# Chapter 9

# **Coordination Compounds**

# Solutions

# **SECTION - A**

# **Objective Type Questions (One option is correct)**

- 1. Select the correct statement.
  - (1) A strong field ligand always forms inner orbital complex
  - (2) A strong field ligand always form diamagnetic complex
  - (3) Zinc forms tetrahedral complexes in compounds with coordination number four
  - (4) Splitting of *d*-orbital does not depends on the nature of central atom

#### Sol. Answer (3)

 $Zn^{2+}$  has  $d^{10}$  configuration so it always forms  $sp^3$  complexes.

Wavelength of absorbed light by [CoCl(NH<sub>3</sub>)<sub>5</sub>]<sup>2+</sup>, [Co(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup>, [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [Co(CN)<sub>6</sub>]<sup>3-</sup> are (in nm) P, Q, R and S respectively. The correct order of wavelength is

(1) P > Q > R > S (2) S > R > Q > P (3) P > Q > S > R (4) S > Q > R > P

#### Sol. Answer (1)

With same metal as strength of ligand increases, gap between  $t_{2g}$  and  $e_g$  increases so lower wavelength is absorbed by electron.

 Complex compound P exists as two stereoisomers X<sub>1</sub> and X<sub>2</sub>. Assume both isomers of P on reaction with Br<sup>-</sup> replace one ammonia molecule by Br<sup>-</sup>

 $X_1 \xrightarrow{Br} Only One isomer (Z)$ 

 $X_2 \xrightarrow{Br} Two isomer (Y_1 + Y_2)$ 

(P: Tetraammine dibromide cobalt (III) chloride)

Select the correct statement.

- (1) Out of  $Y_1$  and  $Y_2$ , only one is optically active
- (2)  $X_1$  is Cis while  $X_2$  is trans
- (3)  $Y_1$ ,  $Y_2$ , Z,  $X_1$  and  $X_2$  all are optically inactive
- (4)  $Y_1$  and  $Y_2$  cannot show geometrical isomerism

Sol. Answer (3)

 $P = [Co(NH_3)_4Br_2]CI$ X<sub>1</sub> = trans form of P

 $X_2 = Cis$  form of P

X<sub>1</sub>, X<sub>2</sub>, Y<sub>1</sub>, Y<sub>2</sub>, Y and Z all are optically inactive

- 4. X and Y are neutral ligands. Both X and Y form octahedral complex with Ferrous ion viz.  $[FeX_6]^{2^+}$  and  $[FeY_6]^{2^+}$ . Complex  $[FeX_6]^{2^+}$  is diamagnetic while  $[FeY_6]^{2^+}$  is paramagnetic. On the basis of these information select the correct statement.
  - (1)  $[FeY_6]^{2+}$  is  $d^2sp^3$  hybridised
- (2)  $[FeX_6]^{2+}$  is  $d^2sp^3$  hybridised
- (3) Magnetic moment of [FeY<sub>6</sub>]<sup>2+</sup> is 2.83 B.M
- (4) Magnetic moment of  $[FeY_6]^{2+}$  is 1.73 B.M

# Sol. Answer (2)

Fe<sup>2+</sup> has configuration

|A| 4s<sup>0</sup>3d<sup>6</sup>

If complex is diamagnetic then ligand must be strong field while in paramagnetic ligand must be weak.

- 5. Consider the following statement about C.F.T :
  - S1 : Degeneracy of p subshell remain unaffected in both square planar as well as octahedral field.
  - **S2** : Degeneracy of p subshell remain unaffected in octahedral field but gets destroyed in square planar field.
  - **S3** : Degeneracy of p subshell remain unaffected in square planar field but degeneracy is destroyed in octahedral field.

The incorrect statement is

(1) Only S1 and S2 (2) Only S1 and S3 (3) Only S2 and S3 (4) Only S1

Sol. Answer (2)

P-Subshell have  $P_x$ ,  $P_y$  and  $P_z$ . In octahedral field energy of each orbital remains same but in square planar field energy of electron is affected.

- 6. With the help of crystallography, it is found that C–O distance in gaseous free carbon monoxide is 112.8 pm but in [V(CO)<sub>6</sub>]<sup>-</sup> is greater than 112.8 pm. The C–O bond length increase in [V(CO)<sub>6</sub>]<sup>-</sup> is due to
  - (1) Vanadium donates the d-electrons in  $\pi$  orbital of CO
  - (2) Vanadium donates the d-electron in  $\sigma$  orbital of CO
  - (3) Vanadium donates the d-electron in  $\sigma^{*}$  orbital of CO
  - (4) Vanadium donates the d-electron in  $\pi^*$  orbital of CO

#### Sol. Answer (4)

LUMO of CO is  $\pi^*$  so V<sup>-</sup> donate electron in  $\pi^*$  of CO so C–O bond order decreases

- 7. An inorganic compound 'A' having IUPAC naming Bromidochloridobis (ethane -1,2-amine) Cobalt (III) chloride. Which of the following isomerism(s) is shown by A?
  - (1) Only geometrical, optical and linkage isomerism
  - (2) Only geometrical, optical and ionisation isomerism
  - (3) Only geometrical and Ionisation isomerism
  - (4) Only ionisation and optical isomerism

#### Sol. Answer (2)

[Co(en)<sub>2</sub>BrCl]Cl shows geometrical, optical and Ionisation isomerism.

