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CHEMISTRY

TARGET : JEE Advanced - 2021

CAPS – 8

Coordination Compound

Answer Key

1.	(D)	**2.**	(C)	**3.**	(A)	**4.**	(D)	**5.**	(A)
6.	(B)	**7.**	(A)	**8.**	(C)	**9.**	(B)	**10.**	(B)
11.	(C)	**12.**	(B)	**13.**	(D)	**14.**	(A)	**15.**	(ABD)
16.	(ABD)	**17.**	(ABCD)	**18.**	(ABC)	**19.**	(2.00)	**20.**	(1.00)
21.	(7.0)	**22.**	(B)	**23.**	(D)	**24.**	(D)		

Solution

1. (I) Both Co^{2+} and Co^{3+} are stabilized in the presence of strong field ligands due to higher CFSE values.

(II) Because of higher Z_{eff} value on the valence shell of Pd^{2+} and Pt^{2+} cations they, always form inner orbital complex.

(III) $[Ni(CO)_4]$; sp^3, tetrahedral, $\mu = 0$ BM

$[Ni(CN)_4]^{4-}$; sp^3, tetrahedral, $\mu = 0$ BM

(IV) $Ni^{2+} = 3d^8$

2. Order of strength of ligand: en > NH_3 > H_2O

$\therefore$ Order of Δ_0 is $\Delta_{en} > \Delta_{NH_3} > \Delta_{H_2O}$

3. Peroxide ion is diamagnetic while dioxygen is paramagnetic.

Conc. H_2SO_4 can dehydrate water of crystallization from $[CrCl(H_2O)_5]Cl_2.H_2O$ but it cannot remove those water molecules which are working as ligands.

4. $[Co(en)_3][Cr(C_2O_4)_3]$, $[Co(C_2O_4)(en)_2][Cr(C_2O_4)_2(en)]$,

$[Cr(C_2O_4)(en)_2][Co(C_2O_4)_2(en)]$

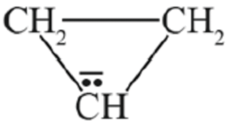
$[Co(en)_3]$ $[Co(C_2O_4)_3]$, Total coordination isomers = 4

$[Cu(NH_3)_4][CuCl_4]$, $[CuCl(NH_3)_3][CuCl_3(NH_3)]$ Total coordination isomers = 2

$[Ni(en)_3][Co(NO_2)_6]$, $[Ni(NO_2)_2(en)_2][Co(NO_2)_4(en)]$,

$[Co(NO_2)_2(en)_2][Ni(NO_2)_4(en)]$, $[Co(en)_3][Ni(NO_2)_6]$ Total number of coordination isomers = 4

5. No vacant 'd' or π^* orbitals on



6. (A) The complexes $[Cr(en)_2Cl_2]^+$ and $[Co(C_2O_4)_2(NH_3)_2]^-$ contain different ligands and different metal ions. Hence, they have different stabilities.

(B) Both complexes are of the type $[M(AA)_2a_2]^{n\pm}$. Hence, they have equal number of stereoisomers.

(C) $[Cr(en)_2Cl_2]^+$ is paramagnetic with 3 unpaired electrons and $[Co(C_2O_4)_2(NH_3)_2]^-$ is diamagnetic with zero unpaired electrons.

7. $K_3[Fe(CN)_6] + FeCl_3 \rightarrow Fe[Fe(CN)_6] + 3KCl$

8. NO_2 ligands at cis-position only are exchangeable

9. For the given compound two geometrical isomers are possible one is cis and the other is trans. The molecule does not contains any element of symmetry (such as plane of symmetry) and is optically active.

10. Total number of stereo isomers of $[Co(acac)_2BrCl]^-$ are 3, i.e., cis, trans, optical.

11. (Amminebromochloromethylamineplatinum) (II) represents the correct IUPAC name. The ligands are arranged in alphabetical order. The oxidation state of the complex is written in roman parenthesis. The names of the ligand and the metal are correctly spelled.

12. The complex is $[CoNO_3(NH_3)_5]SO_4$.

$$\frac{0.020L \times 0.1mol/L\,NaOH \times 1mol\,acid}{1mol\,NaOH} = 0.0020\,mol\ acid$$

$$\frac{0.0020\,mol}{10^{-3}mol} = 2$$

As 2 moles of acid in the exchanger replaced each 1 mole of complex cations, so the complex must have an oxidation state of +2, so the complex will be $[CoNO_3(NH_3)_5]SO_4$.

