Chapter **Co-ordination Compounds**



Topic-1: Important Terms, Coordination Number, Nomenclature and Isomerism of Coordination Compounds

MCQs with One Correct Answer

- Among the following options, select the option in which each complex in Set-I shows geometrical isomerism and the two complexes in Set-II are ionization isomers of each other. [en = H₂NCH₂CH₂NH₂] [Adv. 2024]
 - (a) Set-I: [Ni(CO)₄] and [PdCl₂(PPh₃)₂] Set-II: [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅(SO₄)]Cl
 - (b) Set-I: [Co(en)(NH₂)₂Cl₂] and [PdCl₂(PPh₂)₂] Set-II: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
 - (c) Set-I: $[Co(NH_3)_3(NO_2)_3]$ and $[Co(en)_3Cl_2]$ Set-II: [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅(SO₄)]Cl
 - (d) Set-I: [Cr(NH₂)₅Cl]Cl, and [Co(en)(NH₃)₂Cl₂] Set-II: [Cr(H2O)6]Cl3 and [Cr(H2O)5Cl]Cl2. H2O
- As per IUPAC nomenclature, the name of the complex $[Co(H_2O)_4(NH_3)_2]Cl_3$ is:
- (a) Tetraaquadiaminecobalt (III) chloride
 - (b) Tetraaquadiamminecobalt (III) chloride
- (c) Diaminetetraaquacoblat (II) chloride
- (d) Diamminetetraaquacobalt (III) chloride
- The correct structure of ethylenediaminetetraacetic acid (EDTA) is

- The ionisation isomer of [Cr(H₂O)₄Cl(NO₂)]Cl is [2010]
 - (a) $[Cr(H_2O)_4(O_2N)]Cl_2$
 - (b) $[Cr(H_2O)_4Cl_2](NO_2)$
 - (c) [Cr(H₂O)₄Cl(ONO)]Cl
 - (d) [Cr(H₂O)₄Cl₂(NO₂)].H₂O
- The IUPAC name of [Ni (NH₃)₄] [NiCl₄] is
 - Tetrachloronickel (II) tetraamminenickel (II)
 - Tetraamminenickel (II) tetrachloronickel (II)
 - (c) Tetraamminenickel (II) tetrachloronickelate (II)
 - (d) Tetrachloronickel (II) tetrachloronickelate (0) Ans. (C)
- Which kind of isomerism is exhibited by octahedral Co(NH₂)₄Br₂Cl? [2005S]
 - (a) Geometrical and Ionization
 - (b) Geometrical and Optical
 - (c) Optical and Ionization
 - (d) Geometrical only
- The complex ion which has no 'd' electron in the central metal atom is
 - (a) [MnO₄]
- (b) [Co(NH₂)₆]³⁺
- (c) [Fe(CN)₆]³⁻
- (d) $[Cr(H_2O)_6]^{3+}$
- Which of the following is an organometallic compound? [1997 - 1 Mark]
 - (a) Lithium methoxide (b) Lithium acetate
- - Lithium dimethylamide (d) Methyl lithium

Integer Value Answer

- Among V(CO)₆, Cr(CO)₅, Cu(CO)₃, Mn(CO)₅, Fe(CO)₅, [Co(CO)₃]³⁻, [Cr(CO)₄]⁴⁻, and Ir(CO)₃, the total number of species isoelectronic with Ni(CO), is [Given, atomic number: V = 23, Cr = 24, Mn = 25, Fe = 26, Co = 27, Ni = 28, Cu = 29, Ir = 77[Adv. 2024]
- The total number of possible isomers for [Pt(NH,),Cl,]Br, [Adv. 2021]
- 11. Total number of cis N Mn Cl bond angles (that is Mn - N and Mn - Cl bonds in cis positions) present in a molecule of cis -[Mn(en),Cl,] complex is (en = NH, CH, CH, NH,) [Adv. 2019]

- 12. The number of geometric isomers possible for the complex $[CoL_2Cl_2]^-(L=H_2NCH_2CH_2O^-)$ is [Adv. 2016]
- 13. Among the complex ions,

 [Co(NH₂-CH₂-CH₂-NH₂)₂Cl₂]⁺, [CrCl₂(C₂O₄)₂]³⁻,

 [Fe(H₂O)₄(OH)₂]⁺, [Fe(NH₃)₂(CN)₄]⁻, [Co(NH₂-CH₂-CH₂-NH₂)₂(NH₃)Cl]²⁺ and [Co(NH₃)₄(H₂O)Cl]²⁺, the number of complex ion(s) that show(s) *cis-trans* isomerism is

 [Adv. 2015]
- 14. In the complex acetylbromidodicarbonylbis (triethylphosphine) iron (II), the number of Fe-C bond(s) is [Adv. 2015]
- 15. EDTA⁴ is ethylenediaminetetraacetate ion. The total number of N—Co—O bond angles in [Co(EDTA)]¹-complex ion is [Adv. 2013]
- The volume (in mL) of 0.1 M AgNO₃ required for complete precipitation of chloride ions present in 30 mL of 0.01 M solution of [Cr(H₂O)₅Cl]Cl₂, as silver chloride is close to
- 17. Total number of geometrical isomers for the complex [RhCl(CO) (PPh₃) (NH₃)] is [2010]
- The number of water molecule(s) directly bonded to the metal centre in CuSO₄.5H₂O is [2009 - 4 Marks]

4 Fill in the Blanks

[1994 - 1 Mark]

(§) 6 MCQs with One or More than One Correct Answer

- 20. The complex(es), which can exhibit the type of isomerism shown by $[Pt(NH_3)_2Br_2]$, is(are) $[en = H_2NCH_2CH_2NH_2]$ [Adv. 2023]
 - (a) [Pt(en)(SCN)₂]
- (b) [Zn(NH₃)₂Cl₂]
- (c) [Pt(NH₃)₂Cl₄] (d) [Cr(en)₂(H₂O)(SO₄)]⁺
 21. The pair(s) of coordination complexes/ions exhibiting the same kind of isomerism is(are) [Adv. 2013]
 - (a) [Cr(NH₃)₅Cl]Cl₂ and [Cr(NH₃)₄Cl₂]Cl
 - (b) $[Co(NH_3)_4Cl_2]^+$ and $[Pt(NH_3)_2(H_2O)Cl]^+$

- (c) $[CoBr_2Cl_2]^{2-}$ and $[PtBr_2Cl_2]^{2-}$
- (d) [Pt(NH₃)₃(NO₃)]Cl and [Pt(NH₃)₃Cl]Br
- 22. The compound(s) that exhibit(s) geometrical isomerism is (are) [2009]
 - (a) [Pt(en)Cl₂]
- (b) [Pt(en)₂]Cl₂
- (c) [Pt(en)₂Cl₂]Cl₂
- (d) $[Pt(NH_3)_2Cl_2]$

Assertion and Reason Statement Type Questions

Each question contains **STATEMENT-1** (Assertion) and **STATEMENT-2** (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is incorrect.
- (d) If Statement -1 is incorrect but Statement -2 is correct.
- 23. Statement-1: The geometrical isomers of the complex [M(NH₃)₄Cl₂] are optically inactive.
 Statement-2: Both geometrical isomers of the complex [M(NH₃)₄Cl₂] possess axis of symmetry. [2008 2 Marks]

10 Subjective Problems

- 24. A, B, and C are three complexes of chromium (III) with the empirical formula H₁₂O₆Cl₃Cr. All the three complexes have water and chloride ion as ligands. Complex A does not react with concentrated H₂SO₄, whereas complexes B and C lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H₂SO₄. Identify A, B and C. [1999 6 Marks]
- 25. Write the formulae of the following complexes:
 - (i) Pentaamminechlorocobalt(III) [1997 1 Mark]
 - (ii) Lithium tetrahydroaluminate(III). [1997 1 Mark]
- 26. Write down the IUPAC names of the following compounds:
 - (i) $[Cr(NH_3)_5CO_3]Cl$ [1996 1 Mark]
 - (ii) $K_3[Cr(CN)_6]$ [1995 1 Mark]
 - (iii) [Co(NH₃)₅ONO]Cl₂ [1995 1 Mark]



Topic-2: Bonding, Stability and Application of Coordination Compounds

MCQs with One Correct Answer

- 1. The reaction of Pb(NO₃)₂ and NaCl in water produces a precipitate that dissolves upon the addition of HCl of appropriate concentration. The dissolution of the precipitate is due to the formation of [Adv. 2022]
 - (a) PbCl,
- (b) PbCl₄
- (c) [PbCl,]2-
- (d) [PbCl₆]²-
- 2. The calculated spin only magnetic moments of [Cr(NH₃)₆]³⁺ and [CuF₆]³⁻ in BM, respectively, are (Atomic numbers of Cr and Cu are 24 and 29, respectively) [Adv. 2021]
 - (a) 3.87 and 2.84
- (b) 4.90 and 1.73

- (c) 3.87 and 1.73
- (d) 4.90 and 2.84
- 3. The geometries of the ammonia complexes of Ni²⁺, Pt²⁺ and Zn²⁺ respectively, are [Adv. 2016]
 - (a) octahedral, square planar and tetrahedral
 - (b) square planar, octahedral and tetrahedral
 - (c) tetrahedral, square planar and octahedral
 - (d) octahedral, tetrahedral and square planar
- 4. Consider the following complex ions, P, Q and R.
 - $P = [\text{FeF}_6]^{3-}, Q = [\text{V}(\text{H}_2\text{O}_6]^{2+} \text{ and } R = [\text{Fe}(\text{H}_2\text{O})_6]^{2+}]^{2+}$

