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NCERT Solutions for Coordination Compounds

- 1. Write the formulas for the following coordination compounds: (i)Tetraamminediaquacobalt(III) chloride (ii)Potassium tetracyanidonickelate(II) (iii)Tris(ethanp-1,2-diamine) chromium(III) chloride (iv)Amminebromidochloridonitrito-N- platinatc(II) (v)Dichloridobis(ethane-1,2-diamine) platinum (IV) nitrate (vi)Iron(III)hexacyanidoferrate(II) Ans: (i) $[CO(NH_3)_4(H_2O)_2]Cl_3$. $(ii)K_2[Ni(CN)_4]$ (iii)[Cr(en)₃]Cl₃ (iv)[Pt (NH₃) Br Cl (N0₂)] $^{-}$ $(v)[PtCl_2(en)_2](N0_3)_2$ $(vi)Fe_4[Fe(CN)_6]_3$ 2. Write IUPAC names of following co-ordination compounds: (a) $[CO(NH_3)_6]Cl_3$ (b) [CO(NH₃)Cl]Cl₂ (C) $K_3[Fe(CN)_6]$ (d) $[K_3[Fe(C_2O_4)_3]$ (e) $K_2[PdCl_4]$ (f) [Pt(NH₃)₂ClNH₂CH₃]Cl. (C. B. S. E. Delhi2013)
- (a) hexaamminecobalt (III) chloride

Ans:

- (b) pentaamminechloridocobalt (III) chloride
- (c) potassium hexacyanoferrate (III)
- (d) potassium trioxalatoferrate (III)
- (e) potassium tetrachloridoplatinum (II)
- (f) diamminechlorido (methylamine) platinum(II) chloride.

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3. Indicate the types of isomerism exhibited by the following complexes and draw the structures for these isomers:

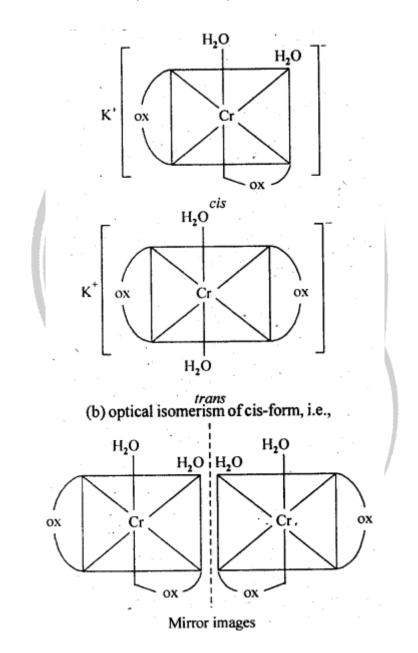
(i)K [Cr $(H_2O)_2(C_2O_4)_2$]

(ii)[CO (en)₃]Cl₃

(iii)[$CO(NH_3)_5(NO_2)(NO_3)_2$], .

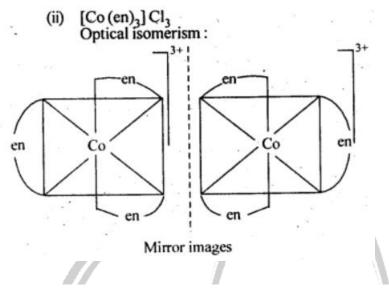
 $(iv)[Pt(NH_3)(H_2O)]$

Ans: (i)(a) geometrical isomerism (cis and tram)

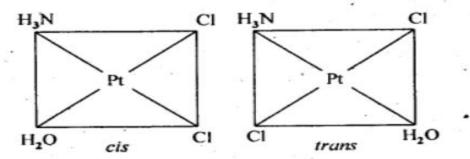


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- (iii) $[Co (NH_3)_5 NO_2] (NO_3)_2$ - Ionisation isomerism : $[Co (NH_3)_5 (NO_2)] (NO_3)_2$ and $[Co (NH_3)_5 (NO_3)] (NO_2) (NO_3)$ - Linkage isomerism : $[(Co (NH_3)_5 (NO_2)] (NO_3)_2$ and $[Co (NH_3)_5 (ONO)] (NO_3)_2$
- (iv) [Pt (NH₃) (H₂O) Cl₂] Geometrical isomerism:



