Coordination Compounds

ANSWERS

1. *dsp*³ hybridisation

2. (a) K₂[Zn(OH)₄]
Potassium tetrahydroxidozincate(II)
(b) [Pt(NH₃)₆]Cl₄
Hexaammineplatinum(IV) chloride

EXAM

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- **3.** +1
- 4. $[RhCl(PPh_3)_3]$
- 5. Both are tetrahedral

OR

Fe exists as Fe²⁺. Fe(II) in $[Fe(H_2O)_6]^{2+} = 3d^6 4s^0 4p^0 4d^0$. As water is a weak ligand, pairing does not occur and the 6 electrons pairs available from each water molecule moves to one 4s, three 4p and two 4d orbitals. Thus, the hybridisation involved is sp^3d^2 .

6. Na₂[Zn(OH)₄]

7. +3, 6

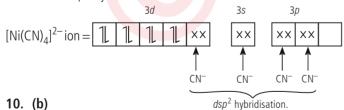
8. Ionisation isomerism : [Co(NH₃)₅Cl]SO₄

and [Co(NH₃)₅SO₄]Cl

OR

The ionisation isomer is $[Co(NH_3)_5SO_4]Br$. The IUPAC name is pentamminesulphatocobalt(III) bromide.

9. (c) : $[Ni(CN)_4]^2$ has square planar geometry explained on the basis of dsp^2 hybridisation

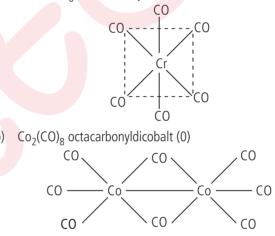


11. (d) : The magnitude of Δ_o varies from stronger to weaker ligands. According to specto-chemical series, F⁻ is a weaker while NH₃ is a stronger ligand. Stronger ligand gives a larger value of Δ_o . **12.** (a) : *cis*-isomer of [PtCl₂(NH₃)₂] is known as *cis*-platin and is used as an antitumor agent in treatment of cancer. **14.** (c) : The primary valencies are normally ionisable and are satisfied by negative ions, while secondary valencies are non-ionisable. These are satisfied by neutral molecules or negative ions.

15. (b)

16. (c) : The crystal field theory is an electrostatic model which considers the metal-ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand.

17. (a) Cr(CO)₆ Hexacarbonylchromium (0)



18. Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). But the fact that the magnetic moment of the complex ion is 5.9 B.M. It should be tetrahedral shape rather than square planar because of the presence of five unpaired electrons in the *d*-orbitals.

OR

In $[Ni(H_2O)_6]^{2+}$, Ni^{2+} ion has two unpaired electron and it shows colour. In $[Ni(CN)_4]^{2-}$, there is no unpaired electron, hence it is colourless.

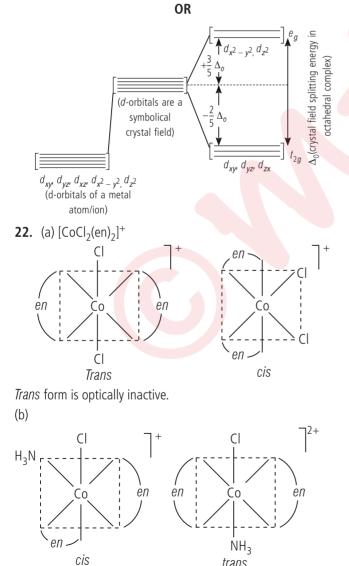
19. Tetrahedral complexes do not show geometrical isomerism because the relative positions of the unidentate ligands attached to the central metal atom are the same with respect to each other.

20. As the coordination number of cobalt is six therefore the expected formula that explains the above data is formulated as $[Co(NH_3)_4Cl_2]Cl$ tetraamminedichloridocobalt(III) chloride.

13. (b)

21.

Weak field coordination entity	Strong field coordination entity
1. They are formed when the crystal field splitting energy (Δ_o) in octahedral complexes is less than the energy required for an electron pairing in a single orbital (<i>P</i>)	1. They are formed when the crystal field splitting energy (Δ_o) is greater than the <i>P</i> .
2. They are also called high spin complexes.	2. They are called low spin complexes.
3. They are mostly paramagnetic in nature.	3. They are mostly diamagnetic or less paramagnetic than weak field.
 Never formed by CN[−] ligands. 	4. Formed by CN ⁻ like ligands.



trans

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Trans form is optically inactive.

23. Cr^{2+} had d^4 configuration. d^4 ion in a high spin state (weak field) $t^3_{2g} e_q^{1}$ $CFSE = -0.6\Delta_0 = -0.6 \times 13900 \text{ cm}^{-1} = -8340 \text{ cm}^{-1}$ d^4 ion in a low spin state (strong field) $t_{2a}^4 e_q^0$ $CFSE = -1.6\Delta_{o} + P = -1.6(13900 \text{ cm}^{-1}) + 23500 \text{ cm}^{-1}$ $= 1260 \text{ cm}^{-1}$ Since, $\Delta_o < P$, the high spin configuration would be more stable.

OR

Valence bond theory was developed by Pauling. Coordination compounds contain complex ion, in which ligands form coordinate bonds with the metal. Thus, the ligand must have a lone pair of electrons and the metal must have an empty orbital of suitable energy available for bonding. The theory considers which atomic orbitals on the metal are used for bonding. From this, shape and stability of the complex are predicted. The theory has two main limitations. Most transition metal complexes are coloured, but the theory provides no explanation for their electronic spectra. Further, the theory does not explain why the magnetic properties vary with temperature. For these reasons it has largely been superseded by the crystal field theory. However, it is of interest for study as it shows the continuity of the development of modern ideas from Werner's theory.