The correct order of the complex ions, according to their spin-only magnetic moment values (in B.M.) is [Adv. 2013]

(a) R < Q < P

	(c) $R < P < Q$ (d) $Q < P < R$	
5.	$NiCl_2 \{P(C_2H_5)_2(C_6H_5)\}_2$ exhibits temperature dependent	
	magnetic behaviour (paramagnetic/diamagnetic). The	
	coordination geometries of Ni ²⁺ in the paramagnetic and	
	diamagnetic states are respectively [2012]	
	(a) tetrahedral and tetrahedral	
	(b) square planar and square planar	
	(c) tetrahedral and square planar	
	(d) square planar and tetrahedral	
6.	Among the following complexes (K–P)	
	$K_3[Fe(CN)_6](K), [Co(NH_3)_6]Cl_3(L), Na_3[Co(oxalate)_3](M),$	
	the $[Ni(H_2O)_6]Cl_2$ (N), $K_2[Pt(CN)_4]$ (O) and	
	$[Zn(H_2O)_6](NO_3)_2(\mathbf{P})$ the diamagnetic complexes are [2011]	17.
	(a) K, L, M, N (b) K, M, O, P	
	(c) L, M, O, P (d) L, M, N, O	
7.	Geometrical shapes of the complexes formed by the reaction	
/•		
	(a) octahedral, tetrahedral and square planar	(:0
	(b) tetrahedral, square planar and octahedral	(2)
	(c) square planar, tetrahedral and octahedral	18.
	(d) octahedral, square planar and octahedral	
8.	The complex showing a spin-only magnetic moment of	
	2.82 B.M. is: [2010]	
	(a) [Ni(CO) ₄] (b) [NiCl ₄] ²⁻	19
	(c) $[Ni(PPh_3)_4]$ (d) $[Ni(CN)_4]^{2-}$	
9.	The spin only magnetic moment value (in Bohr magneton	
۶.	units) of Cr(CO) ₆ is [2009]	
	/ 10	
10		
10.	Both [Ni (CO) ₄] and [Ni (CN) ₄] ²⁻ are diamagnetic. The	20
	hybridisations of nickel in these complexes, respectively,	
	are [2008]	
	(a) sp^3, sp^3 (b) sp^3, dsp^2	
	(c) dsp^2 , sp^3 (d) dsp^2 , sp^2	
11.	Among the following metal carbonyls, the C-O bond or-	21
	der is lowest in [2007]	-1
	(a) $[Mn(CO)_6]^+$ (b) $[Fe(CO)_5]$	
	(c) [Cr(CO) ₆] (d) [V(CO) ₆]	
12.	$Ag^{+} + NH_{3} \rightleftharpoons [Ag(NH_{3})]^{+}; k_{1} = 6.8 \times 10^{-3}$	
		(:(
	$[Ag(NH_3)]^+ + NH_3 \Longrightarrow [Ag(NH_3)_2]^+; k_2 = 1.6 \times 10^{-3}$	
	then the formation constant of $[Ag(NH_3)_2]^+$ is $[2006-3M,-1]$	22
	(a) 6.8×10^{-6} (b) 1.08×10^{-5}	
	(c) 1.08×10^{-6} (d) 6.8×10^{-5}	60
13.		
13.		23
	(a) $\sqrt{3}$ (b) $\sqrt{8}$ (c) $\sqrt{15}$ (d) $\sqrt{24}$	6
14.		(1)
- "	(a) [PdCl ₄] ²⁻ (b) [Ni(CN) ₄] ²⁻	24
	(a) $[PdCl_4]^{2-}$ (b) $[Ni(CN)_4]^{2-}$ (c) $[Pd(CN)_4]^{2-}$ (d) $[NiCl_4]^{2-}$	The state of
1-	(c) [ru(CN) ₄] (d) [NiCl ₄]	
15.	The geometry of Ni(CO) ₄ and Ni(PPh ₃) ₂ Cl ₂ are	
	(a) both square planar [1999 - 2 Marks]	
	(b) tetrahedral and square planar, respectively	
	(c) both tetrahedral	
	(d) square planar and tetrahedral, respectively	

(b) Q < R < P

B49 16. Amongst [Ni(CO)₄], [Ni(CN)₄]²-and [NiCl₄²] [1991-1 Mark] (a) [Ni(CO)₄] and [NiCl₄²] are diamagnetic and [Ni(CN)₄]²⁻ is paramagnetic (b) [NiCl₄²⁻] and [Ni(CN)₄]²⁻ are diamagnetic and [Ni(CO)₄] is paramagnetic (c) [Ni(CO)₄] and [Ni(CN)₄]²⁻ are diamagnetic and [NiCl₄²⁻]is paramagnetic (d) [Ni(CO)₄] is diamagnetic and [NiCl₄²⁻] and [Ni(CN),]2- are paramagnetic Amongst the following, the lowest degree of paramagnetism per mole of the compound at 298 K will be shown by [1988 - 1 Mark] (a) MnSO₄.4H₂O (b) CuSO₄.5H₂O (c) FeSO₄.6H₂O (d) NiSO, 6H,O Integer Value Answer Among [Co(CN)₄]⁴, [Co(CO)₃(NO)], XeF₄, [PCl₄]⁺, $[PdCl_4]^{2-}$, $[ICl_4]^{-}$, $[Cu(CN)_4]^{3-}$ and P_4 the total number of species with tetrahedral geometry is [Adv. 2024] Among the following complexes, the total number of [Adv. 2024] diamagnetic species is $[Mn(NH_3)_6]^{3+}, [MnCl_6]^{3-}, [FeF_6]^{3-}, [CoF_6]^{3-}, [Fe(NH_3)_6]^{3+},$ and $[Co(en)_3]^{3+}$ [Given, atomic number: Mn = 25, Fe = 26, Co = 27; $en = H_2NCH_2CH_2NH_2$ Among the species given below, the total number of diamagnetic species is Hatom, NO, monomer, O, (superoxide), dimeric sulphur in vapour phase, Mn₃O₄, (NH₄)₂[FeCl₄],(NH₄)₂[NiCl₄], [Adv. 2018] K2MnO4, K2CrO4 For the octahedral complexes of Fe3+ in SCN- (thiocyanato-S) and in CN-ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is [Adv. 2015] [Atomic number of Fe = 26] Fill in the Blanks The type of magnetism exhibited by $[Mn(H_2O)_6]^{2+}$ ion is [1994 - 1 Mark] True / False

Both potassium ferrocyanide and potassium ferricyanide

Given: Atomic numbers of Fe, Co, Ni and Cu are 26, 27, 28

6 MCQs with One or More than One Correct Answer
The pair(s) of complexes wherein both exhibit tetrahedral

are diamagnetic.

geometry is(are) (Note: py = pyridine

and 29, respectively)

[1989 - 1 Mark]

[Adv. 2021]

- (a) $[FeCl_4]$ and $[Fe(CO)_4]^{2-}$
- (b) [Co(CO)₄] and [CoCl₄]²
- (c) [Ni(CO)₄] and [Ni(CN)₄]²-
- (d) [Cu(py)₄]⁺ and [Cu(CN)₄]³⁻
- 25. Choose the correct statement(s) among the following:
 - (a) [FeCl₄] has tetrahedral geometry. [Adv. 2020]
 - (b) [Co(en)(NH₃)₂Cl₂]⁺ has 2 geometrical isomers.
 - (c) [FeCl₄] has higher spin-only magnetic moment than $[Co(en)(NH_3),Cl_3]^+$.
 - (d) The cobalt ion in [Co(en)(NH₃)₂Cl₂]⁺ has sp³d² hybridization.
- 26. The correct option(s) regarding the complex $[Co(en)(NH_3)_3(H_2O)]^{3+}$ (en = $H_2NCH_2CH_2NH_3$) is (are)
 - (a) It has two geometrical isomers
 - (b) It will have three geometrical isomers if bidentate 'en' is replaced by two cyanide ligands
 - (c) It is paramagnetic
 - (d) It absorbs light at longer wavelength as compared to [Co(en)(NH₃)₄]³⁺
- 27. The correct statement(s) regarding the binary transition metal carbonyl compounds is (are) (Atomic numbers: Fe = 26, Ni = 28)[Adv. 2018]
 - (a) Total number of valence shell electrons at metal centre in Fe(CO), or Ni(CO), is 16
 - (b) These are predominantly low spin in nature
 - Metal-carbon bond strengthens when the oxidation state of the metal is lowered
 - The carbonyl C-O bond weakens when the oxidation state of the metal is increased
- Addition of excess aqueous ammonia to a pink coloured aqueous solution of MCl₂.6H₂O(X) and NH₄Cl gives an octahedral complex Y in the presence of air. In aqueous solution, complex Y behaves as 1:3 electrolyte. The reaction of X with excess HCl at room temperature results in the formation of a blue coloured complex Z. The calculated spin only magnetic moment of X and Z is 3.87 B.M., whereas it is zero for complex Y. Among the following options, which statement(s) is (are) correct? [Adv. 2017]
 - Addition of silver nitrate to Y gives only two equivalents of silver chloride
 - (b) The hybridization of the central metal ion in Y is d^2sp^3
 - Z is a tetrahedral complex (c)
 - When X and Z are in equilibrium at 0°C, the colour of the solution is pink
- 29. If the bond length of CO bond in carbon monoxide is 1.128Å, then what is the value of CO bond length in Fe(CO)₅? [2006 - 5M, -1]
- (a) 1.15Å (b) 1.128Å (c) 1.13Å (d) 1.118Å In nitroprusside ion the iron and NO exist as Fe^{II} and NO+ rather than Fe^{III} and NO. These forms can be differentiated by [1998 - 2 Marks]
 - (a) estimating the concentration of iron
 - (b) measuring the concentration of CN
 - measuring the solid state magnetic moment
 - (d) thermally decomposing the compound.