- 8. 0.0036 moles of CrCl<sub>3</sub>. 6H<sub>2</sub>O were passed through cation exchange resin and the solution of acid coming out of it requried 28.8 ml 0.375 M NaOH. Then which of following is correct about complex ?
  - (1) It is inner orbital complex
  - (2) Formula of complex is [Cr(H<sub>2</sub>O)<sub>5</sub>Cl]Cl<sub>2</sub>. H<sub>2</sub>O
  - (3) Primary valency is six
  - (4) Formula of complex is  $[Cr(H_2O)_6]Cl_3$

# Sol. Answer (4)

m mol of  $OH^-$  = 10.8, m mol of compound = 3.6

So 1 mol of compound must give three CI-.

- 9. Which of the following set of statements are correct?
  - S1 : Geometrical isomerism is not observed in complex of co-ordination number 4 having tetrahedral geometry.

(2)

- S2 : Mabcd can have three geometrical isomers, if the complex is square planar
- S3 : Square planar complex do not show optical isomerism.
- **S4** :  $[Pt(gly)_3]^+$  can have both geometrical and optical isomers.
- (1) Only S1

- S1, S2, S3 and S4
- (3) Both S2 and S3 (4) S1, S2 and S3

# Sol. Answer (2)

Tetrahedral complexes do not exhibit geometrical isomerism.

Square planar complex do not exhibit optical isomerism as they have plane of symmetry

mabcd can have three geometrical isomers



[Pt(gly)<sub>3</sub>]<sup>+</sup> forms a facial and meridional isomers. Both exhibit optical isomerism.

- 10. In a nitrosyl complex the odd electron on nitrogen of the co-ordinated nitrosyl is transferred to (n 1) d subshell of the central metal atom. Hence the spin only magnetic moment of the complex K[Cr(CN)<sub>4</sub>(NH<sub>3</sub>)(NO)] (assuming the metal ion to be in the strong field) is
  - (1)  $\sqrt{8}$  BM (2) 0 BM (3)  $\sqrt{24}$  BM (4)  $\sqrt{15}$  BM

# Sol. Answer (1)

The configuration of chromium in the complex after considering nitrosyl electron

 $\mu = \sqrt{2(2+2)} = \sqrt{8}$  BM

11. Identify the correct order of wavelength of light absorbed by the following complex ions.

$$\begin{bmatrix} Co(H_2O)_6 \end{bmatrix}^{+3}, \quad \begin{bmatrix} Co(CN)_6 \end{bmatrix}^{3-}, \quad \begin{bmatrix} Co(I)_6 \end{bmatrix}^{3-}, \quad \begin{bmatrix} Co(en)_3 \end{bmatrix}^{3+} \\ III & IV \end{bmatrix}$$
(1) ||| > | > |V > || (2) || > |V > | > ||| (3) ||| > | > || > |V (4) || > ||| > |V > ||

Sol. Answer (1)

As ligand field strength increases, splitting energy increases and hence wavelength decreases.

Order of field strength  $I^- < H_2O < en < CN^-$ 

- 12. Which of the following is incorrect regarding  $Fe_4[Fe(CN)_6]_3$ ?
  - (1) Coordinated Fe atom is involved in  $d^2sp^3$  hybridisation
  - (2) Blue colour is due to MMCT (Metal-Metal Charge Transfer)
  - (3)  $t_{2\alpha}$  orbital contains six electrons
  - (4) C-N bond length in  $Fe_3[Fe(CN)_6]_2$  is greater than that in  $Fe_4[Fe(CN)_6]_3$

#### Sol. Answer (4)

- \* Fe is involved in d<sup>2</sup>sp<sup>3</sup> hybridisation as CN<sup>-</sup> is stronger ligand.
- \* Electron transfer takes place between Fe<sup>+2</sup> and Fe<sup>+3</sup>, inside and outside of coordination sphere which is MMCT (Metal Metal charge transfer) because of this reason composition of Prussian blue and turnbull's blue are same.
- \* In coordination sphere Fe<sup>+2</sup> have 6 electrons in  $t_{2q}$  orbital.
- In Fe<sub>3</sub>[Fe(CN)<sub>6</sub>]<sub>2</sub>, Fe is in +3 oxidation state of coordination sphere while in Fe<sub>4</sub>[Fe(CN)<sub>6</sub>]<sub>3</sub> Fe is in +2 oxidation state, and +ve charge on metal increases back bonding decreases.

(4)

- 13. Which of the following statements incorrect?
  - (1) In ferrocyanide ion EAN of central metal ion is 36
  - (3)  $[Co(en)_3]^{+3}$  central atom is  $d^2sp^3$  hybridised
- Sol. Answer (4)

 $[Co(NH_3)_6]^{3+}$  and  $[Co(en)_3]^{3+}$  are inner orbital complex.

14. What is wrong about the complex

 $K[Pt(\eta^2 - C_2H_4)CI_3]?$ 

- (1) It is called Zeise's salt
- (3) Oxidation number of Pt is +2

(2) It is only a  $\pi$ -bonded complex

Sol. Answer (2)

It has both  $\sigma$  and  $\pi$  bonding.

