**PHYSICAL / INORGANIC CHEMISTRY**

**DPP**

DAILY PRACTICE PROBLEMS

# DPP No. 9

**Total Marks : 46**

**Max. Time : 50 min.**

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**Topic : Coordination Compounds**

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| **Type of Questions** | | **M.M., Min.** |
|---|---|---|
| Single choice Objective ('–1' negative marking) Q.1 to Q.8 | (3 marks, 3 min.) | [24, 24] |
| Subjective Questions ('–1' negative marking) Q.9 to Q.10 | (4 marks, 5 min.) | [8, 10] |
| Comprehension ('–1' negative marking) Q.11 to Q.12 | (3 marks, 3 min.) | [6, 6] |
| Match the Following (no negative marking) Q. 13 | (8 marks, 10 min.) | [8, 10] |

**1.** In the crystal field of the complex $[Fe(Cl)(CN)_4(O_2)]^{4-}$ the electronic configuration of metal is found to be $t_{2g}^6, e_g^0$ then, which of the following is true about this complex ion:

(A) It is a paramagnetic complex
(B) O–O bond length will be more than found in $O_2$ molecule
(C) Its IUPAC name will be chlorotetracyanosuperoxidoferrate (II) ion
(D) All the above are true

**2.** Which one of the following compounds has the electron-pair geometry as the trigonal bipyramidal with three equatorial positions occupied by lone pairs of electrons ?

(A) $[AlCl_3]$ (B) $XeF_2$ (C) $[Pt(NH_3)_2Cl_2]$ (D) $CH_3 — Mg — Br$.

**3.** **(a)** Spin only magnetic moment of a complex having CFSE = – 0.6 $\Delta_0$ and surrounded by weak field ligands can be:

(A) 1.73 BM (B) 4.9 BM (C) both (A) & (B) (D) None of these

**(b)** Which of the following statements is not correct?
(a) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of CFSE
(b) $[Ni(H_2O)_6]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ have same value of magnetic moment
(A) Only a (B) Only b (C) Both a and b (D) None of these

**4.** Nitroprusside ion is :
A : $[Fe^{II}(CN)_5NO^+]^{2-}$ and not ;
B : $[Fe^{II}(CO)_5NO]^{2+}$. A and B can be differentiated by.
(A) estimating the concentration of iron (B) measuring the concentration of $CN^-$
(C) measuring the magnetic moment (D) thermally decomposing the compound.

**5.** All the following complexes shows a decrease in their weights when placed in a magnetic balance. Then, which of the these has square planar geometry :

(A) $Ni(CO)_4$ (B) $K[AgF_4]$ (C) $Na_2[Zn(CN)_4]$ (D) None of these

**6.** It is given that a complex formed by one $Ni^{2+}$ ion and some $Cl^-$ ions and some $PPh_3$ molecules does not show geometrical isomerism and its solution does not show electrical conductance. Then, which is correct about the complex :

(A) It is square planar (B) It is tetrahedral (C) It is diamagnetic (D) none of the above is correct

**7.** The green coloured complex $K_2[Cr(CN)_4(NH_3)(NO)]$ is paramagnetic and its paramagnetic moment (spin only) is 1.73 B.M. Which of the following is correct about it :
(i) Its IUPAC name is Potassium amminetetracyanonitrosylchromate (II)
(ii) Its IUPAC name is Potassium amminetetracyanonitrosoniumchromate (I)
(iii) Hybridisation state of chromium is $sp^3d^2$ (iv) It cannot show geometrical isomerism
(v) Hybridisation state of chromium is $d^2sp^3$ (vi) It can show linkage isomerism
(A) (ii), (iii),(iv) (B) (i),(iii), (vi) (C) (i), (v) (D) (ii), (v), (vi)

**8.** Which are correct statements ?

(A) $[Ag(NH_3)_2]^+$ is linear with sp hybridised $Ag^+$ ion.

(B) $NiCl_4^{2-}$ , $VO_4^{3-}$ and $MnO_4^-$ have tetrahedral geometry

(C) $[Cu(NH_3)_4]^{2+}$ , $[Pt(NH_3)_4]^{2+}$ and $[Ni(CN)_4]^{2-}$ have $dsp^2$ hybridisation of the metal ion

(D) $Fe(CO)_5$ have bipyramidal structure with $dsp^3$ hybridised iron.

**9.** In each of the following pair of complexes, choose the one that absorbs light at a longer wave length.

(a) $[Co(NH_3)_6]^{2+}$ , $[Co(H_2O)_6]^{2+}$ (b) $[FeF_6]^{3-}$ , $[Fe(CN)_6]^{3-}$ (c) $[Cu(NH_3)_4]^{2+}$ , $[CuCl_4]^{2-}$

**10.** Observed (expermiental) lattice energies (in KJ/mol) of octahedrally coordinated crystals of VO and FeO are – 3917 and – 3923 respectively. The lattice energies of these crystals in the absence of CFSE are – 3691 and – 3856 kJ/mol respectively. Assuming that oxide ion ($O^{2-}$) is a weak field ligand, calculate CFSE value of $V^{2+}$ and $Fe^{2+}$ ion.