- Among the following ions which one has the highest paramagnetism? [1993 - 1 Mark]
 - (a) [Cr(H₂O)₆]³⁺
- (b) [Fe(H₂O)₆]²⁺
- (c) [Cu(H,O)₆]²⁺
- (d) [Zn(H,O),]2+
- Match the Following
- Match the electronic configurations in List-I with appropriate metal complex ions in List-II and choose the correct option. [Adv. 2023]

[Atomic number: Fe = 26, Mn = 25, Co = 27]

List-I List-II

- (1) [Fe(H₂O)₆]²⁺
- [Mn(H,O),]2
- [Co(NH₂)₆]³

[CoCl.]2-

- [FeCl,]
- (5) (a) $P \rightarrow 1$; $Q \rightarrow 4$; $R \rightarrow 2$; $S \rightarrow 3$
- (b) $P \rightarrow 1$; $Q \rightarrow 2$; $R \rightarrow 4$; $S \rightarrow 5$
- (c) $P \rightarrow 3$; $Q \rightarrow 2$; $R \rightarrow 5$; $S \rightarrow 1$
- (d) $P \rightarrow 3$; $Q \rightarrow 2$; $R \rightarrow 4$; $S \rightarrow 1$
- 33. List-I contains metal species and List-II contains their properties. [Adv. 2022]

List-I List-II

(I) [Cr(CN)₆]4-

- (P) t_{2a} orbitals contain 4 electrons
- (II) [RuCl_]2-
- (Q) $\mu(\text{spin-only}) = 4.9 \text{ BM}$
- (III) [Cr(H₂O)₆]²⁺
- (R) low spin complex ion
- (IV) [Fe(H,O)₆]²⁺
- (S) metal ion in 4+ oxidation state
- (T) d⁴ species

[Given: Atomic number of Cr = 24, Ru = 44, Fe = 26]

Match each metal species in LIST-I with their properties in LIST-II, and choose the correct option

- (a) $I \rightarrow R$, T; $II \rightarrow P$, S; $III \rightarrow Q$, T; $IV \rightarrow P$, Q
- (b) $I \rightarrow R$, S; $II \rightarrow P$, T; $III \rightarrow P$, O; $IV \rightarrow O$, T
- (c) $I \rightarrow P, R; II \rightarrow R, S; III \rightarrow R, T; IV \rightarrow P, T$
- (d) $I \rightarrow Q$, T; $II \rightarrow S$, T; $III \rightarrow P$, T; $IV \rightarrow Q$, R
- 34. Match each set of hybrid orbitals from List-I with complex(es) given in List-II [Adv. 2018]

List-I

List-II

- (A) dsp^2 (B) sp^3
- (p) [FeF₆]4-
- (C) sp^3d^2
- (q) [Ti(H,O),Cl₃] (r) $[Cr(NH_2)_6]^{3+}$
- (D) d^2sp^2
- [FeCl,]2
- [Ni(CO),]
- [Ni(CN)4]2

The correct option is

- (a) A-t; B-s, w; C-q, r; D-p
- (b) A-t, w; B-s; C-q; D-p, q
- (c) A-w; B-s, t; C-p; D-q, r
- (d) A-s, w; B-t, w; C-p, q; D-r

35. Match each coordination compound in List-I with an appropriate pair of characteristics from List-II and select the correct answer using the code given below the lists.

[40] {en = H₂NCH₂CH₂NH₂; atomic numbers : Ti = 22; Cr = 24; Co = 27; Pt = 78} [Adv. 2014]

List-I

List-II

- (A) [Cr(NH₃)₄Cl₂]Cl
- (p) Paramagnetic and exhibits ionisation isomerism
- (B) [Ti(H₂O)₅Cl](NO₃)₂
- (q) Diamagnetic and exhibits cis-trans isomerism
- (C) [Pt(en)(NH₃)Cl]NO₃
- (r) Paramagnetic and exhibits *cis-trans* isomerism
- (D) [Co(NH₃)₄(NO₃)₂]NO₃ (s) Diamagnetic and exhibits ionisation isomerism

Code:

Cou	~ .			
	A	В	C	D
(a)	(s)	(q)	(r)	(p)
(b)	(r)	(p)	(s)	(q)
(c)	(q)	(p)	(r)	(s)
(d)	(p)	(r)	(s)	(a)

36. Match the complexes in Column-I with their properties listed in Column-II. [2007]

Column-I

Column-II

- (A) [Co(NH₃)₄(H₂O)₂] Cl₂
- p) geometrical isomers
- (B) [Pt(NH₃)₂Cl₂] (C) [Co(H₂O)₂Cl]C
- (q) paramagnetic(r) diamagnetic
- (C) [Co(H₂O)₅Cl]Cl (D) [Ni(H₂O)₆]Cl₂
- (s) metal ion with +2 oxidation state

8 Comprehension/Passage Based Questions

The coordination number of Ni²⁺ is 4.

 $NiCl_2 + KCN(excess) \longrightarrow A (cyano complex)$

 $NiCl_2 + Conc. HCl(excess) \longrightarrow B$ (chloro complex)

- 37. The IUPAC name of A and B are [2006 5M, -2]
 - (a) Potassium tetracyanonickelate (II), potassium tetrachloronickelate (II)
 - (b) Tetracyanopotassiumnickelate (II), tetrachloropotassiumnickelate (II)
 - (c) Tetracyanonickel (II), tetrachloronickel (II)
 - (d) Potassium tetracyanonickel (II), potassium tetrachloronickel (II)
- 38. Predict the magnetic nature of A and B [2006 5M, -2]
 - (a) Both are diamagnetic
 - (b) A is diamagnetic and B is paramagnetic with one unpaired electron
 - (c) A is diamagnetic and B is paramagnetic with two unpaired electrons
 - (d) Both are paramagnetic
- 39. The hybridization of A and B are [2006 5M, -2]
 - (a) dsp^2 , sp^3
- (b) sp^3 , sp^3
- (c) dsp^2 , dsp^2
- (d) sp^3d^2 , d^2sp^3

9 Assertion and Reason Statement Type Questions

Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement -2.
- (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement -1.
- (c) If Statement -1 is correct but Statement -2 is incorrect.
- (d) If Statement -1 is incorrect but Statement -2 is correct.
- Statement-1: [Fe(H₂O)₅NO]SO₄ is paramagnetic.
 Statement-2: The Fe in [Fe(H₂O)₅NO]SO₄ has three unpaired electrons. [2008]

10 Subjective Problems

41. $Fe^{3+} \xrightarrow{SCN^{-}} (A) \xrightarrow{Blood red} \xrightarrow{excess} (B)$

What are (A) and (B)? Give IUPAC name of (A). Find the spin only magnetic moment of (B). [2005 - 4 Marks]

- 42. Nickel chloride, when treated with dimethylgyloxime in presence of ammonium hydroxide, a bright red precipitate is obtained. Answer the following. [2004 4 Marks]
 - (a) Draw the structure of the complex showing H-bonds
 - (b) Give oxidation state of nickel and its hybridisation
 - (c) Predict the magnetic behaviour of the complex
- Write the IUPAC nomenclature of the given complex along with its hybridisation and structure.

 $K_2[Cr(NO)(NH_3)(CN)_4], \mu = 1.73 \text{ BM } [2003-4 \text{Marks}]$

44. Deduce the structure of [NiCl₄]²⁻ and [Ni(CN)₄]²⁻ considering the hybridization of the metal ion. Calculate the magnetic moment (spin only) of the species. [2002 - 5 Marks]

- 45. A metal complex having composition Cr(NH₃)₄Cl₂Br has been isolated in two forms (A) and (B). The form (A) reacts with AgNO₃ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridization of chromium in each. Calculate their magnetic moments (spinonly value). [2001 5 Marks]
- **46.** Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case. [2000 4 Marks]
- 47. A compound of vanadium has a magnetic moment of 1.73 BM. Work out the electronic configuration of the vanadium ion in the compound. [1997 2 Marks]
- 48. Identify the complexes which are expected to be coloured. Explain [1994 2 Marks]
 - (i) $[Ti(NO_3)_4]$
- (ii) [Cu(NCCH₃)₄]⁺BF₄⁻
- (iii) [Cr(NH₃)₆]³⁺3Cl⁻
- (iv) K₃[VF₆]

? AnswerKey

inc. Draw the structures of County (a) ". Income had and

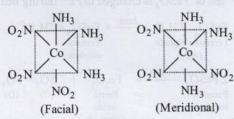
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1,	(c)	2.	(d)	3.	(c)	4.	(b)	5.	(c)	6.	(a)	7.	(a)	8.	(d)	9.	(3)	10.	(6)
11.	(6)	12.	(5)	13,	(6)	14.	(3)	15.	(8)	16.	(6)		(3)	18.			(5)	10.	(0)
19.	(Hexa	mine	cobalt (I	II) chl	oride)	20.	(c, d)	21.	(b, d)			23.			.,,				
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1.	(c)	2.	(a)		(a)	4.	(b)		(c)	A	(c)			8.		av. B		10.	(b)
11.	(c) (d)				(a)			5.	N STATE OF	6.		7.	(b)	8.	(b)	9.	(a)	10.	
11.	- Contractor	2.	(a)	3. 13.	(a) (c)	4.	(b) (d)	5. 15.	(c) (c)	6. 16,	(c)	7. 17.	(b) (b)	8. 18.	(b) (5)	9. 19.	(a) (1)	20.	(1)
1. 11. 21. 29.	(d)	2. 12.	(a) (b)	3. 13.	(a) (c) ism)	4. 14.	(b)	5. 15.	(c)	6. 16,	(c) (c)	7. 17.	(b) (b) (a, c)	8.	(b) (5)	9. 19.	(a)	20.	(1)

Hints & Solutions

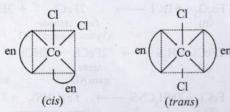
Topic-1: Important Terms, Coordination Number, Nomenclature and Isomerism of Coordination Compounds

(c) Complexes of type [Ma₃b₃]^{h+} form facial and meridional isomers.