15. Cis-di-µ-chloro-bis [Chloro(triphenylphosphine) platinum (II)] is



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(2) In  $[Co(NH_3)_6]^{3+}$  central atom is  $d^2sp^3$  hybridised

Four ligands surrounds the platinum atom

(4)  $[Co(en)_3]^{+3}$  is outer orbital complex

### Sol. Answer (2)



- 16. The IUPAC name of ferrocence is
  - (1) bis ( $\mu^5$ –Cyclopentadienyl) iron(0)
  - (3) bis ( $\eta^5$ –Cyclopentadienyl) iron(II)
- Sol. Answer (3)



bis ( $\eta^5$  –Cyclopentadienyl) iron (II)

- 17. The wave number of the radiation absorbed by [CoCl<sub>6</sub>]<sup>-4</sup> is 18000 cm<sup>-1</sup>, then the wave number of the radiation absorbed by [CoCl<sub>4</sub>]<sup>-2</sup> will be
  - (1)  $1800 \text{ cm}^{-1}$  (2)  $1000 \text{ cm}^{-1}$  (3)  $8000 \text{ cm}^{-1}$  (4)  $9000 \text{ cm}^{-1}$
- Sol. Answer (3)

$$\Delta_t = \frac{4}{9} (\Delta_0) \qquad \left[ \text{as E} = \frac{hc}{\lambda} = hc\overline{v} \therefore E \propto \overline{v} \right]$$
$$= \frac{4}{9} (18000) = 8000 \,\text{cm}^{-1}$$

- 18. Select the incorrect statement.
  - (1) Greater is the oxidation state of central metal ion greater is the stablility of the complex
  - (2) Chelate complexes have low stability constants
  - (3) CO forms stabilise complex because of its synergic bonding.
  - (4) Greater is the "stability constant" of a complex , greater is its stability

# Sol. Answer (2)

Chelate Complexes have greater stability.

- 19. Which of the following is the correct statement?
  - (1) The  $\pi$ -bond between metal and carbonyl. Carbon reduces the bond length of C–O in carbon monoxide
  - (2)  $dz^2$  orbital of central metal atom/ion is used in  $dsp^2$  hybridization
  - (3)  $\ddot{P}(CH_3)_3$  is a  $\pi$ -acid ligand
  - (4) All negative ligands are stronger than neutral ligands

# Sol. Answer (3)

Due to metal carbonyl bond, bond order between C and O reduces and hence bond length increases.

- $\rightarrow$  dx<sup>2</sup>–y<sup>2</sup> orbital of central metal atom is used in  $dsp^2$
- $\rightarrow$  P(CH<sub>3</sub>)<sub>3</sub> ligand can act as a sigma donar and a  $\pi$  acceptor ligand due to the presence of vacant *d*-orbitals
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- (2) bis ( $\eta^{10}$ –Cyclopentadienyl) iron(0)
- (4) bis ( $\mu^{10}$ –Cyclopentadienyl) iron(II)

20. In the isoelectronic species of metal carbonyl the C-O bond strength is expected to increase in the order.

(1)  $[Mn(CO)_6]^+ < [Cr(CO)_6] < [V(CO)_6]^-$  (2)  $[V(CO)_6]^- < [Cr(CO)_6] < [Mn(CO)_6]^+$ 

(3) 
$$[V(CO)_6]^- < [Mn(CO)_6]^+ < [Cr(CO)_6]$$

(4) 
$$[Cr(CO)_6] < [Mn(CO)_6]^+ < [V(CO)_6]^-$$

Sol. Answer (2)

More the number of  $e^-$  in d-orbitals of metal atom, will give more electrons into  $\pi^*$  MO of CO and hence bond order between C and O decreases

21. What will be the value of crystal field stabilisation energy of  $[Mn(H_2O)_6]^{+2}$ ?

Sol. Answer (2)

 $Mn^{+2} \rightarrow [Ar] 4s^0 3d^5$ 

22. How many total isomers including constitutional isomers and stereoisomers are possible for complex [Rh(en)<sub>2</sub>(NO<sub>2</sub>)(SCN)]<sup>+</sup>?

Sol. Answer (2)



Total number of isomers = 2 + 1 + 2 + 1 + 2 + 1 + 2 + 1 = 12

23. If the number of chelate rings in brown ring complex is "a" and in [Fe(EDTA)]<sup>-1</sup> is "b" and five membered rings in [Ni(DMG)<sub>2</sub>] is "c". Then what will be the value of (b + c − a)?



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(4)