4. Give evidence that [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅SO₄]Cl are ionisation isomers.

Ans: When dissolved in water, they give different ions in solution which can be tested by adding $AgNO_3$ solution and $BaCl_2$ solution, i.e.,

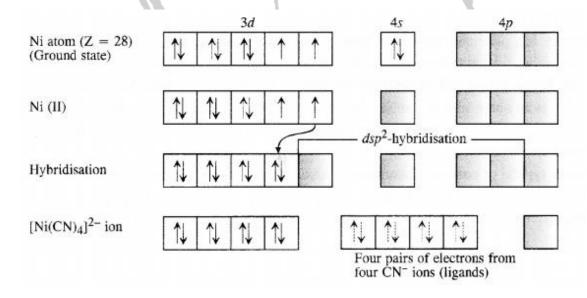
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$$[\text{Co (NH}_3)_5 \text{ Cl] SO}_4(aq) + \text{BaCl}_2(aq) \rightarrow \\ \text{BaSO}_4(s) \downarrow \\ \text{ppt} \\ [\text{Co (NH}_3)_5 \text{ Cl] SO}_4(aq) + \text{AgNO}_3(aq) \rightarrow \\ \text{No reaction} \\ [\text{Co (NH}_3)_5 \text{ SO}_4] \text{ Cl}(aq) + \text{BaCl}_2(aq) \rightarrow \\ \text{No reaction} \\ [\text{Co (NH}_3)_5 \text{ SO}_4] \text{ Cl } (aq) + \text{AgNO}_3(aq) \rightarrow \\ \text{AgCl } (s) \downarrow \\ \text{ppt} \\]$$

Hence, the two are ionisation isomers.

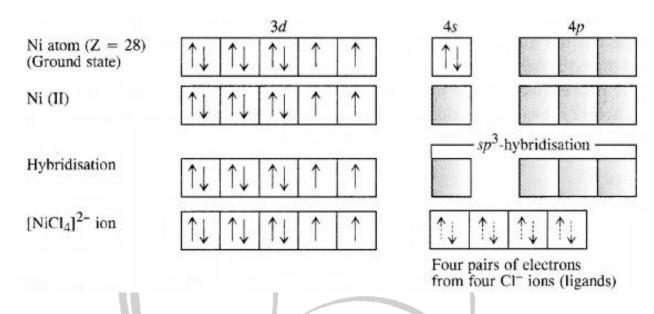
5. Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic. (Rajasthan Board 2012) Ans: Outer electronic configuration of nickel (Z=28) in ground state is $3d^84s^2$. Nickel in this complex is in + 2 oxidation state. It achieves + 2 oxidation state by the loss of the two 4s-electrons. The resulting Ni^{2+} ion has outer electronic configuration of $3d^8$. Since CN^- ion is a strong field, under its attacking influence, two unpaired electrons in the 3d orbitals pair up.



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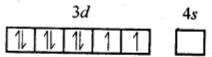
Outer electronic configuration of nickel (Z = 28) in ground state is $3d^84s^2$ Nickel in this complex is in + 2 oxidation state. Nickel achieves + 2 oxidation state by the loss of two 4s-electrons. The resulting Ni²⁺ ion has outer electronic configuration of $3d^8$. Since CP ion is a weak field ligand, it is not in a position to cause electron pairing.



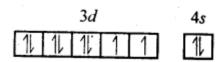
6. [NiCl₄]²⁻ is paramagnetic while [Ni(CO)₄] is diamagnetic though both are tetrahedral.Why?

Ans:

In $[\text{NiCl}_4]^{2-}$, Ni is in +2 oxidation state Ni (28): $3d^84s^2$ Ni²⁺: $3d^84s^0$



Cl⁻ is weak field ligand. It does not pair up $e^{-1}s$. Hence, it is paramagnetic In [Ni (CO)₄], Ni is in 0 O.S. Ni (28): $3d^8 4s^2$



CO is strong field ligand, as it pairs the $4s e^{-1}s$ with $3d e^{-1}s$ to give $3d^{10} 4s^0$. So, no unpaired e^- and hence, the complex is diamagnetic.