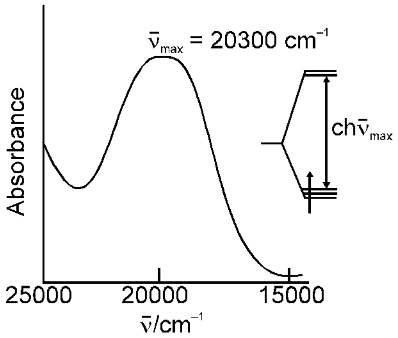
**Comprehension # (Q.11 to Q.12)**

**Read the following passage based on Applications of crystal field theory to explains magnetic and spectral properties of complexes carefully and answer the questions (11- 12).**

With the help of CFT number of unpaired electron in a compound can be calculated and we can calculate its paramagnetic moment(due to spin only), by the formula :

$\mu = \sqrt{n(n+2)}$ Bohr magneton (BM). where n is the number of unpaired electron in the complex.

For spectral analysis the separation between $t_{2g}$ and $e_g$ orbitals, called ligand field splitting. Parameter $\Delta_0$ (for octahedral complexes) should be known to us, which can be easily calculated by observing the absorption spectrum of one electron complex. Figure shows the optical absorption spectrum of the $d^1$ hexaaquatitanium(III) ion $[Ti(H_2O)_6]^{3+}$. The CFT assigns the first absorption maximum at 20,300 $cm^{-1}$ to the transition $e_g \leftarrow t_{2g}$. For multielectronic($d^2$ to $d^{10}$) system, the calculation of $\Delta_0$ by absorption spectrum is not that easy as the absorption spectrum will also be affected by electron-electron repulsions.



**11.** The crystal field stabilization energy (CFSE) for complex given in the passage, $[Ti(H_2O)]^{3+}$ will be (in kJ/mol) :

(A) 243 kJ/mole (B) 97 kJ/mole (C) 194 kJ/mole (D) 143 kJ/mole

**12.** The magnetic moments of following, arranged in increasing order will be (atomic number of Co = 27)

(1) $Co^{3+}$ (octahedral complex with a strong field ligand)

(2) $Co^{3+}$ (octahedral complex with a weak field ligand)

(3) $Co^{2+}$ (tetrahedral complex)

(4) $Co^{2+}$ (square planar complex)

(A) 1 > 2 > 3 > 4 (B) 2 > 3 > 4 > 1 (C) 3 > 2 > 4 > 1 (D) 2 > 4 > 3 > 1

**13.** **Match the pairs of complexes listed in column-I with the method(s) used for their differentiation listed in column-II.**

| **Column – I** | **Column–II** |
|---|---|
| (A) $[Cr(H_2O)_6]Cl_3$ and $Cr(H_2O)_5Cl]\ Cl_2.H_2O$ | (p) Can be differentiated by amount, nature or colour of precipitate formed. |
| (B) $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$ | (q) Can be differentiated by electrical conduction measurement method (appreciable difference) |
| (C) $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_6]Cl_3$ | (r) Can be differentiated using cryoscopic measurement method. |
| (D) $[Cu(H_2O)_4]SO_4.H_2O$ and $[Cu(H_2O)_6](NO_3)_2$ | (s) Can be differentiated by heating with concentrated $H_2SO_4$ |

# Answer Key

## DPP No. # 9

**1.** D **2.** B **3.** **(a)** C **(b)** A **4.** C **5.** B

**6.** B **7.** D **8.** ABCD

**9.** Stronger field ligand will split more so, more energy is required to transition of electrons from $t_{2g}$ to $e_g$ so, smaller wavelength light is required.

**10.** – 226, – 67. **11.** B **12.** B **13.** (A-p,q,r,s); (B-p,q); (C-p,q,r); (D-p,r,s)

# Hints & Solutions

## PHYSICAL / INORGANIC CHEMISTRY

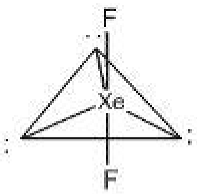
## DPP No. # 9

**1.** The given complex is actually.

$$\left[\underset{+2}{Fe}\underset{-1}{(Cl)}\underset{-4}{(CN)_4}\underset{-1}{(O_2)}\right]^{4-}$$

hence Fe(II) is $t_{2g}^{6}$, $e_g^{0}$ due to effect of strong ligands but it is paramagnetic due to $O_2^{-1}$ ligand.

**2.**



**3.** **(a)** The options can give CFSE = – 0.6 $\Delta_0$ with weak field ligands $\Rightarrow$ $d^4$ and $d^9$.
**(b)** Ammonia is a stronger field ligand than water.
So, CFSE of $[Ni(NH_3)_6]^{2+}$ is greater than $[Ni(H_2O)_6]^{2+}$

**4.** In A, $NO^+$ has no unpaired $e^-$s. So, complex is diamagnetic but in B, NO is odd $e^-$ molecule, having one odd $e^-$. So, B is paramagnetic.