4

Sol.	Answer (2)								
	In brown ring complex								
	$[Fe(H_2O)_5(NO)] SO_4 a = 0$								
	$[Fe(EDTA)]^{-1} b = 5$								
	and in Ni(DMG) <sub>2</sub> c = 2								
	b + c – a = 5 + 2 – 0 = 7								
24.	Choose the incorrect regarding stability.								
	(a) $[Fe(phen)_3]^{+2} > [Fe(phen)_3]^{+3}$	(b)	$[Fe(CN)_6]^{-4} > [Fe(CN)_6]^{-4}$	,] <sup>_3</sup>					
	(c) $Fe(dipy)_{3}^{+3} > Fe(dipy)_{3}^{+2}$								
	(1) a, b (2) b, c	(3)	a, c	(4)	a, b, c				
Sol.	Answer (1)								
	Due to synergic bonding.								
25.	Which of the following compound may be optical activ	/e?							
	(1) $Co(en)_2 Cl_2$	(2)	[Rh Cl Br NH <sub>3</sub> PH <sub>3</sub> ] <sup>-</sup>						
	(3) $Cu(en)_2Cl_2$	(4)	All of these						
Sol.	Answer (1)			S					
	Cu(en) <sub>2</sub> Cl <sub>2</sub> does not form isomer.								
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	Objective Type Questions (More	than	one options are correc	ct)					
1.	Objective Type Questions (More Identify the colourless complexes.	than •	one options are correc	ct)					
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1. Sol. 2. Sol. 3.	<b>Objective Type Questions (More</b> Identify the colourless complexes. (1) Ti(NO <sub>3</sub> ) <sub>4</sub> (2) [Cu(NCCH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup> BF <sub>4</sub> <sup>-</sup> Answer (1, 2) Ti <sup>+3</sup> and Cu <sup>+</sup> have no unpaired e <sup>-</sup> in <i>d</i> orbital. So, their Which of the following complexes are paramagnetic? (1) Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (2) [MnCl <sub>4</sub> ] <sup>2-</sup> Answer (1, 2) Ni <sup>+2</sup> and Mn <sup>+2</sup> have unpaired e <sup>-</sup> , so these are paramagnetic Identify the incorrect statements about [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> . (1) The complex is tetrahedral (3) Cu <sup>2+</sup> in the complex is <i>dsp</i> <sup>2</sup> hybridised Answer (1, 4)	(3) (3) (3) (3) (3) (2) (4)	one options are correct [Cr(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> bounds are colourless. [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> The complex is square Cu <sup>2+</sup> in the complex is	(4) (4) (4)	$K_3[VF_6]$ [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> ar				
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<ol> <li>Sol.</li> <li>Sol.</li> <li>Sol.</li> <li>Sol.</li> </ol>	<b>Objective Type Questions (More</b> Identify the colourless complexes.(1) Ti(NO3)4(2) $[Cu(NCCH3)4]^+BF4^-$ Answer (1, 2)Ti*3 and Cu* have no unpaired e <sup>-</sup> in <i>d</i> orbital. So, theirWhich of the following complexes are paramagnetic?(1) Ni(H2O)6]2+(2) $[MnCl4]2^-$ Answer (1, 2)Ni*2 and Mn*2 have unpaired e <sup>-</sup> , so these are paramagneticIdentify the incorrect statements about $[Cu(NH3)4]^2+$ .(1) The complex is tetrahedral(3) Cu2+ in the complex is $dsp^2$ hybridisedAnswer (1, 4) $[Cu(NH3)4]^2+$ is paramagnetic square planar complex $[Co(NH3)5NO2SO4$ shows	(3) (3) (3) (3) (2) (4) (4)	one options are correct [Cr(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> bounds are colourless. [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> The complex is square Cu <sup>2+</sup> in the complex is hich Cu <sup>+2</sup> show <i>dsp</i> <sup>2</sup> hyl	(4) (4) (4) s <i>sp</i> <sup>2</sup> f	$K_3[VF_6]$ [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> ar hybridised				
<ol> <li>Sol.</li> <li>Sol.</li> <li>Sol.</li> <li>Sol.</li> </ol>	<b>Objective Type Questions (More</b> Identify the colourless complexes. (1) Ti(NO <sub>3</sub> ) <sub>4</sub> (2) [Cu(NCCH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup> BF <sub>4</sub> <sup>-</sup> Answer (1, 2) Ti <sup>+3</sup> and Cu <sup>+</sup> have no unpaired e <sup>-</sup> in <i>d</i> orbital. So, their Which of the following complexes are paramagnetic? (1) Ni(H <sub>2</sub> O) <sub>6</sub> ] <sup>2+</sup> (2) [MnCl <sub>4</sub> ] <sup>2-</sup> Answer (1, 2) Ni <sup>+2</sup> and Mn <sup>+2</sup> have unpaired e <sup>-</sup> , so these are paramage Identify the incorrect statements about [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> . (1) The complex is tetrahedral (3) Cu <sup>2+</sup> in the complex is <i>dsp</i> <sup>2</sup> hybridised Answer (1, 4) [Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> is paramagnetic square planar complex [Co(NH <sub>3</sub> ) <sub>5</sub> NO <sub>2</sub> ]SO <sub>4</sub> shows (1) Ionisation isomerism	(3) (3) (3) (3) (1) (2) (4) (4) (2)	one options are correct [Cr(NH <sub>3</sub> ) <sub>6</sub> ]Cl <sub>3</sub> bounds are colourless. [Zn(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup> The complex is square Cu <sup>2+</sup> in the complex is hich Cu <sup>+2</sup> show <i>dsp</i> <sup>2</sup> hyl Coordination isomerism	<b>:t)</b> (4) (4) (4) ⇒ plan; ⇒ <i>sp</i> <sup>2</sup> I bridisa n	$K_3[VF_6]$ [Co(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup> ar hybridised				

#### **Sol.** Answer (1, 3)

 $[Co(NH_3)_5NO_2]SO_4$  can show linkage and ionization isomerism. Linkage isomerism is due to presence of ambidient  $NO_2^-$  ligand.

- 5. Which complexes show geometrical isomerism?
  - (1) Tetrahedral (2) Octahedral (3) Squa
    - Square planar (4) Linear

**Sol.** Answer (2, 3)

Octahedral and square planar complexes can show geometrical isomerism.



