PHYSICAL / INORGANIC CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

DPP No. 11

Total Marks : 53

Max. Time : 53 min.

Topic : Coordination Compounds

Type of Questions		**M.M., Min.**
Single choice Objective ('–1' negative marking) Q.1 to Q.3	(3 marks, 3 min.)	[9, 9]
Multiple choice objective ('–1' negative marking) Q.4 to Q.5	(4 marks, 4 min.)	[8, 8]
True False ('–1' negative marking) Q.6	(3 marks, 3 min.)	[3, 3]
Subjective Questions ('–1' negative marking) Q.7 to Q.10	(4 marks, 4 min.)	[16,16]
Match the column ('–1' negative marking) Q.11	(4 marks, 4 min.)	[4, 4]

1. Among the following which one of the following IUPAC name is not correctly mentioned ?

(A) Linkage isomer of $[Pt(NH_3)_2Cl(NO_2)]$; Diamminechloridonitrito-O-platinum(II)

(B) Ionization isomer of $[Pt(NH_3)_2Cl\ (NH_2CH_3)]Br$; Diamminebromido(methylamine)platinum(II) chloride.

(C) One of the hydrate isomer of $[Cr(H_2O)_5Cl]Cl_2.H_2O$; Hexaaquachromium(III) chloride.

(D) One of the coordination isomer of $[Co(NH_3)_6][Cr(CN)_6]$; Hexacyanidocobaltate(III) hexaamminechromium(III).

2. Match the complex ions listed in column-I with the characteristics listed in column-II using the codes given below.

Column-I	**Column-II**
(a) $[Ni\ (NH_3)_6]^{2+}$	(p) d^2sp^3 and diamagnetic
(b) $[Cr\ (NH_3)_6]^{3+}$	(q) sp^3d^2 and diamagnetic
(c) $[Co\ (NH_3)_6]^{3+}$	(r) sp^3d^2 and two unpaired electrons
(d) $[Zn\ (NH_3)_6]^{2+}$	(s) d^2sp^3 and three unpaired electrons.

	a	b	c	d		a	b	c	d
(A)	r	s	p	q	(B)	s	r	q	p
(C)	r	s	q	p	(D)	p	q	r	s

3. Consider the following complex :

$[Cr(NH_3)_4(NO_2)_2]$: inner orbital complex.

The oxidation number, number of d-electrons, number of unpaired d-electrons on the metal ion and number of isomers are respectively :

(A) 3, 3, 3, 2 (B) 2, 4, 0, 6 (C) 2, 4, 2, 6 (D) 2, 4, 4, 4

4. In which of the following complexes more than one type of structural isomerism are possible ?

(A) $[Co(NH_3)_5\ (NO_2)]Cl$ (B) $[Co(NH_3)_5(H_2O)](NO_2)_3$

(C) $[Pt(NH_3)_4][Pt(SCN)_4]$ (D) $[Cr(NH_3)_4\ (NO_2)_2]\ (NO_3)_2$

5. Consider the following statements.

(i) Blue salt $K_4[Mn(CN)_6]$. $3H_2O$ is isostructural with the hexacyanoferrate (II) and the former complex is paramagnetic but later one is diamagnetic.

(ii) In the series of isoelectronic species $[V(CO)_6]^-$, $[Cr(CO)_6]$ and $[Mn(CO)_6]^+$, from vanadium to manganese complexes there is a reduction in the strength of the bonding between metal and carbon and an increase in that in the carbonyl group (i.e. CO).

(iii) Chlorotristriphenylphosphinerhodium (I) is a square planar diamagnetic complex which is used as a homogeneous catalyst in hydrogenation of alkenes.

(iv) Like $[Co(NH_3)_4Cl_2]^+$ ion, $[Co(en)_2Cl_2]^+$ ion can exist in cis and trans forms and neither can display optical activity.

(v) Ni $(CO)_4$ and $NiCl_2(PPh_3)_2$ have same hybridisation but different, magnetic moment and effective atomic number

Which of the above statements are correct ?

(A) (i), (iii) and (v) (B) (ii), (iii) and (iv) (C) (ii), (iii) and (v) (D) (iii), (iv) and (v)

6. **S_1 :** CO forms strong complexes with transition elements because the drift of π electron density from metal to carbon tends to make the ligand more negative and so enhances its σ donor power.

S_2 : Amongst $[V(CO)_5]^{3-}$, $[V(CO)_6]^-$ and $[V(CO)_6]$, the C–O bond length is smallest in $[V(CO)_5]^{3-}$.

S_3 : The crystal field theory attributes the colour of the coordination compound to d–d transition of the electron.

