

2016

CHEMISTRY

Paper : 203

INORGANIC CHEMISTRY-II

Full Marks : 80

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following questions: (any five) 2X5=10
- (i) Illustrate with diagram the tetragonal distortion of an octahedral complex. What will be the point group of symmetry of the distorted structure?
 - (ii) What are the two different structures possible for a metal complex with coordination number seven?
 - (iii) What conditions a metal must fulfil in order to show coordination number more than seven?
 - (iv) Why high coordination numbers are common for transition metals occurring on the left of the periodic table?
 - (v) Explain why ground state configurations of the neutral transition metals are $3d^n4s^2$ and not $3d^{n+2}4s^0$.
 - (vi) Predict the coordination geometries of $[\text{NiBr}_4]^{2-}$ and $[\text{AuCl}_4]^-$; justify your answer.
2. Answer the following questions: (any five) 5X5=25
- (i) The $10Dq$, value of the complex $[\text{CoF}_6]^{3-}$ is 13100

cm^{-1} . Illustrate the meaning of D and q. What should be the expected value of "R" for the complex $[\text{RhF}_6]^{3-}$ and "t" for a Co(II) complex? Assign the transition for Co(III) complex. $1+1+3=5$

(ii) What is spectrochemical series? Write the spectrochemical series. Explain why the trend in the series cannot be explained by CFT but MOT can.

$$1+1+3=5$$

(iii) What do you mean by pairing energy? What are the two contributions of electron pairing energy? Out of d^4 , d^5 , d^6 and d^7 , which has the largest pairing energy (for high spin and for low spin) and why? $1+1+3=5$

(iv) Cobalt forms a series of amine complexes. What are the two different experiments with which Werner was able to give not only the correct molecular formula but also the famous postulates of Werner's theory that "metal possesses fixed coordination number"?

Complex	Colour	Early Name
$\text{CoCl}_3 \cdot 6\text{NH}_3$	Yellow	Luteo
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Purple	Purpureo Complex
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	Praseo Complex
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Violet	Violeo Complex

(v) In a metal complex of tetrahedral field symmetry, why the energy of t_2 orbitals are lower compared to that in the hypothetical spherical field symmetry? "The electron pairing energy is composed of two terms." Explain the statement.

(vi) Explain with suitable examples what you mean by charge transfer spectra.

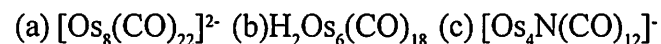
(2)

P.T.O.

3. Answer the following questions: (any four) $5 \times 4 = 20$

(i) Discuss the structure and bonding in $\text{Re}_2\text{Cl}_8^{2-}$.
 (ii) Give few examples of π -acid ligands. Explain why they are called π -acids and comment on their utility in complex formation.

(iii) Find the structure and draw the structure of the following from total electron counts-



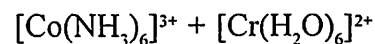
(iv) Explain the structure and bonding of metal-nitrosyl complex.

(v) Explain the three observed characteristics in the chemistry of phosphine on increasing the Tolman's cone angle by substituting bulky groups in PL_3 .

4. Answer from the following questions: (any three) $5 \times 3 = 15$

(i) Explain what you mean by 'labile' and 'inert' complexes. Why the high-spin d^4 complex ion $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is labile, but the low-spin d^4 complex ion $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is inert?

(ii) Is the reaction



Likely to proceed by an inner-sphere or outer-sphere mechanism? Explain your answer.

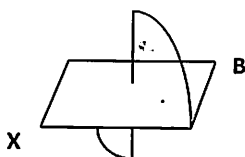
(iii) Define *trans* effect. Illustrate *trans* effect using reaction $[\text{PtCl}_4]^{2-}$ and $[\text{Pt}(\text{NH}_3)_4]^{2+}$.

(3)

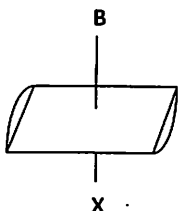
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- (iv) Show that the first two products of structure (i) would be Δ rather than E and in case of (ii) both Δ and \square in a dissociative mechanism :

(a)



(b)



- (v) A strong δ - donor or π -acceptor ligand greatly accelerates the substitution of a ligand that lies in the *trans* position in a square planar complex. Explain the above statement and answer why NH_3 is a stronger *trans* director than H_2O .

5. Answer any two from the following questions: $5 \times 2 = 10$

- (i) What is the most common oxidation state of lanthanides and why? Give a brief description of separation of lanthanides. $1+2+2=5$
- (ii) Explain the lanthanoid contraction.
- (iii) Explain the spectra of lanthanide and actinide complexes.