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7. $[Fe (H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain Ans:
Fe $(H_2O)_6$] ³⁺ Fe (26): $3d^6 4s^2$
Here, Fe is in +3 state. Thus, $Fe^{3+}: 3d^5 4s^0$
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$
H ₂ O being a weak field ligand does not pair up
the e ⁻¹ s and hence the complex is strongly paramagnetic. [Fe (CN) ₆] ³⁻ Fe (26): $3d^6 4s^2$ Here, Fe is in +3 state, So Fe ³⁺ : $3d^5 4s^0$
3d 4s
CN ⁻ being a strong field ligand pairs up the e ⁻¹ s so that we have
3d 4s
11 11 1
Due to only one unpaired e-, the complex is weakly paramagnetic
8. Explain $[CO(NH_3)_6]^{2+}$ is an inner orbital complex. whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital

complex.
Ans:

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Compiled by: Dapinderjeet Singh $[Co(NH_3)_6]^{3+}$ $Co(27):3d^74s^2$ Here, Co is in +3 state, so Co^{3+} : $3d^6 4s^2$ In presence of NH₁, two d e⁻¹s pair up leaving two d-orbitals empty. Hence, hybridisation is d^2sp^3 i.e., inner orbital complex. [Ni (NH₃)₆]²⁺ Here, Ni is in +2 state. Thus, Ni²⁺: 3d⁸4s⁰ In presence of NH₃, de-1s do not pair up. The hybridisation is sp^3d^2 i.e., outer orbital complex. 9. Predict the number of unpaired electrons in the square planar [Pt(CN)₄]²⁻ ion. [Pt (CN)₄]²⁻: The outer shell electronic configuration of Pt is $5d^96s^1$. In +2 state of Pt, it is $5d^8$, i.e., 6p For square planar geometry, hybridisation is dsp^2 . Hence, the two $d e^{-1}$ s pair up to make one d-orbital empty. So, there is no unpaired e-.

Ans:

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10. The hexaaquamanganese (II) ion contains five unpaired electrons while the hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

Ans: Mn(II) ion has $3d^5$ configuration. In the presence of H₂O molecules acting as weak field ligands, the distribution of these five electrons is $t^3_{2g}e^2$ i. e., all the electrons remain unpaired to form a high spin complex. However, in the presence of CN⁻ acting as strong field ligands, the distribution of these electrons is t52ge0g i.e., two t_{2g} orbitals contain paired electrons while the third t_{2g} orbital contains one unpaired electron. The complex formed is a low spin complex.

11. Explain the bonding in coordination compounds in terms of Werner's postulates.

Ans: The main postulates of Werner's theory of coordination compounds are as follows:

- (a)Metals possess two types of valencies called
- (i) primary valency which are ionisable; (ii) secondary valency which are non-ionisable
- (b)Primary valency is satisfied by the negative ions and it is that which a metal exhibits in the formation of its simple salts.
- (c)Secondary valencies are satisfied by neutral ligand or negative ligand and are those which metal exercises in the formation of its complex ions. Every cation has a fixed number of secondary valencies which are directed in space about central metal ion in certain fixed directions, e.g., In CoCl₃-6NH₃, valencies between Co and Cl are primary valencies and valencies between Co and NH₃ are secondary. In COCl₃-6NH₃, six ammonia molecules linked to Co by secondary valencies are directed to six corners of a regular octahedron and thus account for structure of COCl₃-6NH₃ as follows:

$$\begin{bmatrix} H_3N & NH_3 \\ & NH_3 \\ & NH_3 \end{bmatrix}^{3+} 3 CI^{-}$$

In modern theory, it is now referred as coordination number of central metal atom or ion.

12. FeSO₄ solution mixed with $(NH_4)_2SO_4$ solution in 1 : 1 molar ratio gives the test of Fe²⁺ ion but CuSO₄ solution mixed with aqueous ammonia in 1 : 4 molar ratio does not give the test of Cu²⁺ ion. Explain why?