S_4 : The number of electrons in t_{2g} orbitals in $[Cr(NH_3)_4(NO_2)_2](ClO_4)$ is 3.

(A) T F T T (B) F F T T (C) T F T F (D) T T T F

7. What is the $[Cd^{2+}]$ in 1.0L of solution prepared by dissolving 0.0010mol $Cd(NO_3)_2$ & 2 mol NH_3 ? K_d for the dissociation of $Cd(NH_3)_4^{2+}$ into Cd^{2+} & 4 NH_3 is 2×10^{-7}. Neglect the amount of cadmium in complexes containing fewer than 4 ammonia molecules.

8. How many of total isomers are possible for the complex $[Co(NH_3)_4(NO_2)_2]NO_3$?

9. Among the following complexes, how many have 'spin only' magnetic moment of 2.83 B.M. ?

$[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$, $[NiCl_2(PPh_3)_2]$, $[NiCl_4]^{2-}$, $[NiF_6]^{2-}$, $[NiF_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[Ni(H_2O)_6]^{2+}$

10. Total no. of isomers (including stereoisomers) for the complex $[Pd(NH_3)(H_2O)(NO_2)_2]$ are :

11.

	Column-I		**Column-II**
(A)	$[Cr(en)_3]^{3+}$	(p)	Paramagnetic
(B)	$[Mn(CN)_6]^{3-}$	(q)	$\mu_{spin} = \sqrt{15}$ B.M.
(C)	$[Co(H_2O)_6]^{2+}$	(r)	Two unpaired electrons
(D)	$[Fe(CN)_6]^{3-}$	(s)	Inner orbital complex.

Answer Key

DPP No. # 11

1.	D	**2.**	A	**3.**	C	**4.**	ABCD	**5.**	AC
6.	A	**7.**	$[Cd^{2+}] = 1.25 \times 10^{-11}$.			**8.**	10	**9.**	6
10.	7	**11.**	(A – p, q, s) ; (B – p, r, s) ; (C – p, q) ; (D – p, s)						

Hints & Solutions

PHYSICAL / INORGANIC CHEMISTRY

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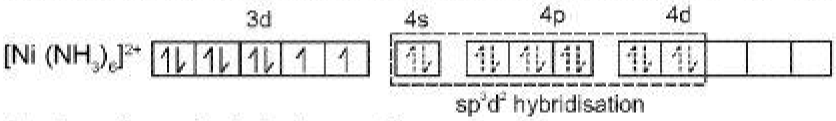
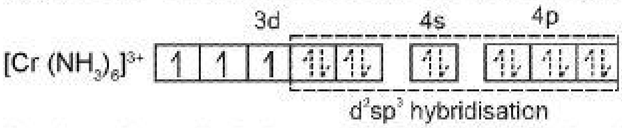
1. (A) $[Pt(NH_3)_2Cl(NO_2)]$ and $[Pt(NH_3)_2Cl(ONO)]$ are linkage isomers.
(B) $[Pt(NH_3)_2Cl\,(NH_2CH_3)]Br$ and $[Pt(NH_3)_2Br\,(NH_2CH_3)]Cl$ are ionisation isomers.
(C) $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_6]Cl_3$ are hydrate isomers.
(D) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$ are coordination isomers.
Correct IUPAC name is hexaamminechromium(III) hexacyanidocobaltate(III).

2. (a) $_{28}Ni$ is in +2 oxidation state with electron configuration $[Ar]^{18}\ 3d^8\ 4s^0$, so

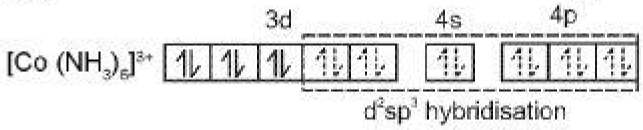


Number of unpaired electrons = 2
(b) $_{24}Cr$ is in +3 oxidation state with electron configuration $[Ar]^{18}\ 3d^3\ 4s^0$; so



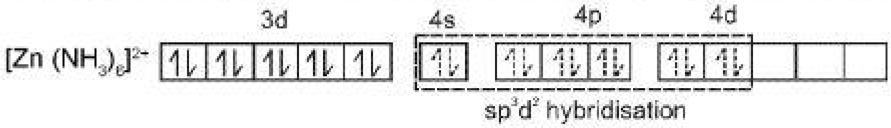
Number of unpaired electrons remains three, whether ligand is strong field or weak field ligand when electron configuration is $3d^3$.