Inner orbital complex – $[Co(NH_3)_6]^{3+}$ Outer orbital complex – $[CoF_6]^{3-}$

24. Ligand on the basis of their ligating ability can be classified as : Monodentate : (Unidentate; dentate = tooth or place of (i) attachment). When the ligands can donate the pair of electrons from one atom it is called monodentate ligands.

e.g., NH₃, H₂O, CN⁻ etc.

(ii) **Didentate :** When the ligand can donate the pair of electrons through two atoms of the ligand, it is called didentate ligand.

e.g., ethylene diamine
$$\begin{pmatrix} CH_2 - \dot{N}H_2 \\ | \\ CH_2 - \dot{N}H_2 \end{pmatrix}$$
; oxalate ion $\begin{pmatrix} COO^- \\ | \\ COO^- \end{pmatrix}$

Polydentate ligands : When the ligand has three or more atoms through which it can donate electron pairs, then the ligands are called polydentate ligands.

e.g., EDTA (Ethylenediaminetetraacetate ion)

$$\begin{pmatrix} -00CCH_2 \\ -00CCH_2 \end{pmatrix}$$
 $\ddot{N} - CH_2 - CH_2 - \ddot{N} \begin{pmatrix} CH_2COO^- \\ CH_2COO^- \end{pmatrix}$

25. When excess of aqueous KCN is added to the aqueous solution of CuSO₄ octahedral complex of hexacyanocuprate (II) ion is formed.

Coordination Compounds

$$CuSO_{4(aq)} + 6KCN_{(aq)} \longrightarrow K_4[Cu(CN)_6] + K_2SO_4$$

Potassium
hexacyanocuprate (II)

After the formation of this complex when H_2S gas is passed through the solution no precipitates of CuS (copper sulphide) are formed as Cu^{2+} ion is not free, they are forming complex compound with the CN^- radicals which due to its covalent nature does not breaks.

26.

Double salt	Complex compound
1. The constituent simple salts are in equimolar proportions.	1. The constituent simple salts may or may not be in equimolar proportions.
2. These dissociate in aqueous solutions.	2. The complex ion does not dissociate in aqueous solution.
3. These contain ionic bonds.	3. These may have ionic as well as coordinate bonds.

27. (i) It is because the relative position of the ligands attached to the central metal atom are the same with respect to each other.

(ii) It is because the *trans* isomer has a plane of symmetry and can be divided into two equal halves.

(iii) Chelating ligand can form a ring with central metal. Therefore it have ability to regulate electron within ring. Because of it there is more force of attraction b/w central metal ion and chelating ligand.

28. (i) K[Cr(H₂O)₂(C₂O₄)₂]

IUPAC name : Potassium diaquadioxalatochromate(III)

Oxidation state of Cr = +3

Electronic configuration : [Ar] $3d^3 (t_{2a}^3 e_a^0)$

The complex will show geometrical isomerism and optical isomerism.

The magnetic moment is $\mu = 3.87$ B.M.

(ii) CrCl₃(*py*)₃

IUPAC name : Trichlorotripyridinechromium(III)

Oxidation state of Cr = +3

Electronic configuration = $[Ar]3d^3 (t_{2a}^3 e_a^0)$

The complex will exist as facial and meridional isomers. The magnetic moment is $\mu = 3.87$ B.M.

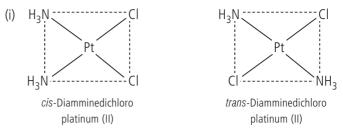
(iii) K₄[Mn(CN)₆]

IUPAC name : Potassium hexacyanomanganate(II)

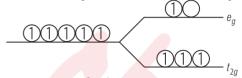
Oxidation state of Mn = +2,

Electronic configuration = $[Ar]3d^5 (t_{2g}^5 e_g^0)$

The complex will have $\mu = 1.73$ B.M.



(ii) When $\Delta_o < P$ is is weak field high spin situation. As a result, one electron entered in e_a orbital and 3 electrons in t_{2a} .



Electronic configuration : $t_{2a}^3 e_a^1$

(iii) Ni(CO)₄ : The outermost electronic configuration will be $3d^8 4s^2 4p^0$.

CO is the strong ligand, causes pairing up of the 4s electrons into the 3d electrons.



Thus, the hybridisation will be sp^3 (tetrahedral) Ni(CO)₄ will be diamagnetic in nature.

29. (i) Three ion, $[Co(NH_3)_6]^{2+}$, $2CI^-$

(ii) Orbital splitting energies are not sufficiently large enough to cause pairing.

(iii) Hexaamminenickel(II) chloride

(iv) Cs[FeCl₄]

Oxidation state of Fe = +3

Coordination number = 4

Shape -Tetrahedral

Magnetic moment $\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.95$ B.M.

30. (i) I_3^-

(ii) Bis-(ethane-1, 2-diammine) copper (II) nitrate.

(iii) Alfred Werner first time did the systematic study of coordination compounds.

(iv) The colour of the coordination entity is decided by the colour of the spectrum absorbed in the d-d transition of electron. The colour shown is always the complementary to the colour absorbed.

(v) When a multidentate ligand forms cyclic ring with metal atom/ion with no unfavorable steric effects, the stability of the complex is increased further and this effect is called macrocyclic effect.

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