**5.** Diamagnetic complexes shows decrease in weight when placed in magnetic balance.
$Ni(CO)_4$ → Tetrahedral & diamagnetic
$K[AgF_4]$ → Square planar & diamagnetic
$Na_2[Zn(CN)_4]$ → Tetrahedral & diamagnetic

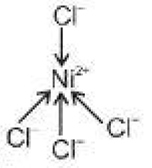
**6.** It is not showing geometrical isomerism $\Rightarrow$ Tetrahedral & paramagnetic.

**7.** The complex is actually

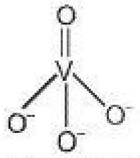
$K_2\left[\overset{(I)}{Cr}(CN)_4\,(NH_3)(\overset{+}{NO})\right]$ in which Cr(I) is $d^2sp^3$ hybridised with one unpaired electron.

**8.** (A) $H_3N \to Ag^+ \leftarrow NH_3$ (linear & sp hybridisation)

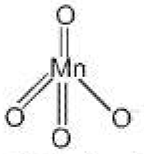
(B)



$sp^3$ Tetrahedral

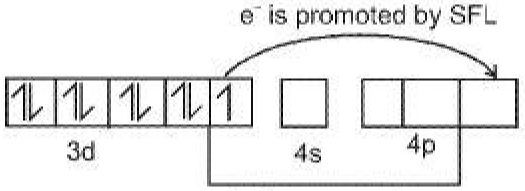


$sp^3$ Tetrahedral



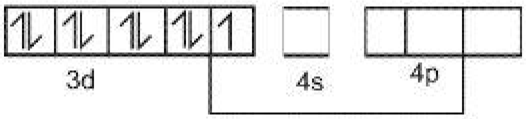
$sp^3$ Tetrahedral

(C) $[Cu(NH_3)_4]^{2+} \to$ $Cu^{2+} \to 3d^9, 4s^0$



$dsp^2$, square planar

$[Ni(CN)_4]^{2-} \to$ $Ni^{2+} \to 3d^8, 4s^0$



$dsp^2$, square planar

$[Pt(NH_3)_4]^{2+}$
4d & 5d metals always forms square planar with 4 ligands.
(D) $Fe(CO)_5$ ; $Fe \to 3d^6, 4s^2$

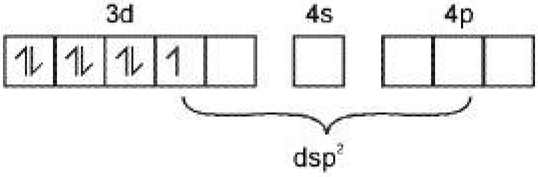
$dsp^3$, TBP

**9.** Stronger field ligand will split more so, more energy is required to transition of electrons from $t_{2g}$ to $e_g$ so, smaller wavelength light is required.

**10.** CFSE of $V^{2+}$ = – 3917 – (– 3691).
= – 226 kJ/mol.
CFSE of $Fe^{2+}$ = observed L.E. – L.E. (in absence of CFSE).
= – 3923 – (– 3856) = – 67 kJ/mol.

**11.** $Ti^{+3}$ is $3d^1$ system, $\Delta_o = 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2$ J/ion
$= 6.63 \times 10^{-34} \times 3 \times 10^8 \times 20300 \times 10^2 \times 10^{-3} \times 6.02 \times 10^{23}$ kJ/mol = 243 kJ/mol.
Now, CFSE $= 0.4 \times \Delta_o = 0.4 \times 243 = 97.2$ kJ/mol.

**12.** (1) ⇅ ⇅ ⇅ D (0) , (2) ⇅ ↿ ↿ P (4) , (3) ⇅ ⇅ P(3),

(4)  P(1)

**13.** (A) $[Cr(H_2O)_6]Cl_3\ (aq) \rightleftharpoons [Cr(H_2O)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$

$[Cr(H_2O)_5Cl]\ Cl_2.H_2O\ (aq) \rightleftharpoons [Cr(H_2O)_5Cl]^{2+}\ (aq) + 2Cl^-\ (aq)$

(B) $[Co(NH_3)_5Br]SO_4\ (aq) \rightleftharpoons [Co(NH_3)_5Br]^{2+}\ (aq) + SO_4^{2-}\ (aq)$

$[Co(NH_3)_5SO_4]Br\ (aq) \rightleftharpoons [Co(NH_3)_5SO_4]^+\ (aq) + Br^-\ (aq)$

(C) $[Co(NH_3)_5Cl]Cl_2\ (aq) \rightleftharpoons [Co(NH_3)_5Cl]^{2+}\ (aq) + 2Cl^-\ (aq)$

$[Co(NH_3)_6]Cl_3\ (aq) \rightleftharpoons [Co(NH_3)_6]^{3+}\ (aq) + 3Cl^-\ (aq)$

(D) $[Cu(H_2O)_4]SO_4.H_2O\ (aq) \rightleftharpoons [Cu(H_2O)_4]^{2+}\ (aq) + SO_4^{2-}\ (aq)$

$[Cu(H_2O)_6](NO_3)_2\ (aq) \rightleftharpoons [Cu(H_2O)_6]^{2+}\ (aq) + 2NO_3^-\ (aq)$