(c) $_{27}Co$ is in +3 oxidation state with electron configuration $[Ar]^{18}\,3d^6\,4s^0$, so



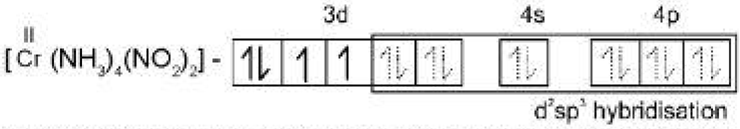
All electrons are paired, so complex ion is diamagnetic.

(d) $_{30}Zn$ is in +2 oxidation state with electron configuration $[Ar]^{18}\,3d^{10}\,4s^0$, so



All electrons are paired, so complex ion is diamagnetic.

3. $_{24}Cr$ is in +2 oxidation state with $[Ar]^{18}3d^4$ configuration. It is inner orbital complex, so ;



Number of d-electrons is four and number of unpaired electrons is two.

It shows geometrical and linkage isomers.

$NO_2 - NO_2$	cis-trans.
$NO_2 - ONO$	cis-trans.
$ONO - ONO$	cis-trans.

Total number of isomers = 6.

4. (A) $[\overset{II}{Co}(NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}(NH_3)_5(ONO)]Cl$ - linkage isomerism

$[\overset{II}{Co}(NH_3)_5(NO_2)]Cl$ and $[\overset{II}{Co}(NH_3)_5Cl]NO_2$ - ionization isomerism

(B) $[\overset{III}{Co}(NH_3)_5(H_2O)](NO_2)_3$ and $[\overset{III}{Co}(NH_3)_5(NO_2)](NO_2)_2.H_2O$ - hydrate isomerism

$[\overset{III}{Co}(NH_3)_5(NO_2)](NO_2)_2.H_2O$ and $[\overset{III}{Co}(NH_3)_5(ONO](NO_2)_2.H_2O$

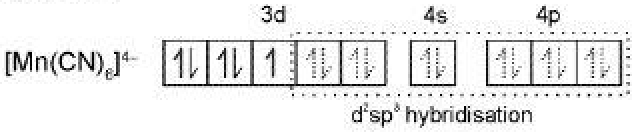
(C) $[\overset{II}{Pt}(NH_3)_4]^{2+}\,[\overset{II}{Pt}(SCN)_4]^{2-}$ and $[\overset{II}{Pt}(NH_3)_3(SCN)]^{+}\,[\overset{II}{Pt}(NH_3)(SCN)_3]^{-}$ - coordination isomerism

$[\overset{II}{Pt}(NH_3)_4]^{2+}\,[\overset{II}{Pt}(SCN)_4]^{2-}$ and $[\overset{II}{Pt}(NH_3)_4]^{2+}\,[\overset{II}{Pt}(NCS)_4]^{2-}$ - linkage isomerism

(D) $[Cr(NH_3)_4(NO_2)_2](NO_3)_2$ and $[Cr(NH_3)_4(NO_3)_2](NO_2)_2$ - ionization isomerism

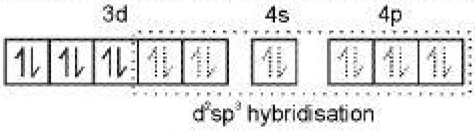
$[Cr(NH_3)_4(NO_2)_2](NO_3)_2$ and $[Cr(NH_3)_4(ONO)_2](NO_3)_2$ - linkage isomerism

5. (i) $_{25}Mn$ is in + II oxidation state. The electronic configuration of Mn^{2+} is $[Ar]^{18}\,3d^5\,4s^0$. The CN^- is strong field ligand, so



It is inner orbital / low spin octahedral complex with one unpaired electron.

Similarly for $[Fe(CN)_6]^{4-}$



It is inner orbital / low spin octahedral complex with no unpaired electron.

(ii) As the negative charge on the metal increases from the manganese complex to vanadium complex, it is delocalised on to the ligands by the π back bonding. This strengthen the metal-carbon bond and weaken the C–O bond (as bond order of CO decreases).

(iii) $[RhCl(PPh_3)_3]$ is Wilkinson's catalyst. Because of $4d^8$ configuration its higher CFSE favours square planar low spin complex (i.e. dsp^2). It is used as homogeneous catalyst for the hydrogenation of alkenes.

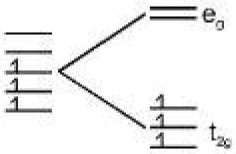
(iv) False statement : trans $[Co(en)_2Cl_2]^+$ has a centre and several planes of symmetry but the cis-form has neither, and (+) and (–) forms of cis $[Co(en)_2Cl_2]^+\,Cl^-$ have been separated.

6. **S_1 :** Correct statement.

S_2 : As electron density on metal ion increases, the back donation into antibonding π orbitals of CO weakens the C–O bond and thus there is increase in inter atomic distance. Hence, C–O bond length is biggest in $[V(CO)_5]^{3-}$.