Set-I:



Complexes of type $[MX_2(L-L)_2]^{\pm}$ give cis and trans isomers



Set-II: [Co(NH₃)₅Cl]SO₄ and [Co(NH₃)₅SO₄]Cl are ionisation isomers.

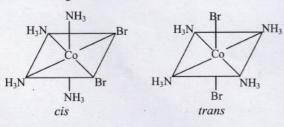
- 2. (d) [Co(H₂O)₄(NH₃)₂]Cl₃ = Diamminetetraaquacobalt (III) chloride.
- 3. (c) The correct structure of EDTA is

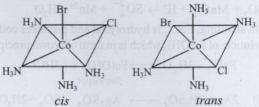
$$HOOC-H_2C$$

 $HOOC-H_2C$
 $N-CH_2-CH_2-N$
 CH_2-COOH
 CH_2-COOH

- 4. (b) Ionisation isomer of $[Cr(H_2O)_4Cl(NO_2)]Cl$ is $[Cr(H_2O)_4Cl_2]NO_2$.
- (c) The correct IUPAC name of the given compound is tetraamminenickel (II) - tetrachloronickelate (II) thus (c) is the correct answer.
- (a) Co(NH₃)₄Br₂Cl will show both geometrical and ionization isomerism.

[Co(NH₃)₄Br₂]Cl and [Co(NH₃)₄BrCl]Br are ionization isomers and geometrical isomers are





7. (a) In $[MnO_4]^-$, Mn is in +7 oxidation state. Electronic configuration of Mn (Z = 25): $[Ar] 3d^54s^2$ Electronic configuration of Mn⁷⁺: $[Ar] 3d^04s^0$ Central atom in other ions have definite number of d electrons.

$$\begin{bmatrix} \text{Co(NH}_3)_6 \end{bmatrix}^{3+} & \begin{bmatrix} \text{Fe(CN)}_6 \end{bmatrix}^{3-} & \begin{bmatrix} \text{Cr(H}_2\text{O)}_6 \end{bmatrix}^{3+} \\ \text{in Co}^{3+} = \text{Six} & \text{in Fe}^{3+} = \text{Five} & \text{in Cr}^{3+} = \text{three} \end{bmatrix}$$

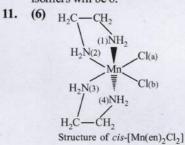
- (d) Organometallic compounds are those compounds in which metal atom is directly bonded with C-atom. H₃C-Li.
- 9. (3) Species having the equal number of valence shell electron are considered as isoelectonic species.

Valence electron in Ni (CO), = 18

Species		Total valence electrons
a a pile		in species
V(CO) ₆	(Tasta	17
Cr(CO) ₅	-	16
Cu(CO) ₃	-	17
Mn(CO) ₅	-	17
Fe(CO) ₅	-	18
[Co(CO),]3-	-	18
[Cr(CO) ₄] ⁴		18
Ir(CO) ₃	_ ,	15

Note: Total valence electrons = Valence electron of metal + Electron donated by ligand.

- 10. (6) Possible isomers are
 - (I) $[Pt(NH_3)_4 Cl_2] Br_2 \Rightarrow GI = 2$
 - (II) $[Pt(NH_3)_4 Br_2] Cl_2 \Rightarrow GI = 2$
 - (III) $[Pt(NH_3)_A BrCl] Br.Cl \Rightarrow GI. = 2$
 - I, II, III are ionisation isomers of given complex and each exhibits two geometrical isomers. Therefore total possible isomers will be 6.



Number of cis N - Mn - Cl bonds, *i.e.* Mn - N and Mn - Cl bonds are in adjacent positions.

1 - Cl(a) - Mn - N(1) 2 - Cl(a) - Mn - N(2)

3 - Cl(a) - Mn - N(4) 4 - Cl(b) - Mn - N(4)

5 - Cl(b) - Mn - N(3) 6 - Cl(b) - Mn - N(1)

Hence, the answer is 6.

Note: All adjacent positions (at 90°) are cis to each other.

12. (5) $[CoL_2Cl_2]^-$ ($L = H_2NCH_2CH_2O^-$)

L is unsymmetrical didentate ligand.

So, the complete is equivalent to $[M(AB)_2a_2]$ Possible G.I. are

13. (6) All the complexes given show *cis-trans* isomerism $[Co(NH, -CH, -CH, -NH_2), Cl_1]^+, [CrCl_1(C,O_4)_2]^{3-}$

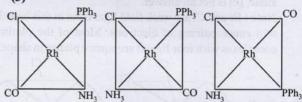
$$\begin{array}{c|cccc}
Cl & & & & \\
Cl & &$$

[Co(NH,-CH,-CH,-NH,),(NH,)Cl]+ (Co(NH,),(H,O)Cl]2+

14. (3)
$$CH_3$$
 C Fe^{+2} Br

Total no. of N - Co - O bonds are 8.

- 16. (6) $m \text{ moles of [Cr (H}_2\text{O})_5\text{Cl]Cl}_2 = 0.01 \times 30 = 0.3$ $m \text{ moles of Cl}^- = 0.3 \times 2 = 0.6$ [1 mole of complex gives 2 Cl $^-$ ions] $m \text{ moles of Ag}^+ = m \text{ moles of Cl}^ 0.1 \times V = 0.6$ V = 6 mL
- 17. (3)



The number of geometrical isomers is 3.

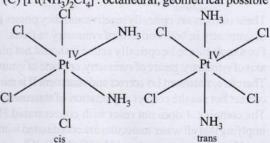
 (4) The number of water molecules directly bonded to the metal centre in CuSO₄.5H₂O is 4.

19. Hexammine cobalt (III) chloride

20. (c, d)
$$[Pt(NH_3)_2 Br_2]$$

Hybridisation : dsp^2 , geometry : square planar, show geometrical isomerism

- (A) [Pt(en)(SCN)₂]: square planar, geometrical not possible
- (B) [Zn(NH₃)₂Cl₂]: tetrahedral, geometrical not possible
- (C) [Pt(NH₃)₂Cl₄]: octahedral, geometrical possible



(D) [Cr(en)₂(H₂O)SO₄]⁺ : Octahedral, geometrical isomerism possible.

$$\begin{array}{c|c} & H_2O & \\ & H_2O & \\ & III & \\ & SO_4 & \\ &$$

21. (b,d) The pair of complex ions [Co(NH₃)₄Cl₂]⁺ and [Pt(NH₃)₂(H₂O)Cl]⁺ show geometrical isomerism.

The pair of complexes [Pt(NH₃)₃(NO₃)]Cl and [Pt(NH₃)₃Cl]Br show ionisation isomerism. The other pairs

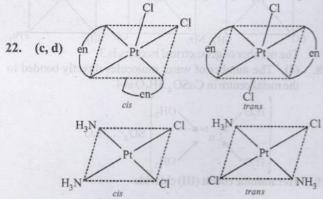
given do not have same type of isomerism.

The complex $[CoBr_2Cl_2]^{2-}$ will show sp^3 hybridisation. The tetrahedral shape will not show any kind of isomerism.

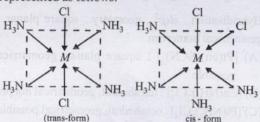
(c) The complex $[PtBr_2Cl_2]^{2-}$ will show dsp^2 hybridisation. The square planar shape will show geometrical isomerism.

Henc, (c) is not an answer.

Note: Br and Cl are weak field ligand but in this case they will cause pairing of electrons. Most of the platinum complexes with four ligand are square planar in shape.



23. (b) The geometrical isomers of [M(NH₃)₄Cl₂] can be represented as follows:-



These isomers are optically inactive and they posses plane of symmetry in both and axis of symmetry in trans.

For a molecule to be optically active it should not possess axis of symmetry, centre of symmetry, or plane of symmetry. Therefore, statement I is correct and statement II is partially correct but not the correct explanation of statement I.

24. The complex A does not react with concentrated H₂SO₄ implying that all water molecules are coordinated with Cr³⁺ ion. Hence, its structure would be [Cr(H₂O)₆]Cl₃.

The compound *B* loses 6.75% of its original mass when treated with concentrated H₂SO₄. This loss is due to the removal of water molecules which is/are not directly coordinated to Cr³⁺ ion.