Ans: When FeSO₄ and $(NH_4)_2SO_4$ solutions are mixed in 1 : 1 molar ratio, a double salt known as Mohr's salt is formed. It has the formula FeSO₄. $(NH_4)_2SO_4.6H_2O$. In aqueous solution, the salt dissociates as :

$$FeSO_4.(NH_4)_2SO_4.6H_2O(aq) \xrightarrow{(aq)} Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O$$

The solution gives the tests for all the ions including Fe2+ ions. On the other hand, when $CuSO_4$ and NH_3 are mixed in the molar ratio of 1 : 4 in solution, a complex $[Cu(NH_3)_4]SO_4$ is formed. Since the Cu^{2+} ions are a part of the complex entity (enclosed in square bracket), it will not give their characteristic tests as are given by Fe^{2+} ions.

13. Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

Ans: Coordination entity: It constitutes of a central atom/ion bonded to fixed number of ions or molecules by coordinate bonds e.g. [COCl₃(NH₃)₃], [Ni (CO)₄] etc.

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Ligand: The ions/molecules bound to central atom/ion in coordination entity are called ligands. Ligands in above examples are CL, NH₃, CO Coordination number: This is the number of bond formed by central atom/ion with ligands. Coordination polyhedron: Spatial arrangement of ligands defining the shape of complex. In above cases Co and Ni polyhedron are octahedral and tetrahedral in $[CoCl_3 (NH_3)_3]$ and $[Ni(CO)_4]$ respectively. Homoleptic: Metal is bound to only one kind of ligands eg Ni in $[Ni(CO)_4]$ Heteroletric Metal is bound to more than one kind of ligands eg $[CoCl_3(NH_3)_3]$

14. What is meant by unidentate didentate and ambidentate ligands? Give two examples for each.

Ans: A molecule or an ion which has only one donor atom to form one coordinate bond with the central metal atom is called unidentate ligand, e.g., Cl- and NH₃.

A molecule or ion which contains two donor atoms and hence forms two coordinate bonds with the central metal atom is called adidentate

A molecule or an ion which contains two donor atoms but only one of them forms a coordinate bond at a time with the central metal atom is called

15. Specify the oxidation numbers of the metals in the following coordination entities: (i) $[Co(H_2O)(CN)(en)_2]^{2+}$ (ii) $[CoBr2(en)_2]^+$ (iii) $[PtCl_4]^{2-}$ (iv) $K_3[Fe(CN)_6]$ (v) $[Cr(NH_3)_3CI_3]$ Ans:

(i)
$$[Co(H_2O)(CN)(en)_2]^{2+}$$
 $x+0+(-1)+0=+2$
(ii) $[CoBr_2(en_2)]^+$ $x+2(-1)+0=+1$
(iii) $[PtCl_4]^{2-}$ $x=+3$
(iv) $K_3[Fe(CN)_6]$ $x=+3$
(v) $[Cr(NH_3)_3Cl_3]$ $x+0+3(-1)=0$
 $x=+3$

- 16. Using IUPAC norms, write the formulae for the following
- (a) tetrahydroxozincate(II)
- (b) hexaammineplatinum (TV)
- (c) potassiumtetrachloridopalladate(II)
- (d) tetrabromidocuprate (II)
- (e) hexaaminecobalt(III) sulphate
- (f) potassiumtetracyanonicklate (II)