S_3 : Correct statement.

S_4 : Electron distribution of $3d^3$ configuration of Cr^{3+}



So, t_{2g} orbitals contain 3 electrons.

7.

$$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+} \qquad K_f = \frac{1}{K_d}.$$

10^{-3} $\quad$ 2

≈ 0 $\quad$ $2-4\times10^{-3}\approx2$ $\quad$ 10^{-3}.

$[Cd^{2+}]_0 = 10^{-3}$ M $\qquad$ $[NH_3]_0 = 2$ M.

$$K_f = \frac{[Cd(NH_3)_4]^{2+}}{[Cd^{2+}][NH_3]^4} = \frac{10^{-3}}{[Cd^{2+}][2]^{+}} = \frac{10^7}{2}.$$

$$\Rightarrow \quad [Cd^{2+}] = \frac{1}{8} \times 10^{-10} = \mathbf{1.25 \times 10^{-11}\ M.}$$

8. NO_2–NO_2 ⟶ 2 (cis/trans)

NO_2–ONO ⟶ 2 (cis/trans)

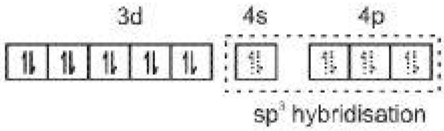
ONO–ONO ⟶ 2 (cis/trans)

NO_2–NO_3 ⟶ 2 (cis/trans)

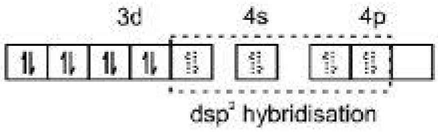
ONO–NO_3 ⟶ 2 (cis/trans)

Total = 10 isomers.

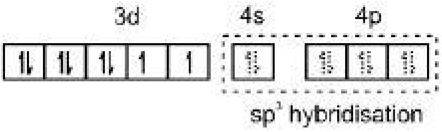
9. $[Ni(CO)_4]$,



$[Ni(CN)_4]^{2-}$,

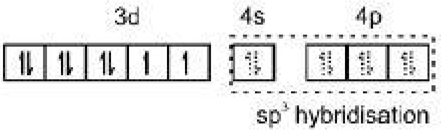


$[NiCl_2(PPH_3)_2]$,



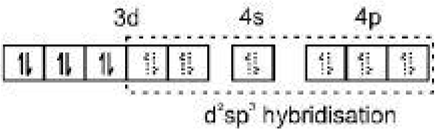
$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[NiCl_4]^{2-}$,

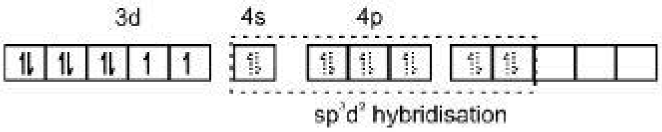


$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[NiF_6]^{2-}$,

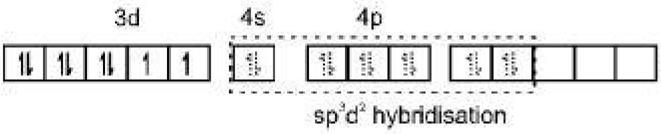


$[NiF_6]^{4-}$,



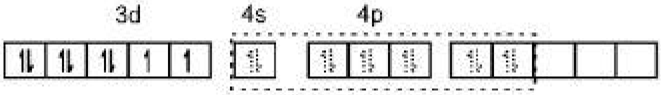
$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

$[Ni(NH_3)_6]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

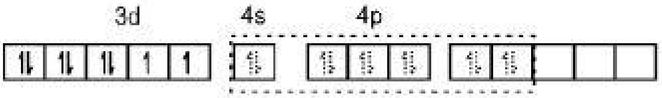
$[Ni(NH_3)_6]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

sp^3d^2 hybridisation

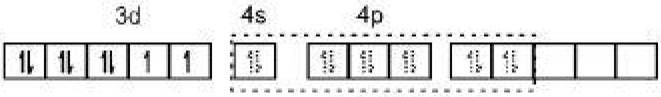
$[Ni(en)_3]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

sp^3d^2 hybridisation

$[Ni(H_2O)_6]^{2+}$,



$\mu_{B.M.} = \sqrt{2(2+2)} = 2.83$

sp^3d^2 hybridisation

Note : With coordination number six and oxidation state +2, two (n–1) d-orbitals are not available for d^2sp^3 hybridisation.
Hence, nd orbitals participitate in hybridisation.

10. (A) (NO_2) (NO_2) → cis + trans
(B) (ONO) (NO_2) → 3
(C) (ONO) (ONO) → cis + trans