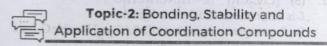
The mass of water molecules removed per mole of the complex

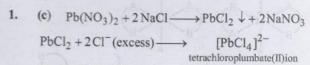
$$= \frac{6.75}{100} \times \text{molar mass of the complex} = \frac{6.75}{100} \times 266.5 \text{ g}$$
$$= 17.98 \text{ g}$$

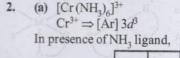
This corresponds to one mole of water. Hence, the structure of the compound B will be $[Cr(H_2O)_5Cl](H_2O)Cl_2$. The compound C loses 13.5% of its mass when treated with concentrated H_2SO_4 which is twice of the mass lost

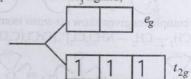
by the compound B. Hence, the structure of the compound C will be $[Cr(H_2O)_4Cl_3](H_2O)_2$ Cl.

- 25. (i) [CoCl(NH₃)₅]²⁺ Formula of pentaamminechlorocobalt (III)
 - (ii) LiAlH $_4$ Formula of lithium tetrahydroaluminate (III)
- 26. (i) Pentaamminecarbonatochromium (III) chloride.
 - (ii) Potassium hexacyanochromate (III)
 - (iii) Pentaamminenitrito-o-cobalt (III) chloride









Number of unpaired electrons = 3

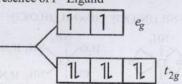
$$\mu = \sqrt{n(n+2)}$$
 B.M.

$$\mu = \sqrt{3(3+2)} \text{ B.M.} = 3.87 \text{ B.M.}$$

 $[CuF_{6}]^{3-}$

$$Cu^{3+} \Rightarrow [Ar] 3d^8$$

In presence of F-Ligand



Number of unpaired electrons = 2

$$\mu = \sqrt{n(n+2)}$$
 B.M.

$$\mu = \sqrt{2(2+2)}$$
 B.M. = 2.84 B.M.

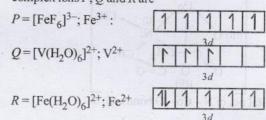
3. (a) Ni²⁺ with NH₃ shows CN = 6 forming [Ni(NH₃)₆]²⁺ $(sp^3d^2 \text{ hybridisation, Octahedral})$

 Pt^{2+} with NH_3 shows CN = 4 forming $[Pt(NH_3)_4]^{2+}$

 $(d^2sp$ hybridisation, square planner)

 Zn^{2+} with NH₃ shows CN = 4 forming $[Zn(NH_3)_4]^{2+}$ (sp^3 hybridisation, tetrahedral)

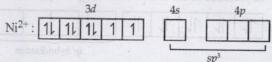
(b) The electronic configuration of central metal ion in complex ions *P*, *Q* and *R* are



Higher the no. of unpaired electron(s), higher will be magnetic moment.

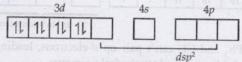
Thus, the correct order of spin only magnetic moment is Q < R < P

5. (c) In both states (paramagnetic and diamagnetic) of the given complex, Ni exists as Ni²⁺ whose electronic configuration is [Ar] 3d⁸4s⁰.



In the above paramagnetic state, the geometry of the complex is sp^3 giving tetrahedral geometry.

The diamagnetic state is achieved by pairing of electrons in 3d orbital.



Thus, the geometry of the complex will be dsp^2 giving square planar geometry.

6. (c)

Complex	No. of electrons in outer d orbital	No. of unpaired electron (s)
[Fe(CN) ₆] ³⁻ (K)	3d ⁵	1 (CN causes pairing of electrons)
$[Co(NH_3)_6]^{3+}$ (L)	3d ⁶	0(NH ₃ causes pairing of electrons)
[Co(oxal.) ₃] ³⁻ (M)	3d ⁶	0(oxalate causes pairing of electrons)
$[Ni(H_2O)_6]^{2+}$ (N)	3d 8	1M ni 2 M (d),
[Pt(CN) ₄] ²⁻ (O)	5d ⁸	0(CN causes pairing of electrons)
$[Zn(H_2O)_6]^{2+}$ (P)	3d 10	NISO "0H"O pas

Thus L, M, O and P are diamagnetic.

7. **(b)** Ni⁺² + 4Cl⁻
$$\longrightarrow$$
 [NiCl₄]²⁻ $\stackrel{sp^3}{}$

[NiCl₄]²⁻, = $3d^8$ configuration with nickel in + 2 oxidation state, Cl⁻ being weak field ligand does not compel for pairing of electrons.

sp³ hybridisation Hence, complex has tetrahedral geometry

$$\begin{bmatrix} CI \\ \downarrow \\ Ni \\ CI \end{bmatrix}^{2-}$$

$$Ni^{+2} + 4CN^{-} \longrightarrow [Ni(CN)_{4}]^{2-}$$

 $[Ni(CN)_4]^{2-} = 3d^8$ configuration with nickel in + 2 oxidation state, CN⁻ being strong field ligand compels for pairing of electrons.

dsp² hybridisation

Hence, complex has square planar geometry.

$$Ni^{+2} + 6H_2O \longrightarrow [Ni(H_2O)_6]^{2+}$$

 $[Ni(H_2O)_6] = 3d^8$ configuration with nickel in + 2 oxidation state. As with $3d^8$ configuration two *d*-orbitals are not available for d^2sp^3 hybridisation. So, hybridisation of Ni (II) is sp^3d^2 and Ni (II) with six co-ordination will have octahedral geometry.

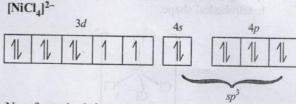
$$\begin{bmatrix} H_2O & OH_2 \\ N_1 & OH_2 \\ H_2O & OH_2 \end{bmatrix}^{2}$$

Note: With water as ligand, Ni (II) forms octahedral complexes.

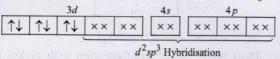
8. **(b)**
$$[\text{NiCl}_4]^{2-}$$
, O.S. of Ni = +2
Ni(28) = $3d^8 4s^2$

3*d* 4*s* 4*p*

CI being weak ligand it cannot pair up the two electrons present in 3d orbital

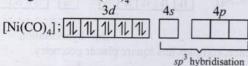


No. of unpaired electrons = 2 Magnetic moment, μ = 2.82 BM. 9. (a) Chromium in Cr(CO)₆ is in zero oxidation state and has [Ar]¹⁸ 3d⁵4s¹ as the electronic configuration. However, CO is a strong ligand, hence pairing up of electrons takes place leading to following configuration in Cr(CO)₆.

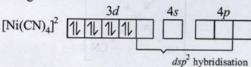


Since, the complex has no unpaired electron, its magnetic moment is zero.

(b) In carbonyls, O.S. of metal is zero.
 In [Ni(CO)₄], the oxidation state of nickel is zero. Its configuration in Ni(CO)₄ is



In [Ni(CN)₄]²⁻ the oxidation state of Ni is 2+ and its configuration is



Thus, the hybridisations of nickel in these compounds are sp^3 and dsp^2 respectively.

- 11. (d) An anionic carbonyl complex can delocalise more electron density to antibonding pi-orbital of CO and hence, lowers the bond order.
- 12. (b) The required reaction is

$$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+; K = ?$$

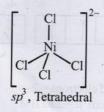
From the given equations, we have

$$k_1 = \frac{[\text{Ag}(\text{NH}_3)]^+}{[\text{Ag}^+][\text{NH}_3]}; \ k_2 = \frac{[\text{Ag}(\text{NH}_3)_2]^+}{[\text{Ag}(\text{NH}_3)]^+[\text{NH}_3]}$$

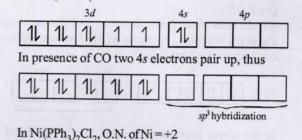
.. The value of K is given by $K = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 1.08 \times 10^{-5}$.

- 13. (c) $\mu = \sqrt{n(n+2)}$ BM ($\mu = \text{spin magnetic moment}$)

 Here Co is present as Co²⁺ ion which has 3 unpaired electrons. So the spin magnetic moment will be $\sqrt{3(3+2)}$, i.e. $\sqrt{15}$ BM.
- 14. (d) The configuration of Ni^{2+} is $3d^8$. For the elements of the first transition series, Cl^- behaves as a weak field/high spin ligand. Hence, Ni in $[NiCl_4]^{2-}$ is sp^3 hybridised leading to tetrahedral shape.



15. (c) In metal carbonyl the metal is in zero oxidation state. In Ni(CO)₄, O.N. of Ni = 0 For Ni (Z = 28)



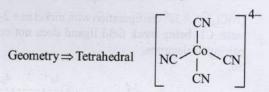
PPh₃ and Cl⁻ can't pair up d-electrons, leading to sp^3 hybridization and tetrahedral geometry.

sp3 hybridization

16. (c)

Atom/Ion Complex	Configuration	No. of unpaired electrons	Magnetic nature
$Ni^{2+}(d^8)$ $[NiCl_4]^{2-}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2 2	Paramagnetic
[Ni(CN) ₄] ²⁻	T↓ ↑↓ ↑↓ ↑↓ : : : : : Rearrangement dsp^2	0	Diamagnetic
Ni (<i>d</i> ⁸ s ²) [Ni(CO) ₄]	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	2 0	Paramagnetic Diamagnetic

- 17. (b) Mn²+ in MnSO₄·4H₂O has d⁵ configuration (five unpaired electrons); Cu²+ in CuSO₄·5H₂O has d⁰ configuration (one unpaired electron); Fe²+ in FeSO₄·6H₂O has d⁶ configuration (four unpaired electron); and Ni²+ in NiSO₄·6H₂O has d⁶ configuration (two unpaired electron). Thus, CuSO₄·5H₂O has lowest degree of paramagnetism.
 18. (5) [Co(CN)₄]⁴-⇒ Co⁰ 3d⁴4s²⇒ 3d⁰
- 18. (5) $[Co(CN)_4]^{4-2} \Rightarrow Co^0 \quad 3d^74s^2 \Rightarrow 3d^9$ Due to SFL, CN-pairing and transference of electron takes place and hybridisation is sp^3 .