86	Co	ordination Compounds				Solut	tions of	Assignment (Level-II)	
11.	[Cr(	(CN) <sub>6</sub> ] [Co(NH <sub>3</sub> ) <sub>6</sub> ] contai	ins						
	(1)	Cationic complex	(2)	Anionic complex	(3)	Neutral ligands	(4)	Anionic ligands	
Sol.	Ans	swer (1, 2, 3, 4)							
	[Cr liga	$(CN)_6][Co(NH_3)_6]$ is a nd while $NH_3$ is a neutr	comp al liga	blex in which both ca ind.	tionic	and anionic part are	comple	ex, CN⁻ is a negative	
12.	Wh	ich of the following invo	lves s	p <sup>3</sup> hybridisation?					
	(1)	Ni(CO) <sub>4</sub>	(2)	[ZnCl <sub>4</sub> ] <sup>2-</sup>	(3)	[Ni(CN) <sub>4</sub> ] <sup>2-</sup>	(4)	[Cu(NH <sub>3</sub> ) <sub>4</sub> ] <sup>2+</sup>	
Sol.	Ans	swer (1, 2)							
	[Ni(	$(CO)_4$ ] and $[ZnCl_4]^{-2}$ N	li and	Zn involves sp <sup>3</sup> hybrid	dised.				
13.	Oth	er theories explaining the	he boi	nding in coordination	compo	ounds are			
	(1)	Ligand field theory			(2)	Molecular orbital the	ory		
	(3)	VSEPR theory			(4)	Atomic orbital theory	,		
Sol.	Ans	swer (1, 2)							
	Bor	nding in coordination co	mpou	nd is explained by					
	(1)	Ligand field theory.							
	(2)	M.O. Theory.					2		
14.	On is o	On mixing aqueous solution of copper sulphate with aqueous solution of ammonia a deep blue coloured solution s obtained. Choose the correct options :							
	(1)	The blue coloured solu	ition s	hows presence of Cu	<sup>2+</sup> ions				
	(2)	The blue coloured solu	ition d	loes not show presen	ce of (	Cu <sup>2+</sup> ions			
	(3)	The blue coloured solu	ition s	hows the presence of	[Cu(N	$[H_3)_4]^{2+}$ ions			
	(4)	The blue coloured solu	ition d	loes not show the pre	sence	of $[Cu(NH_3)_4]^{2+}$ ions			
Sol.	Ans	swer (2, 3)	4			STED			
	Blue	e colour is due to [Cu(I	NH <sub>3</sub> ) <sub>4</sub>	] <sup>+2</sup> complex which is	squa	re planar and <i>dsp</i> <sup>2</sup> hy	bridise	d.	
15.	The	e formation of complexe	s whic	ch involves <i>d</i> -orbitals	of oute	er shell are called			
	(1)	Low spin complexes		AL ON	(2)	High spin complexes	5		
	(3)	Inner orbital complexes	S		(4)	Outer orbital complex	xes		
Sol.	Ans	swer (2, 4)							
	Invo	olvement of <i>d</i> -orbital of	outer	shell is called high sp	oin cor	nplex and outer orbita	l comp	lex.	
16.	Wh	ich of the following ligar	nds ar	e $\pi$ acceptor?					
	(1)	NO	(2)	NO <sup>+</sup>	(3)	PF <sub>3</sub>	(4)	H <sub>2</sub> O	
Sol.	Ans	swer (1, 2, 3)							
	NO	, NO⁺, PF₃ from synerg	ic bor	iding.					
17.	[Co	(en) <sub>2</sub> NO <sub>2</sub> Br]Cl can exhi	bit						
	(1)	Geometrical isomerism	ı		(2)	Optical isomerism			
	(3)	Linkage isomerism			(4)	Ionisation isomerism			

Solu	utions of Assignment (Level-	II)				Coordinatio	on Compounds	87	
Sol	. Answer (1, 2, 3, 4)								
	NO <sub>2</sub> <sup>-</sup> can act as ambiden	t ligan	d.						
18.	Which of the following co	mplex	es may be coloured du	ue to o	d-d transition?				
	(1) [Ni(CO) <sub>4</sub> ]	(2)	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	(3)	[Cu(H <sub>2</sub> O) <sub>4</sub> ] <sup>+2</sup>	(4)	K <sub>3</sub> [Cu(CN) <sub>4</sub> ]		
Sol	. Answer (2, 3)								
	K₃[Fe(CN) <sub>6</sub> ] and [Cu(H₂O)₄] <sup>2+</sup> are paramagnetic, so show d-d transition.								
19.	Stability of the complex m	nay de	pend on						
	(1) Oxidation state			(2)	No. of <i>d</i> orbitals	in metal ior	ı		
	(3) Nature of ligands			(4)	Geometry of con	nplex			
Sol	. Answer (1, 2, 3, 4)								
	Square planar.								
20.	20. Which of following ions favour square planar geometry?								
	(1) Au <sup>+3</sup>	(2)	lr+	(3)	Pt <sup>+2</sup>	(4)	Hg <sup>+2</sup>		
Sol	. Answer (1, 2, 3)					10			
	Hg⁺² favour tetrahedral ge	ometr				ilons			
	SECTION - C								

#### Linked Comprehension Type Questions

### **Comprehension-I**

Consider the following isomers of  $[Co(NH_3)_4Br_2]^+$ . The black sphere represents Co, grey spheres represent  $NH_3$  and unshaded spheres represent Br.