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- (g) potassiumtrioxalatochromate(III)
- (h) pentaamminenitrito-O-cobalt(III)
- (i) diamminedichloridoplatinum(II)
- (j) pentaamminenitrito-N-cobalt (III).
- Ans: (a) [Zn(OH)₄]₂₋
- (b) $[Pt(NH_3)_6]^{4+}$
- (c) $K_2[PdCl_4]$
- (d) [Cu(Br)₄]²⁻
- (e) $[CO(NH_3)_6]_2 (SO_4)_3$
- (f) $K_2[Ni(CN)_4]$
- (g) K_3 [Cr(OX)₃]
- (h) [CO(NH₃)₅ONO]₂₊
- (i) $[Pt(NH_3)_2Cl_2]$
- (j) $[CO(NH_3)_5NO_2]^{2+}$.
- 17. Using IUPAC norms write the systematic names of the following:
- (i) [Co(NH₃)₆]CI₃,
- (ii)[Pt(NH₃)₂CI (NH₂CH₃)] Cl
- (iii) $[Ti(H_20)_6]3+$
- (iv) [Co(NH3)₄Cl(N02)]CI
- $(v)|Mn(H_20)_6|^{2+}$
- (vi)[NiCl₄]²⁻
- (vii)[Ni(NH₃)₆]CI₂
- $(viii)[Co(en)_3]^{3+}$
- (ix) $[Ni(CO)_4]$
- Ans: (i) Hexaammine cobalt (III) chloride.
- (ii) Diammine chlorido (methylamine) platinum (II) chloride.
- (iii) Hexaaquatitanium (III) ion.
- (iv) Tetraammine chlorido nitrito-N-cobalt (IV) chloride.
- (v)Hexaaquamanganese (II) ion.
- (vi)Tetrachloridonickelate (II) ion.
- (vii)Hexaammine nickel (II) chloride.
- (viii)Tris (ethane -1,2-diamine) cobalt (III) ion.
- (ix) Tetra carbonyl nickel (0)

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18. List various types of isomerism possible for coordination compounds, giving an example of each.

Ans: Coordination compounds exhibit stereo isomerism and structural isomerism. Two types of stereoisomerism and their examples are as follows.

(i) Geometrical isomerism

(ii) Optical isomerism.

Four types of structural isomerism are as follows:

- (i) Linkage isomerism [Co (NH₃)₅NO₂] Cl₂ and [Co (NH₃)₅ ONO] Cl₂
- (ii) Coordination isomerism [Co (NH₃)₆] [Cr (CN)₆] and [Cr (NH₃)₆] [Co (CN)₆]
- (iii) Ionisation isomerism [Co (NH₃)₅ SO₄] Br and [Co (NH₃)₅ Br] SO₄
- (iv) Solvate or hydrate isomerism [Cr (H2O)6] Cl2 and [Cr (H2O)5 Cl] Cl. H2O

19. How many geometrical isomers are possible in . the following coordination entities? (i) $[Cr(C_2O_4)_3]^3$ (ii) $[CoCl_3(NH_3)_3]$

Ans: (i) $[Cr(C_2O_4)_3]^{3-}$ => No geometrical isomers are possible in this coordination entity.

(ii) [Co(NH₃)₃ Cl₃] => Two geometrical isomers are possible (fac and mer) in this coordination entity.

20. Draw the structures of optical isomers of

- (i) $[Cr(C_2O_4)_3]^{3-}$
- (ii)[PtCl₂(en)₂]₂₊
- (iii)[Cr(NH₃)₂Cl₂(en)]⁺

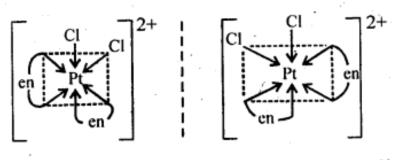
Ans:

(i)
$$[Cr(C_2O_4)_3]^{3-} \Rightarrow [Cr(ox)_3]^{3-}$$

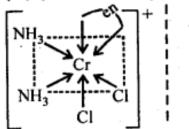
$$\begin{bmatrix} ox & \\ cr & \\ ox & \\ (dextro) \end{bmatrix}^{-3} \qquad \begin{bmatrix} ox & \\ Cr & \\ ox & \\ (laevo) \end{bmatrix}$$

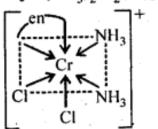
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(ii) (cis-isomer only) Cis - [PtCl2(en)2]2+



(iii) (cis-isomer only) Cis - [Cr(NH₃)₂Cl₂(en)]⁺

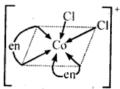


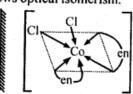


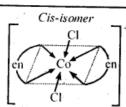
21. Draw all the isomers (geometrical and optical) of

- $(i)[CoCl_2(en)_2]$ +
- (ii)[Co(NH $_3$) CI (en) $_2$] $^{2+}$
- (iii) $[Co(NH_3)_2Cl_2(en)]$ +

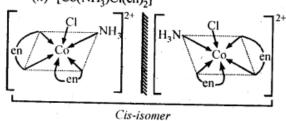
(i) [CoCl₂(en)₂]⁺ has 2 geometrical isomers. Further cis-form shows optical isomerism.