[Co(CO)₃NO] Co⁰ $\Rightarrow 3d^74s^2 \Rightarrow 3d^9$ due to SFL, CO and NO $\Rightarrow sp^3$ hybridisation

$$XeF_4 \Rightarrow 4bp + 2lp = sp^3d^2$$

Square planar

$$F \times \dot{x}\dot{e} < F$$

 $PCl_4^+ \Rightarrow 4pb + 0lp$

$$sp^3 \Rightarrow$$
 tetrahedral

 $[PdCl_4]^{2-} \Rightarrow Pd^{2+}, Cl^-$ behaves as SFL $Pd^{2+} \Rightarrow 4d^8 \Rightarrow dsp^2 \Rightarrow$ square planar

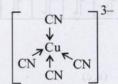
$$ICl_4^- \Rightarrow 4bp + 2lp$$

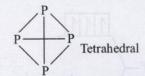
$$sp^3d^2$$

square planar

$$[Cu(CN)_4]^{3-} \Rightarrow Cu^{+1} \Rightarrow 3d^{10}$$

Tetrahedral





19. (1) $[Mn(NH_3)_6]^{3+} \Rightarrow d^4$ system : $\boxed{1 \ 1 \ 1 \times \times \times}$, NH_3 strong field, ligand. Paramagnetic $[MnCl_6]^{3-} \Rightarrow d^4$ system : $\boxed{1 \ 1 \ 1 \ 1}$, Cl^- a weak

 $[MnCl_6]^{3-} \Rightarrow d^4$ system : $\boxed{1\ |\ 1\ |\ 1\ |\ 1}$, Cl^- a weak field ligand. Paramagnetic

 $[FeF_6]^{3-} \Rightarrow d^5$ system : 1 1 1 1 1 1, F⁻ a weak field ligand. Paramagnetic

 $[\text{CoF}_6]^{3-} \Rightarrow \text{d}^6 \text{ system} : \boxed{1 \ | \ 1 \ | \ 1 \ | \ 1}, \text{ F}^- \text{ a weak}$ field ligand. Paramagnetic

 $[Fe(NH_3)_6]^{3+} \Rightarrow d^5 \text{ system} : 1 1 1 \times \times, NH_3 a$ strong field ligand. Paramagnetic

 $[\text{Co(en)}_3]^{3+} \Rightarrow d^6 \text{ system}: \boxed{1\!\!1 \ 1\!\!1 \ 1\!\!1 \times \times \times}, \text{ en a strong}$ field ligand. Diamagnetic

Only 1 complex is diamagnetic.

20. (1)

• H-atom =1s¹ Paramagnetic

• $NO_2 = \sqrt{\frac{0}{N}}$ odd electron species Paramagnetic

• O_2^- (superoxide) = One unpaired electron in π^* M.O.

Paramagnetic

• S_2 (in vapour phase) = same as O_2 , two unpaired e⁻s are present in $\pi^*M.O$.

Paramagnetic

• $Mn_3O_4 = 2MnO \cdot MnO_2$

Paramagnetic

• $(NH_4)_2[FeCl_4] = Fe^{2+} = 3d^6 4s^0$

Paramagnetic

• $(NH_4)_2[NiCl_4] = Ni = 3d^8 4s^2$

 $Ni^{2+} = 3d^8 4s^0$ Paramagnetic

•
$$K_2MnO_4 = 2K^+ \begin{bmatrix} O \\ Mn \\ O \end{bmatrix}$$
, $Mn^{6+} = [Ar] 3d^1$

Paramagnetic

•
$$K_2 \text{CrO}_4 = 2K^+ \begin{bmatrix} O \\ Cr \\ O & O \end{bmatrix}$$
, $Cr^{6+} = [Ar] 3d^0$

Diamagnetic

21. (4) Fe(26)
$$\longrightarrow$$
 [Ar]₁₈ $3d^64s^2$
Fe³⁺ \longrightarrow [Ar]₁₈ $3d^54s^0$

SCN- is weak field ligand hence pairing will not occur.

$$: Fe^{3+} \longrightarrow \boxed{111111}$$

Unpaired electrons = 5

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

$$=\sqrt{35}$$
 B.M. = 5.92 B.M.

CN⁻ is strong field ligand hence pairing will take place.

$$\therefore Fe^{3+} \longrightarrow \boxed{1 | 1 | 1 |}$$

Unpaired electrons = 1

Magnetic moment = $\sqrt{1(1+2)}$ B.M. = $\sqrt{3}$ B.M. = 1.732

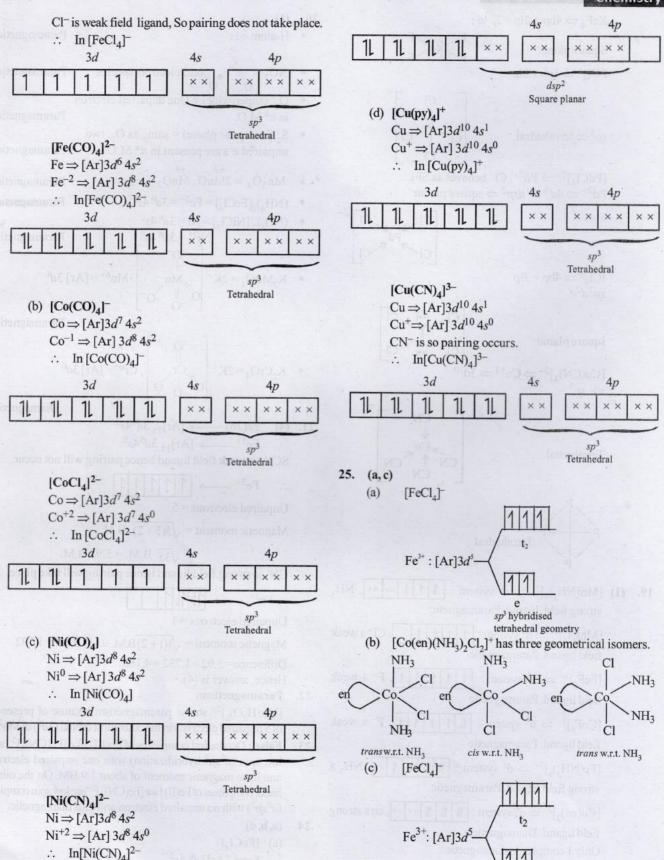
Difference = 5.92 - 1.732 = 4.188

Hence, answer is (4).

22. Paramagnetism;

 $[Mn(H_2O)_6]^{2+}$ shows paramagnetism because of presence of 5 unpaired electrons in the outer most orbital $(3d^5)$ of Mn^{2+} .

- 23. False: Octahedral complexes of Fe(III) like $[Fe(CN)_6]^{3-}$ are low spin (d^2sp^3) hybridization) with one unpaired electron and have magnetic moment of about 1.9 BM. On the other hand, complexes of Fe(II) like $[Fe(CN)_6]^{2-}$ are low spin complex (d^2sp^3) with no unpaired electron and thus diamagnetic.
- 24. (a, b, d)
 - (a) $[\text{FeCl}_4]^ \text{Fe} \Rightarrow [\text{Ar}] 3d^6 4s^2$ $\text{Fe}^{+3} \Rightarrow [\text{Ar}] 3d^5 4s^0$

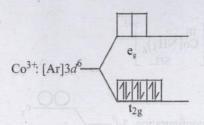


Number of unpaired electrons (n) = 5

Spin only magnetic moment = $\sqrt{n(n+2)}B.M.$

= 5.92 B.M.

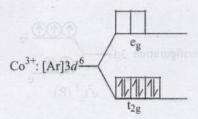
[Co(en)(NH₃)₂Cl₂]+



Number of unpaired electrons (n) = 0 Spin only magnetic moment = $\sqrt{n(n+2)}$ B.M.

= 0

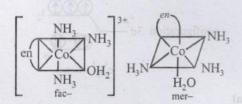
(d) [Co(en)(NH₃)₂Cl₂]⁺



 d^2sp^3 hybridisation, octahedral geometry

26. (a, b, d)

(a) [Co(en)(NH₃)₃(H₂O)]³⁺ has 2 geometrical isomers.



(b) Compound [Co(CN)₂(NH₃)₃(H₂O)]⁺ will have three geometrical isomers.

$$\begin{bmatrix} H_{2}O \\ H_{3}N \\ CO \\ CN \\ mer^{-}, cis^{-} \end{bmatrix}^{+} \begin{bmatrix} H_{2}O \\ H_{3}N \\ CO \\ M_{3}N \\ NH_{3} \\ fac^{-}, cis^{-} \end{bmatrix}^{+} \begin{bmatrix} H_{2}O \\ H_{3}N \\ CO \\ NC \\ NC \\ NH_{3} \\ fac^{-}, trans^{-} \end{bmatrix}^{+}$$

[Note: fac- and mer- w.r.t. NH₃, cis- and trans- w.r.t. -CN] (c) [Co(en)(NH₃)₃(H₂O)]³⁺ is diamagnetic Due to the presence of strong field ligand 'en' d⁶ system (Co³⁺) forms low spin (l.s) complex in Oh splitting of d-orbitals.