(d)

- 1. Which of the following are cis-isomers?
  - (1) Isomers (a) and (b)
  - (3) Isomers (b) and (d)

- (2) Isomers (a) and (c)
- (4) Isomers (c) and (d)

Sol. Answer (2)

cis isomers are (a) and (c)



- 2. Which of the following are trans-isomers?
  - (1) Isomers (a) and (b)
  - (3) Isomers (b) and (d)

#### Sol. Answer (3)

Trans-isomers are (b) and (d)



- 3. Which structures are identical?
  - (1) None of the structures are identical
  - (2) Structure (a) = structure (b) and structure (c) = structure (d)
  - (3) Structure (a) = structure (c) and structure (b) = structure (d)
  - (4) Structure (a) = structure (d) and structure (b) = structure (c)

#### Sol. Answer (3)

Structure (a) is identical to (c) while structure (b) is identical to (d).

#### **Comprehension-II**

A coordination compound is a complex in which the numbers of ions or molecules attached to the central metal atom or ion is beyond the number possible, on the basis of electrovalent or covalent bonding. The extra groups or ions are linked to the metal by coordination bonds in which the linked group (L) is the donor and metal (M) is the acceptor *i.e.*  $M \leftarrow L$ . Coordination compounds are mainly of two types:

- (i) Neutral compounds like [Fe(CO)<sub>5</sub>]
- (ii) Ionic compounds, which consists of ions

in which atleast one is  $\sigma$  complex ion. e.g.  $K_4[Fe(CN)_6]$  complex ion : A complex ion is an electrically charged radical which consists of a metal atom or ion surrounded by a group of ions or neutral molecules. For example,  $[Cu(NH_3)_4]^{2+}$ ,  $[Fe(CN)_6]^{3-}$ . Ligands are defined as molecules or ions having atleast one pair of electrons for donation. Ligands are also known as Lewis bases.

1. How many ions are produced by  $[Co(NH_3)_6]Cl_3$  in solution?

(3) 3

(4) 2

Sol. Answer (2)

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

2. Which of the following is non-ionizable?

(1)  $[Co(NH_3)_3Cl_3]$  (2)  $[Co(NH_3)_4Cl_2]Cl$  (3)  $[Co(NH_3)_5Cl]Cl_2$  (4)  $[Co(NH_3)_6]Cl_2$ 

Sol. Answer (1)

 $[Co(NH_3)_3Cl_3]$  is non-ionizable.

- 3. AgCl dissolves in  $NH_4OH$  due to the formation of
  - (1)  $[Ag(NH_4)_2CI]$  (2)  $[Ag(NH_4)_3]CI$  (3)  $[Ag(NH_3)_2]CI$  (4)  $[Ag(NH_3)_2OH]$

Sol. Answer (3)

 $AgCI + NH_4OH \longrightarrow [Ag(NH_3)_2]CI$ 

- (2) Isomers (a) and (c)
- (4) Isomers (c) and (d)

#### Comprehension-III

	$X \longrightarrow$ Isomer					
	$A \xrightarrow{AgNO_3} Yellow ppt$					
	$B \xrightarrow{AgNO_3} White ppt$					
	Complexes 'A' and 'B' are hexacoo	rdinated complexes				
1.	Compound A may show					
	(1) Geometrical isomerism		(2)	Linkage isomerism		
	(3) Optical isomerism		(4)	All of these		
Sol.	Answer (4)					
	$B = [Co(en)_2(Br)(NO_2)]CI, A = [Co(en)_2(Br)(NO_2)]CI, $	n) <sub>2</sub> CINO <sub>2</sub> ]Br				
2.	How many total optically active form	ns of 'A' and 'B' are p	ossil	ole?		
	(1) 2 (2) 10	)	(3)	8	(4)	4
Sol.	Answer (3)					
	Only trans form are optically active				5	
		SECTION	I - C	)		
		Matrix-Match Typ	e Qu	lestions	1	
1.	Match the column			1 11 estim		
	Column I		Co	olumn II.		
	(A) [Ni(CN) <sub>4</sub> ] <sup>2-</sup>	(p)	d <sup>2</sup> .	sp <sup>3</sup>		
	(B) [Ni(CO) <sub>4</sub> ]	(q)	sp	$^{3}d^{2}$		
	(C) $[Co(en)_3]^{3+}$	(r)	ds	$p^2$		
	(D) [Co(Br) <sub>3</sub> Cl <sub>3</sub> ] <sup>3-</sup>	(s)	sp	3		
Sol.	Answer A(r), B(s), C(p), D(q)	A COL WISON				
	$[Ni(CN)_4]^{-2} \longrightarrow dsp^2$	Ar b.				
	$[Ni(CO)_4] \longrightarrow sp^3$					
	$[\operatorname{Co}(\operatorname{en})_3]^{+3} \longrightarrow d^2 s p^3$					
	$[\text{CoBr}_3\text{Cl}_2]^{-3} \longrightarrow sp^3d^2$					
2.	Match the column					
	Column I		Co	olumn II		
	(A) Glycinate ion	(p)	Bio	dentate		
	(B) EDTA	(q)	He	exadentate		
	(C) Oxalate	(r)	Mo	onodentate		
	(D) Sulphate	(s)	Le	wis base		

- **Sol.** Answer A(p, s), B(q, s), C(p, s), D(p, r, s)
  - Glycinate ion  $\rightarrow$  Bidentate, Lewis base

EDTA  $\rightarrow$  hexadentate, Lewis base

 $\mathsf{Oxalate} \to \mathsf{Bidentate}, \, \mathsf{Lewis} \, \, \mathsf{base}$ 

Sulphate  $\rightarrow$  Monodentate, Lewis base, sometimes bidentate also

3. Match the complex with its oxidation state of central metal

#### Column I

- (A) [Fe(CN)<sub>6</sub>]<sup>4-</sup>
- (B) [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>
- (C) [NiCl<sub>4</sub>]<sup>2-</sup>
- (D) [CoF<sub>6</sub>]<sup>3-</sup>
- **Sol.** Answer A(p, r), B(q, r), C(p, s), D(q, s)