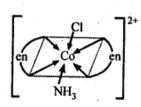




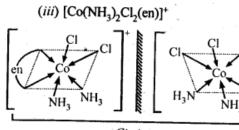


(ii) [Co(NH₃)Cl(en)₂]²⁺

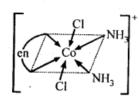




Trans-isomer



Cis-isomer



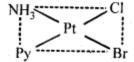
Trans-isomer

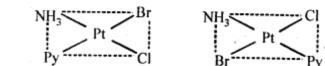
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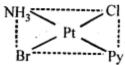
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22. Write all the geometrical isomers of [Pt(NH₃)(Br)(Cl) (Py)] and how many of these will exhibit optical isomerism?

Ans: Three isomers of [Pt(NH3)(Br)(Cl)(Py)] are possible.

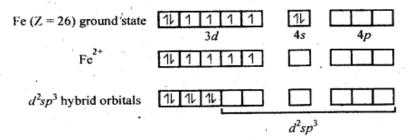






These are obtained by keeping the position of one of the ligand, say NH3 fixed and rotating the positions of others. This type of isomers do not show any optical isomerism. Optical isomerism only rarely occurs in square planar or tetrahedral complexes and that too when they contain unsymmetrical chelating ligand.

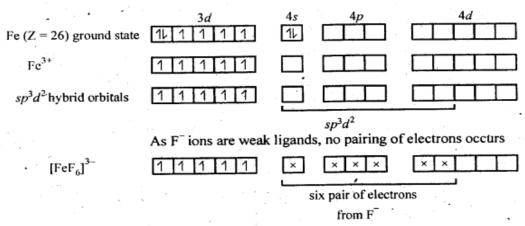
- 23. Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
- (i) $[Fe(CN)_6]^{4-}$
- (ii) [FeF₆]³⁻
- (iii) $[Co(C_2O_4)_3]^{3-}$
- (iv) $[CoF_6]^{3-}$
- (i) $[Fe(CN)_6]^{4-}$ is d^2sp^3 hybridised, octahedral in shape and diamagnetic in nature.



Pairing of electrons takes place because of strong CN ligand

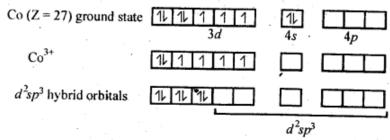
 $[Fe(CN)_6]^4$ $1 | 1 | 1 | 1 | \times \times$ six pair of electrons from CN

(ii) $[FeF_a]^{3-}$ is sp^3d^2 hybridised, octahedral in shape and paramagnetic in nature.

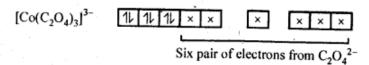


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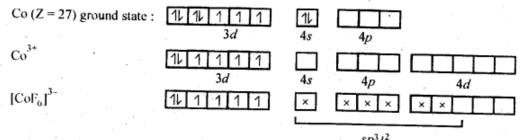
(iii) $[Co(C_2O_4)_3]^{3-}$ is d^2sp^3 hybridised, octahedral in shape and diamagnetic in nature.



Paring of electrons occurs due to strong C₂O₄²⁻ ligands

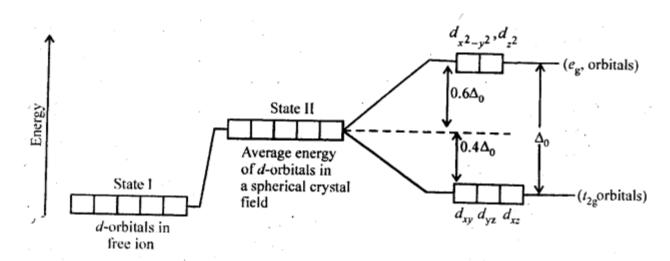


(iv) $[CoF_6]^{3-}$ is sp^3d^2 hybridised, octahedral in shape and paramagnetic in nature.



As F ions are weak ligands, pairing of electrons does not take place.