(d) [Co(en)(NH₃)₄]³⁺ has larger gap between e_g and t_{2g} than [Co(en)(NH₃)₃(H₂O)]³⁺.
 So, [Co(en)(NH₅)₃(H₂O)]³⁺absorbs light at longer wavelength as compared to [Co(en)(NH₃)₄]³⁺.

27. (b, c)

(a) [(Fe(CO₅)] & [Ni(CO)₄] complexes have 18-electrons in their valence shell.

For transition elements of 3d-series, the valence shells are 3d- and 4s.

- (b) Due to strong ligand field, carbonyl complexes are predominantly low spin complexes.
- (c) As electron density increases on metals (with lowering oxidation state on metals), the extent of synergic bonding increases. Hence, M-C bond strength increases.
- (d) While positive charge on metals increases and the extent of synergic bond decreases and hence, C-O bond becomes stronger.
- **28. (b, c, d)** Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M. where, n = No. of unpaired electrons Given for X and Z, $\mu = 3.87$ B.M.

i.e.
$$\sqrt{n(n+2)} = 3.87$$

 $n^2 + 2n - 15 = 0$: $n = 3$

 $n + 2n - 13 - 0 \dots n - 3$

For complex Y(1:3 electrolyte) given $\mu = 0$

i.e.
$$\sqrt{n(n+2)} = 0 \Rightarrow n = 0$$

 $CoCl_2.6H_2O$ or $[Co(H_2O)_6)]$ Cl_2 (X) is pink coloured compound and octahedral in structure.

On adding excess of HCl at room temperature, $[Co(H_2O)_6]Cl_2(X)$ changes into tetrahedral, $[CoCl_4]^{2-}(Z)$ and on adding excess of NH₃ and NH₄Cl in the presence of air forms $[Co(NH_3)_6]Cl_3(Y)$.

$$[\operatorname{Co}(\operatorname{H}_2\operatorname{O})_6]\operatorname{Cl}_2 \xrightarrow{\operatorname{NH}_3(\operatorname{excess})} [\operatorname{Co}(\operatorname{NH}_3)_6]\operatorname{Cl}_3$$
(X) Pink
(Y)

 $(\mu = 3.87 \, \text{B.M})$ $(\mu = 0.00)$

29. (a, c) The metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fe).

As the bond strength $Fe \leftarrow C \equiv O$

between Fe-C increases, the bond order between C-O decreases and the effective bonding can be represented as Fe-C=O.

This will increase the C-O bond length. Thus, the answers can be $1.13\,\text{\AA}$ or $1.15\,\text{\AA}$.

30. (c) The magnetic moment (μ) of a species is related to its number of unpaired electrons (n) in form of following expressions.

$$\mu = \sqrt{n(n+2)}$$
 B.M

The number of unpaired electrons in the given pairs are as follows:

$$Fe^{2+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^6$$

or
$$\uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow$$
 Thus, here $n = 4$.

$$Fe^{3+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5$$

or
$$\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$$
 Thus, here $n = 5$

NO or
$$\stackrel{+}{N} = \stackrel{-}{O}$$
: $n = 0$; NO or $\stackrel{\times}{N} \stackrel{\times \bullet \bullet}{=} 0$: $n = 1$

The given combinations differ in the number of unpaired electrons. Hence, these can be differentiated by the measurement on the solid state magnetic moment of nitroprusside ion.

31. (b) Highest parmagnetic character will be shown by the ion having maximum number of unpaired electrons in their d-subshells.

25Cr3+ has 3 unpaired electrons;

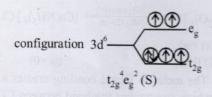
26Fe2+ has 4 unpaired electrons

29Cu2+ has 1 unpaired electrons;

30Zn2+ has no unpaired electrons

So (a), (b) & (c) show paramagnetism. Out of which (b) has the highest paramagnetism.

32. (d) 1.
$$\begin{bmatrix} II \\ Fe(H_2O)_6 \end{bmatrix}^{+2}$$



2.
$$\left[\frac{II}{Mn} (H_2O)_6 \right]^{+2}$$

configuration
$$3d^5$$

$$t_{2g}^{3}e_{g}^{2}(Q)$$

$$e_{g}$$

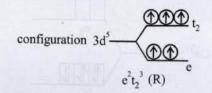
3.
$$\left[\begin{array}{c} III \\ Co(NH_3)_6 \\ SFL \end{array} \right]^{+3}$$

configuration
$$3d^6$$

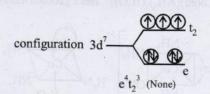
$$t_{2g}^6 e_g^0 (P)$$

$$e_g$$

4.
$$\begin{bmatrix} III \\ Fe Cl_4 \\ WFL \end{bmatrix}$$



5.
$$\left[\begin{array}{c} II \\ CoCl_4 \\ WFL \end{array} \right]^{-2}$$



- 33. (a)
 - (I) $[Cr(CN)_6]^{4-} \Rightarrow Cr^{2+}(d^4) \Rightarrow low spin Oh complex as$ CN- is strong field ligand.

Electronic configuration = $t_{2g}^4 e_g^0$; $\Delta_0 > P$;

$$\mu_{S.O.} = \sqrt{2(2+2)} = 2.82 \text{ BM}$$

(P), (R), (T)

(II) $[RuCl_6]^{2-} \Rightarrow Ru^{4+}(d^4) \Rightarrow Low spin Oh complex as$ Ru is of large size.

Electronic configuration = $t_{2g}^4 e_g^0$; $\Delta_0 > P$;

$$\mu_{S,O} = \sqrt{2(2+2)} = 2.82 \text{ BM}$$

(P), (R), (S), (T)

(III) $[Cr(H_2O)_6]^{2+} \Rightarrow Cr^{2+}(d^4) \Rightarrow$ high spin Oh complex as H_2O is weak field ligand.

Electronic configuration = $t_{2g}^3 e_g^1$; $\Delta_0 < P$;

$$\mu_{S.O.} = \sqrt{4(4+2)} = 4.89 \text{ BM}$$

(O), (T)

(IV) $[Fe(H_2O)_6]^{2+} \Rightarrow Fe^{2+}(d^6) \Rightarrow high spin Oh complex$

Electronic configuration = $t_{2g}^4 e_g^2$; $\Delta_0 < P$;

$$\mu_{S.O.} = \sqrt{4(4+2)} = 4.89 \text{ BM}$$

(P), (Q)

34. (c)

- (p) $[FeF_6]^4$, $Fe^{2+} = 3d^6$ and F^- is weak field ligand
- :. Hybridization is sp^3d^2 (high spin complex)
- (q) $[Ti(H_2O)_3Cl_3]$, $Ti^{3+} = 3d^1$ (No effect of ligand field strength)
- :. Hybridization is d²sp³
- (r) $[Cr(NH_3)_6]^{3+}$, $Cr^{3+} = 3d^3$ (No effect of ligand field strength)
- : Hybridization is d²sp³
- (s) [FeCl₄]²⁻, 3d⁶ and Cl⁻ is weak field ligand
- :. Hybridization is sp³
- (t) $[Ni(CO)_4]$, $Ni = 3d^{10}$ and CO is strong field ligand
- :. Hybridization is sp³
- (w) $[Ni(CN)_4]^{2-}$, $Ni^{2+} = 3d^8$ and CN is strong field ligand
- :. Hybridization is dsp²

35. (b)

Complex	Magnetic character	Isomerism
A, [Cr(NH ₃) ₄ Cl ₂]Cl	Cr ³⁺ is d ³ , hence paramagnetic	cis-trans
B, [Ti(H ₂ O) ₅ Cl](NO ₃) ₂	Ti ³⁺ is d ¹ , hence paramagnetic.	ionization
C, [Pt(en)(NH ₃)Cl]NO ₃	Pt ²⁺ is d ⁸ , complex is square planar, all electrons are paired, hence diamagnetic	ionization
D, [Co(NH ₃) ₄ (NO ₃) ₂]NO ₃	Co ³⁺ is d ⁶ , all electrons are paired due to strong ligands, hence diamagnetic	cis-trans

36. (A): (p), (q) and (s)

In $[\text{Co(NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, Co is in + 2 state having $3d^7$ configuration, which makes it paramagentic due to odd electrons. Moreover, it is an octahedral complex showing *cis-trans* isomerism w.r.t., H₂O.

$$\begin{bmatrix} H_3N & OH_2 & NH_3 \\ H_3N & OH_2 & NH_3 \\ H_3N & OH_2 & OH_2 \end{bmatrix}^{2+} \begin{bmatrix} NH_3 & NH_3 & NH_3 \\ H_3N & OH_2 & OH_2 \\ OH_2 & OH_2 & OH_2 \end{bmatrix}^{2+}$$

$$trans$$

$$Co^{2+} = 3d^7 \text{ (Paramagnetic)}$$

(B): (p), (r) and (s)

In [Pt (NH₃)Cl₂], Pt is in + 2 state with configuration $5d^8$. Since NH₃ is a strong field ligand, it will pair all the electrons making the complex diamagnetic. Moreover, it is a square planar complex showing cis-trans isomerism.

$$\begin{bmatrix} H_3 N & CI \\ H_3 N & Pt & CI \end{bmatrix}$$

$$\begin{bmatrix} H_3 N & CI \\ CI & Pt & NH_3 \end{bmatrix}$$

$$(cis) \qquad (trans)$$

$$Pt^{2+} = 5d^8 4s^0 \text{ (diamagnetic)}$$

(C):(q) and (s)

In $[Co(H_2O)_5Cl]Cl$, Co is in + 2 state with $3d^7$ configuration making it paramagnetic.

