22-23/31451

M.Sc. 3rd Semester Examination-2022-23

CHEMISTRY

Course ID : 31451 **Course Code : CHEM301C**

Course Title : Inorganic Chemistry

Time : 2 Hours *Full Marks* : 40

The figures in the right hand margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

1. Answer ***any five*** of the followings : 2×5=10

(a) $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. – Explain.

(b) What do you mean by kinetically INERT and LABILE complex ?

(c) Define E type and P type delayed florescence.

(d) Calculate the effective magnetic moment of Pr^{3+}.

(e) Greenhouse effect leads to global warming. Which substances are responsible for greenhouse effect ?

(f) The pressure dependence of the replacement of chlorobenzene (PhCl) by piperidine in the complex $[W(CO)_4(PPh_3)(PhCl)]$ has been studied. The volume of activation is found to be $-30.5\ cm^3mol^{-1}$. What does this value suggest about the mechanism?

(g) Compare excited state of meta complexes with organic compounds.

2. Answer ***any four*** of the followings. (5×4=20)

(a) Write down the basic characteristic features of single molecular magnets (SMM). Give an example of a single molecular magnet and calculate its total ground state spin value. Write two applications of single molecule magnets. 2+2+1

(b) Propose the products of the following redox reactions. What are the side products of the reactions? 2+2+1

(f) The pressure dependence of the replacement of chlorobenzene (PhCl) by piperidine in the complex $[W(CO)_4(PPH_3)(PhCl)]$ has been studied. The volume of activation is found to be $+50.3\ cm^3mol^{-1}$. What does this value suggest about the mechanism ?

(g) Compare excited state of metal complexes with organic compounds.

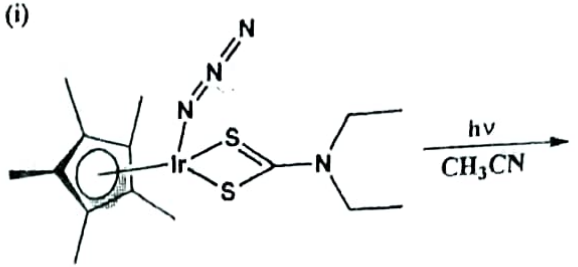
2. Answer ***any four*** of the followings : 5×4=20

(a) Write down the basic characteristic features of single molecular magnets (SMM). Give an example of a single molecular magnet and calculate its total ground state spin value. Write two applications of single molecular magnets. 2+2+1

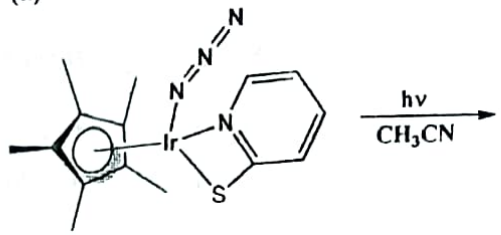
(b) Propose the products of the following related reactions. What are the side products of the reactions ?

(2+2)+1

(i)



(ii)



(2+2)+1

(c) (i) Define Traus Effect. Describe briefly the π-bonding theory of Traus effect.

(ii) "Rate of substitution of $[Cr(H_2O)_6]^{3+}$ is very slow as compare to $[Fe(H_2O)_6]^{3+}$ – Justify. (1+2)+2

(d) What do you mean by oxygen demanding waste ? Mention the differences between BOD and COD. Describe the water quality by BOD/COD ratio.

1+3+1

(e) "The ratio of Φ_{NH_3}/Φ_{NCS^-} of following photoaquation reaction is 15 at 373 nm; 22 at 492 and 8 at 652 nm." – Comment. From the given reaction how do you justify that NH_3 release occurs from quartet state and NCS^- from doublet state ? 2+3

$$[Cr(NH_3)_5(NCS)]^{2+} + H_2O \xrightarrow{h\nu} [Cr(NH_3)_5(H_2O)]^{3+} + NCS^-$$
$$[Cr(NH_3)_5(NCS)]^{2+} + H_2O \xrightarrow{h\nu} [Cr(NH_3)_4(H_2O)(NCS)]^{2+} + NH_3$$

(f) (i) Design two step synthesis of *cis* and *trans*-$[PtCl_2(NO_2)(NH_3)]$ – starting from $[PtCl_4]^{2-}$.

(ii) Calculate the spin-only magnetic moment ($\mu_{s.o.}$) for Co^{3+} (H.S) in B.M unit. Explain why the $\mu_{(observed)}$ value for the same is found to be ~ 5.4 B.M. 3+2

3. Answer ***any one*** of the followings : 10×1=10

(a) (i) What is diamagnetic susceptibility ? Explain why is called an inducted effect ?

Calculate the diamagnetic correction vaue for 2,2'-Dipyridyl ligand.

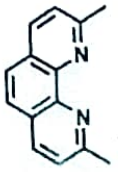
Pascal's atom constant (χ_A)	
atoms	χ_{dia}
H	-2.93×10^{-6}
C	-6.00×10^{-6}
N (open chain)	-5.57×10^{-6}
N (ring)	-4.61×10^{-6}
Pascal's constitutive corrections (λ)	
Atom	χ_{dia}
C (in ring)	-0.24×10^{-6}

All values are in cgs units/gram atom.

(ii) in $[Cu(H_2O)_6]^{2+}$, two water molecules undergo exchange with the bulk solvent molecule much more rapidly than other four – explain.

(iii) Justify the following statement – "rate of hydrolysis in basic aqueous medium of $[Co(NH_3)_5Cl]^{2+}$ is much faster than $[Co(py)_5Cl]^{2+}$ (2+1+3)+2+2

(b) (i) Complete the following reaction sequence. Include the structure of ligand with the additional electron in the square planar complex. What is the charge on the ligand in the square planar complex ?



$\xrightarrow{Cu^I}$ A $\xrightarrow[MLCT]{h\nu}$ B

Cu^I tetrahedral complex Cu^{II} square planar complex

(ii)What is composting ? Describe the windrow method of compositing. (4+1)+(2+3)

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