(6 pages)

DECEMBER 2014 **P/ID 40128/PCHH**

Time : Three hours Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

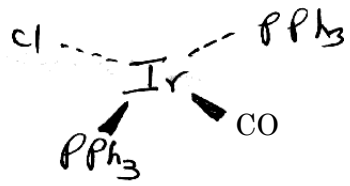
Answer ALL questions.

1. Write any four classical ligands.
2. Explain synergic mechanism in metal complexes.
3. What are the physical techniques used to identify multiple nature of M-CO bond?
4. Find out the product in $RCH=CH_2 + H_2 + CO \longrightarrow$
5. Explain the terms in $\mu = ge(S(S+1))^{1/2}\,\mu_B$.
6. How many proton NMR signals are observed in paramagnetic complex Ni $(CH_3\ NH_2)_6^{+2}$?
7. Explain MORSE potential energy diagram.
8. Explain Pascal's constants k_B and k_A in the case of diamagnetism and what are the units?
9. Explain Doppler broadening and terms in the equation $E_t = E_r + D - R$.
10. What is meant by quadropole coupling constant? Explain with sketch on energy scale.

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) Explain oxidative addition and reductive eliminations with suitable examples. Also explain addition of oxygen. (O_2) in the following complex.



(ii) Which one of the following is the most probable for isolation?

(1) $W_2(CO)_{10}$

(2) $(W_2(CO)_{10})^{-2}$

(3) $[W_2(CO)_{10}]^{+2}$

(4) $[W_2(CO)_{10}]^{+}$ and

(5) $[W_2(CO)_{10}]^{-}$.

Or

(b) (i) Predict the compound in the following reactions

(1) $Ni + 4\,CO \longrightarrow$

(2) $Fe(CO)_5 \xrightarrow{h\gamma}$

(3) $Cr\,Cl_3 + Al + 6\,CO \xrightarrow[\text{Benzene}]{Al\,Cl_3}$

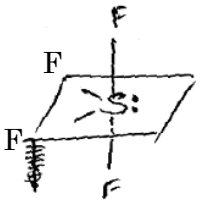
(4) $Re_2O_4 + 17\,CO \xrightarrow[250^\circ C]{350\,\text{atmos}}$

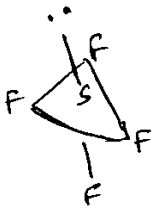
(ii) Describe the bonding present in metal carbonyls with neat sketch.

(iii) How bridging CO group can be differentiated from that of terminal CO group in IR spectra?

12. (a) (i) What is the relevance of blue shift, molar extinction, coefficient, protonation in assignment of electronic transitions?

(ii) Find out the point group in the following structures

(1) 

(2) 

(3) 

Or

(b) Calculate Pascal's constant k_A and k_B for the following compounds

(i) $C_5 H_5N$

(ii) $(CH_3)_2 C = 0$.

Use the data :

$k_C = -6.00 \times 10^{-6}\ cm^3\ mol^{-1}$

$k_H = 2.93 \times 10^{-6}\ cm^3\ mole^{-1}$

$k_N = -4.61 \times 10^{-6}\ cm^3\ mole^{-1}$

$k_O = -4.61 \times 10^{-6}\ cm^3\ mole^{-1}$

$k_{C=O} = 6.3 \times 10^{-6}\ cm^3\ mole^{-1}$.

13. (a) Predict and explain in the case of $(MeP)_4 Pt^{+2}$ diamagnetic complex phosphorous resonance signals if (i) $J_{P-H} > J_{P-Pt}$ and (ii) $J_{P-Pt} > J_{P-H}$.

Or

(b) (i) Write general principles involved in the selection rules and splitting patterns in assigning NQR spectral studies.

(ii) Sketch on energy scale NQR energy levels for $I = 7/2$ and $I = 3/2$, $I = O$ $I = \frac{1}{2}$.

14. (a) (i) Sketch and explain the e.s.r. transitions of H atom. What are the units of energy?

(ii) Explain the importance of derivative curves in e.s.r. transitions after working proton hyperfine splitting in allyl radical.

(iii) Write notes on the following in e.s.r. spectroscopy

(1) Internal standard

(2) Selection rules

(3) Hyperfine splitting in $CH_3^{\cdot}$ radical

(4) Equivalent and non equivalent protons.

Or

(b) Write notes on the following :

(i) Zero field splitting

(ii) Transitions in singlet and triplet states

(iii) Jahn-Teller distortion

(iv) EPR transitions in $CuSiF_6 \cdot 6H_2O$ complex.

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