24. Draw figure to show the splitting of d-orbitals in an octahedral crystal field. Ans:



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25. A solution of $[Ni(H_20)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain. Ans: In $[Ni(H_20)_6]^{2+}$, Ni is in + 2 oxidation state and having 3ds electronic configuration, in which there are two unpaired electrons which do not pair in the presence of the weak H_20 ligand. Hence, it is coloured. The d-d transition absorbs red light and the complementary light emitted is green.

In [Ni(CN)₄]² Ni is also in + 2 oxidation state and having 3d⁸ electronic configuration. But in presence of strong ligand CN⁻ the two unpaired electrons in the 3d orbitals pair up. Thus, there is no unpaired electron present. Hence, it is colourless.

26. [Fe (CN)₆]⁴⁻ and [Fe (H₂O)₆]²⁺ are of different colours in dilute solutions. Why? Ans: In both the complexes, Fe is in + 2 oxidation state with d6 configuration. This means that it has four unpaired electrons. Both CN⁻ ion and H₂O molecules which act as ligands occupy different relative positions in the spectrochemical series. They differ in crystal field splitting energy (Δ_0). Quite obviously, they absorb radiations corresponding to different wavelengths/frequencies from the visible region of light. (VIBGYOR) and the transmitted colours are also different. This means that the complexes have different colours in solutions.

27. What is crystal field splitting energy? How does the magnitude of Δ_0 decide the actual configuration of d-orbitals in a coordination entity?

Ans: When the ligands approach a transition metal ion, the d-orbitals split into two sets, one with lower energy and the other with higher energy. The difference of energy between the two sets of orbitals is called crystal field splitting energy (Δ_0 for octahedral field). If Δ_0 < P (pairing energy), the fourth electron enters

one of the e°g, orbitals giving the configuration $t^3{}_{2g}e^1{}_g$, thus forming high spin complexes. Such ligands for which Δ_0 < P are called weak field ligands. If Δ_0 > P, the fourth electron pairs up in one of the t_{2g} orbitals giving the configuration $t^4{}_{2g}e^1{}_g$ thereby forming low spin complexes. Such ligands for which Δ_0 > P are called strong field ligands.

28. What is meant by the chelate effect? Give an example.

Ans: When a didentate or a polydentate ligand contains donor atoms positioned in such a way that when they coordinate with the central metal ion, a five or a six membered ring is formed, the effect is called chelate effect. For example,

$$\begin{array}{c|c} Cl & & H_2 \\ \hline \\ Cl & & N \\ \hline \\ Cl & & CH_2 \\ \hline \\ N & & CH_2 \\ \hline \\ N & & CH_2 \\ \end{array}$$
 or [PtCl₂(en)]

(Where Toppers make...... Toppers)

29. [Cr(NH ₃) ₆] ³⁺ is paramagnetic while [Ni(CN) ₄] ²⁻ is diamagnetic. Explain why? Ans:
The presence of three unpaired electrons in $[\tilde{Cr}(NH_3)_6]^{3+}$ explains its paramagnetic character.
Cr (Z = 24) in ground state $3d$ $4s$ $4p$
Cr ³⁺
As NH ₃ is a weak ligand does not lead to pairing of electrons
$[Cr(NH_3)_6]^{3+}$ $\uparrow \uparrow \uparrow \uparrow \times $
d^2sp^3 hybridisation
[Ni(CN) ₄] ²⁻ is diamagnetic, since there is no unpaired electrons.
Ni (Z = 28) in ground state $1 \downarrow 1 $
$[Ni(CN)_4]^{2-}$ $1 1 1 1 \times $
30. Amongst the following ions? Which one has the highest magnetic moment value: (i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Fe(H_2O)_6]^{2+}$ Ans: The oxidation states are: Cr (III), Fe (II) and Zn (II). Electronic configuration of $Cr^{3+} = 3d^3$, unpaired electron = 3 Electronic configuration of $Fe^{2+} = 3d^6$, unpaired electron = 4 Electronic configuration of $Zn^{2+} = 3d^{10}$, unpaired electrons = 0 μ = $n(n+2)$ $$ where n is number of unpaiared electrons Hence, (ii) has highest value of magnetic moment.