 $[Fe(CN)_6]^{-4} \longrightarrow Fe^{+II}, d^2sp^3$ , diamagnetic

 $[Co(NH_3)_6]^{+3} \longrightarrow Co^{+3}, d^2sp^3$ , diamagnetic

 $[NiCl_4]^{-2} \longrightarrow Ni^{+2}$  paramagnetic

 $[CoF_6]^{-3} \longrightarrow Co^{+3}$ , paramagnetic

- 4. Match the given compound in column I to the properties given as per VBT in column II
  - Column I
  - (A)  $[Zn(H_2O)_4]^{2+}$
  - (B) [Pt(NH<sub>3</sub>)<sub>4</sub>] [PtCl<sub>4</sub>]
  - (C) Fe<sub>2</sub>(CO)<sub>9</sub>
  - (D)  $[Cu(NH_3)_4]^{2+}$
- **Sol.** Answer A(p, s), B(q, s), C(s, t), D(q, r)
  - Fe<sub>2</sub>(CO)<sub>9</sub> contain M–M bond.
  - In  $[Cu(NH_3)_4]^{2+}$ , Cu has  $dsp^2$  hybridisation.
- 5. Match the compound given in column I to the properties given in column II

# Column I

- (A)  $[Co(en)_2 ClBr]^+$
- (B)  $[Pt(NH_3)_2Cl_2]$
- (C)  $[Cu(NH_3)_6]^{+2}$
- (D) [Ni(dmg)<sub>2</sub>]

### Column II

- (p) Oxidation number of central metal is +2
- (q) Oxidation number of central metal is +3
- (r) Diamagnetic
- (s) Paramagnetic

(p) *sp*<sup>3</sup> hybridisation

Column II

- (q) dsp<sup>2</sup> hybridisation
- (r) Paramagnetic
- (s) Diamagnetic
- (t) Metal metal bond
  - Column II
- (p) Geometrical isomerism
- (q) Optical isomerism
- (r) All bond length are not equal
- (s) Chelation effect is present
- (t) Hydrogen bonding is present in complex

# **Sol.** Answer A(p, q, s), B(p), C(r), D(s, t)

#### Fact.

# **SECTION - E**

#### Assertion-Reason Type Questions

1. STATEMENT-1 : Zeise's salt contain  $C_2H_4$  molecule as one of the ligands. and

STATEMENT-2 : Zeise's salt is an organometallic compound.

Sol. Answer (2)

```
The formula of Zeise salt is [Pt(C_2H_4)Cl_3]^-.
```

2. STATEMENT-1 : Oxidation state of Fe in Fe(CO)<sub>5</sub> is zero.

#### and

STATEMENT-2 : EAN of Fe in its complexes is always 36.

#### Sol. Answer (2)

CO does not carry any charge.

 $EAN = 26 + 2 \times 5 = 36.$ 

3. STATEMENT-1 :  $[Co(NH_3)_3CI_3]$  does not give white ppt with AgNO<sub>3</sub> solution.

# and

STATEMENT-2 : Chlorine is not present in the ionisable part of the given complex.

# Sol. Answer (1)

[Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] does not ionize to give Cl<sup>-</sup>.

4. STATEMENT-1 : Tetrahedral complexes with chiral structure exhibit optical isomerism.

#### and

STATEMENT-2 : They lack plane of symmetry.

#### Sol. Answer (1)

Tetrahedral complex with chiral structure are optically active because these are dissymmetric.

5. STATEMENT-1 : The IUPAC name of  $K_4[Fe(C_2O_4)_3]$  is potassium trioxalatoferrate (III).

#### and

STATEMENT-2 : Oxalate ion is a bidentate ligand.

# Sol. Answer (4)

In  $K_4[Fe(C_2O_4)_3]$ , Fe is in + II oxidation state,  $\begin{bmatrix} COO \\ \\ \\ \\ \\ \\ COO^- \end{bmatrix}$  is a bidentate ligand.

6. STATEMENT-1 : Coordination isomerism occurs when both the cations and anions are complexes. and

STATEMENT-2 : Oxidation state of central metal ion in both coordination spheres is always equal.

#### Sol. Answer (3)

Oxidation state of central metal ion in both coordination sphere may be equal or different.

7. STATEMENT-1 : The  $[Ni(en)_3]Cl_2$  has higher stability than  $[Ni(NH_3)_6]Cl_2$ .

#### and

STATEMENT-2 : Ethylene diamine shows chelation with Ni<sup>+2</sup> ion.

#### Sol. Answer (1)

Due to chelation stability increases.

8. STATEMENT-1 : Co<sup>+2</sup> form octahedral stable complex with excess KCN.

#### and

STATEMENT-2 : CN<sup>-</sup> is stronger ligand than NH<sub>3</sub>.

Sol. Answer (4)

Co<sup>+2</sup> does not form octahedral complex with KCN.

9. STATEMENT-1 : CN<sup>-</sup> may act as bridging ligand.

#### and

STATEMENT-2 : Lone pair resides on carbon as well as on nitrogen.

Sol. Answer (2)

In CN<sup>-</sup> both C & N have lone pair.