(D): (q) and (s)

In $[Ni(H_2O)_6]Cl_2$, Ni is in + 2 state with $3d^8$ configuration. It is attached with weak field ligands, therefore it is paramagnetic.

37. (a)
$$Ni^{2+} \xrightarrow{KCN} K_2[Ni(CN)_4];$$

potassium tetracyano nickelete (II)

$$Ni^{2+} \xrightarrow{KCl} K_2[NiCl_4]$$

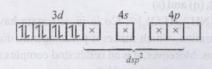
potassium tetrachloro nichelate (II)

38. (c) For
$$[Ni(CN)_4]^{2-}$$
; $Ni = [Ar]3d^84s^2$; $Ni^{2+} = [Ar]3d^8$

	3 <i>d</i>	4s	4p
Ni ²⁺	11111111	12 57 K	

However, CN^- is a strong field ligand so it forces the 3d electrons to pair up and hence the effective configuration in this case will be:

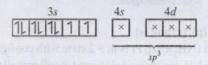
Ni2+ in presence of CN-



Thus, $[Ni (CN)_4]^{2-}$ exhibits dsp^2 hybridization and square planar shape. Since here, number of unpaired electrons is zero, the complex will be *diamagnetic*.

In case of [NiCl₄]²⁻, Cl⁻ is a weak field ligand, so the effective configuration of Ni²⁺ in this complex will be as follows:

Ni2+ in presence of Cl-



So here, Ni^{2+} is sp^3 hybridised and thus, tetrahedral in shape. Since, the complex has two unpaired electrons, it will be *paramagnetic*.

- 39. (a) Discussed above.
- 40. (a) In $[Fe(H_2O)_5NO] SO_4$, Let the oxidation state of Fe be x. Then for $[Fe(H_2O)_5NO]^{2+}$,

$$x+1=+2$$
 or $x=+2-1=+1$

Hence, in this complex the oxidation state of Fe is +1 Electronic configuration of Fe⁺ can be represented as Fe⁺= $1s^22s^22p^63s^23p^63d^7$. This unexpected configuration is due to presence of NO⁺. Due to which 1 electron from $4s^1$ gets shifted to 3d– orbitals.

The $3d^7$ electrons in five 3d- orbitals can be shown as

In it, we find 3 unpaired electrons.

Because of the presence of unpaired electrons the complex is paramagnetic *i.e.* statement 1 is true.

As is clear from above there are three unpaired electrons in this complex *i.e.* statement 2 is true.

Since, paramagnetic behaviour is due to presence of unpaired electrons in it so statement 2 is correct explanation of statement 1.

41.
$$Fe^{3+} + SCN^{-} \longrightarrow [Fe(SCN)(H_2O)_5]^{2+}$$
(excess) (blood red)
(A)

$$[Fe(SCN)(H_2O)_5]^{2+} + 6F^- \longrightarrow [FeF_6]^{3-} + SCN^-$$
(B)

IUPAC name of (A) is pentaaquathiocyanatoferrate (III) ion IUPAC name of (B) is hexafluoroferrate (III)

In $[FeF_6]^{3-}$ coordination no. of Fe = 6In $[FeF_6]^{3-}$ oxidation state of Fe = +3

: It has 5 unpaired electrons, n = 5, Fe³⁺ is $3d^5$

Magnetic moment (μ) = $\sqrt{n(n+2)}$ (B.M.)

$$\sqrt{5(5+2)} = \sqrt{35} = 5.92 \,\mathrm{B.M.}$$

42. (a)
$$H_3C-C = N$$
 $N = C - CH_3$ $H_3C-C = N$ $N = C - CH_3$ $N = C - CH_3$ $N = C - CH_3$ $N = C - CH_3$

Bis(dimethylglyoximato) nickel (II)

- (b) Charge on Ni in the complex is +2 and it is dsp^2 hybridised
- (c) Since number of unpaired electrons in Ni²⁺ is zero, the complex is diamagnetic.
- 43. The spin magnetic moment, m of the complex is 1.73 BM.

$$\mu = \sqrt{n(n+2)} = 1.73 \Rightarrow n = 1$$

It means that nucleus of the complex, chromium ion has one unpaired electron. So the ligand NO is unit positively charged.

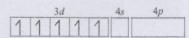
Cr $(z = 24) = 3d^54s^2$, after pairing up of electrons, there shall be one unpaired electron left.

Thus, chromimum can be in Cr+ state.

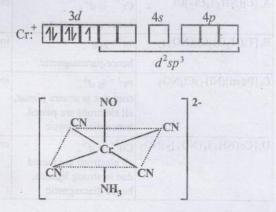
IUPAC name:

Potassium amminetetracyanonitrosochromate (I).

(a) Electronic configuration of Cr⁺:



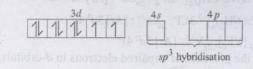
(b) Electronic configuration of Cr⁺ under the influence of strong field ligand CN⁻



So, Hybridization: d2sp3; Shape: Octahedral

44. Cl⁻ is a weak ligand which is unable to pair the electrons of Ni²⁺. Therefore, here hybridisation is sp³ and shape will be tetrahedral.

Electronic configuration of Ni^{+2} (No. of electrons = 26) in presence of Cl^- ion, a weak ligand.

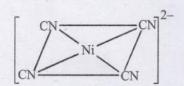


Magnetic moment of [NiCl₄]²⁻ = $\sqrt{2(2+2)}$ = 2.82 BM

On the other hand, CN^- is a stong ligand which pairs up the electrons of Ni^{2+} . Therefore, here hybridisation is dsp^2 and shape will be square planar.

Electronic configuration of Ni²⁺ in presence of CN⁻ ion, a strong ligand.

Magnetic moment of $[Ni(CN)_4]^{2-} = \sqrt{0(0+2)} = 0.0BM$



Square planar dsp2 hybridisation

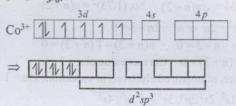
45. Compound (A) on treatment with AgNO₃ gives white precipitate of AgCl, which is readily soluble in dil.aq. NH₃. Therefore it has at least one Cl⁻ ion in the ionization sphere. Furthermore, chromium has coordination number equal to 6. So, its formula is [Cr(NH₃)₄BrCl]Cl.

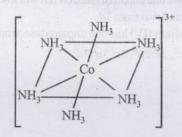
Compound (B) on treatment with AgNO₃ gives pale yellow precipitate of AgBr soluble in conc. NH₃. Therefore it has Br⁻ in the ionization sphere. So, its formula is [Cr(NH₃)₄Cl₂]Br.

State of hybridization of chromium in both (A) and (B) is d^2sp^3 . Spin magnetic moment of (A) or (B),

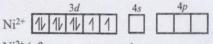
$$\mu_{\text{spin}} = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ BM}$$

46. [Co(NH₁)₆]³⁻

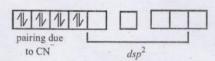




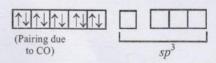
Octahedral complex, d^2sp^3 hybridisation [Ni (CN)₄]²⁻

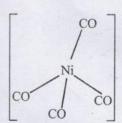


Ni2+ (after rearrangement)



[Ni(CO),]





Tetrahedral (sp3 hybridisation)

47. Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM where $n \rightarrow$ number of unpaired electrons $\mu = 1.73$ BM for vanadium ion

1.73 BM =
$$\sqrt{n(n+2)}$$
 So, $(1.73)^2 = n(n+2)$

$$3.0 = n^2 + 2n$$
 or $n^2 + 2n - 3 = 0$

$$n^2 + 3n - n - 3 = 0$$
 : $n(n+3) - 1(n+3) = 0$

$$(n-1)(n+3) = 0$$
 Correct value of $n=1$

Thus, no. of unpaired electrons in vanadium ion = 1

$$_{23}V = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^3, 4s^2$$

It will have one unpaired electron if it will lose two electrons from 4s and two from 3d.

.. Vanadium (IV) has one unpaired electron.

$$V^{4+} = 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^1$$

- **48.** For the explanation of colouration of complexes, first of all find out the number of unpaired electrons present in outer available *d*-orbitals
 - (i) $[Ti(NO_3)_4]$; 22 Ti^{4+} : [Ar] $3d^0 4s^0$
 - (ii) $[Cu(NC CH_3)_4]^+ BF_4^-;_{29}Cu^+: [Ar] 3d^{10} 4s^0$
 - (iii) $[Cr(NH_3)_6]^{+3} 3Cl^{-}; {}_{24}Cr^{3+} : [Ar] 3d^3 4s^0$
 - (iv) $K_3 [VF_6];_{23}V^{+3}: [Ar] 3d^2 4s^0$

Due to the presence of unpaired electrons in d-orbitals, two complexes *i.e.*, $[Cr(NH_3)_6]^{3+} 3Cl^-$ and $K_3[VF_6]$ are coloured. Others having all paired electrons are colourless.