment on the structural, e.p.r. and redox properties of $[Fe_4S_4]^{n+}$ centers.

[5 +5]

^{129}I Mössbauer parameters for I_2Cl_6 and $I_2Br_2Cl_4$

Compound	δ/mm s^{-1}	e^2qQ/MHz
I_2Cl_6	3.50±0.10	+3060±10
$I_2Br_2Cl_4$	3.48±0.02	+3040±10
	2.82±0.02	+2916±10

(b) The ^{119}Sn Mössbauer spectrum of SnF_4 shows a quadrupole splitting, whereas the spectrum of $SnCl_4$ shows a sharp line with no quadrupole splitting – explain.
(c) FeF_2 shows a positive chemical shift but for $[Fe(CN)_6]^{4-}$ the chemical shift is negative – why?

[5+3+2]

5. (a) Explain the observations:
(i) XPS of the N_2O shows two peaks in N 1*s* region.
(ii) Binding energy for C 1*s* of the CO is 295.8 eV whereas for the CO_2 it is 297.8 eV.
(iii) O_2 shows two unequal peaks for O 1*s* in XPS.
(iv) UPS of the argon shows two peaks of unequal intensities for 2*p* orbitals.
(b) Calculate the energy associated with a velocity of 2 mm s^{-1} in Mössbauer spectroscopy. (E_γ = 14.4 KeV)

[(2+2+2+2)+2]

6. (a)

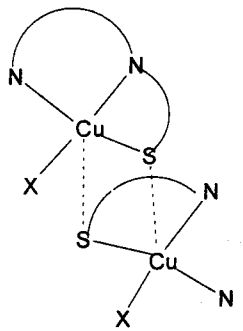


Fig 6(a)

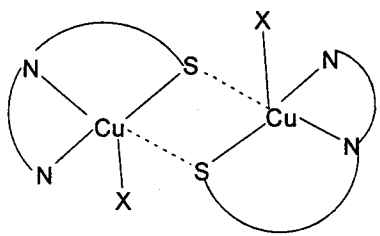


Fig 6(b)

Consider two binuclear Cu(II) complexes given in Figures 6(a) and 6(b). In both the complexes the Cu(II) ions are in a square pyramidal geometry; however, in 6(a) the thiolato bridges are equatorial-axial, whereas in 6(b) they are equatorial-equatorial. Predict with cogent argument the nature of magnetic interaction in these two types of complexes. If the coordination geometry around Cu(II) undergoes distortion towards trigonal bipyramidal will it affect the nature of magnetic interaction?
(b) In oxo or hydroxo bridged complexes (e.g. L_5M-X-L_5; X = O, OH) the magnetic interaction between the metal centers are often dependent upon the M-X-M angle. State the nature of this dependence with proper justification.

[6+4]