10. STATEMENT-1 :  $Co(NH_3)_6^{+3}$  is more stable than  $(Co(en)_2(NH_3)_2)^{+3}$ 

#### and

STATEMENT-2 : Chelation is more in [Co(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>+3</sup> than [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>+3</sup>

#### Sol. Answer (4)

Due to chelation,  $[Co(en)_2(NH_3)_2]$  is more stable.

11. STATEMENT-1 : In square planar complexes,  $d_{x^2-y^2}$  is higher in energy than  $d_{xy}$ 

#### and

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STATEMENT-2 : Ligands approach along x and y axis.
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Sol. Answer (1)
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Fact.

12. STATEMENT-1 : CH<sub>3</sub> MgCl is σ organometallic complex.

#### and

STATEMENT-2 : In ether RMgCl, co-ordination number of Mg is 6.

Sol. Answer (2)

 $CH_3$ –Mg–Cl is  $\sigma$  bonding complex.

13. STATEMENT-1 : Fe(CO)<sub>5</sub> has trigonal bipyramidal shape.

#### and

STATEMENT-2 : Fe(CO)<sub>5</sub> is diamagnetic.

Sol. Answer (2)

 $Fe(CO)_5$  is paramagnetic.

14. STATEMENT-1 : Fe – CN bond length is smaller in  $Fe(CN)_6^{-4}$  than  $Fe(CN)_6^{-3}$ .

#### and

STATEMENT-2 :  $Fe(CN)_6^{-3}$  is more stable than  $Fe(CN)_6^{-4}$ .

#### Sol. Answer (2)

Due to synergic bond.

15. STATEMENT-1 : Ni(dmg)<sub>2</sub> is square planar complex.

#### and

STATEMENT-2 : Chelation effect is present in Ni(dmg)<sub>2</sub>.

Sol. Answer (2)

Ni(dmg)<sub>2</sub> is square planar complex.

# **SECTION - F**

#### **Integer Answer Type Questions**

- 1. How many sp<sup>3</sup> hybridised atoms are there in one molecule of CuSO<sub>4</sub>.5H<sub>2</sub>O?
- Sol. Answer (6)

 $H_2O$  and  $SO_4$  have  $sp^3$  hybridisation.

- 2. How many type of geometrical isomers are possible for  $[M(NH_3)BrCl(H_2O)]$ , where M is Pt<sup>+2</sup>?
- Sol. Answer (3)
  - If M = Pt then geometry is square planar.
- 3. The coordination number of Fe in  $\left[ Fe(\eta^5 C_5H_5)_2 \right]$  is 2x. Then x will be\_\_\_\_\_
- Sol. Answer (5)

Co-ordination number of Fe is 10.

- 4. How many geometrical isomers are possible for [Zn(NH<sub>3</sub>)ClBrPPh<sub>3</sub>]<sup>-</sup>?
- Sol. Answer (0)

It is tetrahedral complex.

- 5. How many geometrical isomers are possible for MA2B2C2?
- Sol. Answer (5)

Fact.

- 6. How many rings are present in [MEDTA]<sup>+n</sup>?
- Sol. Answer (5)

Due to Chelation.

- 7. How many maximum atoms are present in one plane of  $[PtCl_3(\eta^2C_2H_4)]^-$ ?
- Sol. Answer (4)

 $C_2H_4$  is perpendicular to plane of and Cl<sup>-</sup> Pt<sup>+2</sup>

8. How many metal-metal bonds are present in  $Co_4(CO)_{12}$ ?

Sol. Answer (6)

Fact.

Some complexes are given below out of which x complexes are diamagnetic then value of x<sup>2</sup> is K<sub>4</sub>[Fe(CN)<sub>6</sub>], K<sub>3</sub>[Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>], K<sub>2</sub>[Ni(CN)<sub>4</sub>], K<sub>3</sub>[Cu(CN)<sub>4</sub>], K<sub>3</sub>[Fe(CN)<sub>6</sub>], K<sub>2</sub>[PtCl<sub>4</sub>], K<sub>3</sub>[CoF<sub>6</sub>], [Fe(H<sub>2</sub>O)<sub>5</sub>(NO)]<sup>2+</sup>.

Sol. Answer (25)

```
K<sub>4</sub>[Fe(CN)<sub>6</sub>], K<sub>3</sub> [Co(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]
K<sub>2</sub>[Ni(CN)<sub>4</sub>], K<sub>3</sub> [Cu(CN)<sub>4</sub>]
K_2 [Pt(CI)_4]
```

10. The total number of structural isomers of compound  $[Co(H_2O)_2(NH_3)(CN)_3]$  are P then  $3P^2$  is

# Sol. Answer (48)

```
[Co (H<sub>2</sub>O)<sub>2</sub> (NH<sub>3</sub>) (CN)<sub>3</sub>]
[Co (H<sub>2</sub>O)<sub>2</sub> (NH<sub>3</sub>) (CN)<sub>2</sub> (NC)]
[Co (H<sub>2</sub>O)<sub>2</sub> (NH<sub>3</sub>) (CN) (NC)<sub>2</sub>]
[Co (H<sub>2</sub>O)<sub>2</sub> (NH<sub>3</sub>) (NC)<sub>3</sub>]
P = 4
P^2 = 16
```

11. Consider the coordination compound [Co(Gly)<sub>3</sub>]

If number of geometrical isomers is x and y is number of enantiomeric pairs possible, then value of  $x^2 + y^2$  is