13. A: C – C bond length in Zeise's salt is longer than ethylene, indicating some $d\pi - p\pi^*$ backbonding from the platinum atom to C_2H_4.

14. CFSE in octahedral complex.

$$CFSE = \left[-\frac{2}{5}(\text{no. of electron in } t_2g) + \frac{3}{5}(\text{No. of es in eg}\right]\Delta o.$$

S_1 : $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are paramagnetic having four, five and four unpaired electrons respectively.

S_2 : High value of formation constant of a complex indicates its high thermodynamic stability.

S_3 : The crystal field splitting Do, depends upon the field produced by the ligand and charge on the metal ion.

15. $[Tc(CO)_6]^+$ E.A.N. of Tc = 43 – 1 + 6 × 2 = 54 (Xe)

$[Nb(CO)_6]^-$ E.A.N. of Nb = 41 + 1 + 6 × 54 (Xe)

Hence, both complexes are stable and they cannot act as oxidizing or reducing agent.

Extent of $M \xrightarrow{\pi} CO$ back bonding in $[Nb(CO)_6]^-$ is greater than in $[Tc(CO)_6]^+$, hence

Bond order of Nb – C > bond order of Tc – C

Bond order of C – O in $[Tc(CO)_6]^+$ > C – O bond order in $[Nb(CO)_6]^-$

16. Let X be the oxidation number of iron in $Na_2[Fe(CN)_5NO]$

$2(+1) + X + 5(-1) + 1 = 0$ or $X = +2$.

Thus the oxidation number of iron in $Na_2[Fe(CN)_5NO]$ is +2.

In $[Fe(H_2O)_6]^{3+}$

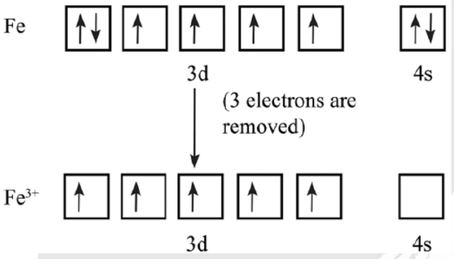
Electronic configuration of Fe is: $[Ar]3d^6 4s^2$

$[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Electronic configuration of $Fe^{+3} = [Ar]3d^5$

Outer electronic configuration of $Fe^{+3} = 3d^5$

Oxidation number of Fe is +3



Its sp^3d^2.

17. cis-$[CoBrCl(en)_2]^+$ will exhibit optical isomerism. No. of geometrical isomers of $[Pt(NO_2)(NH_3)(NH_2OH)py]^{3+}$ and space isomers for $[PtBrCl](NO_2)(NH_3)(py)$ are 30. cis and trans forms are diastereomers to each other.

18. (A) No unpaired electrons in Fe^{2+} but O_2 has unpaired electron.

(B) (O_2) is O_2 i.e., superoxide ion which has B.O (1.5) less than O_2 molecule (2.0) and thus this statement is correct.

(C) Total negative charge of negative ligands in coordination sphere is -6. So oxidation state of Fe is (II) and thus its IUPAC name is correct.

(D) It has a plane of symmetry; thus, it does not show optical isomers.

19. (i) $[Cr(Ox)_3]^{3-}$: optically active.

(ii) $[Pt(Cl_2)(en)]$: Optically inactive

(iii) cis-$[Rh(Cl_2)(NH_3)_4]^+$: optically inactive

(iv) $[Ru(dipy)_3]^{3+}$ optically active

(v) cis-$[Co(NO_2)_3(dien)]$: optically inactive

(vi) trans-$[Co(NO_2)_3(dien)]$: optically inactive

(vii) cis-$[Co(NO_2)_3(NH_3)_3]$: optically inactive

⇒ Total number of optically active complexes = 2

20. $P = NH_2^-, O_2^-, OH^-, Cl^- = 4$

$Q = SO_4^{2-}, NO_2^-, CO_3^{2-}, CH_3COO^- = 4$

R = en, acac, Phen, DMG, Gly = 5

S = DMG, Gly = 2

4 + 4 – 5 – 2 = 1

21. $[PdCl_4]^{2-}$, $[Ni(CN)_4]^{2}$, $[Pd(CN)_4]^{2-}$, Cis platin, Zeise's salt, Willkinson's catalyst, $[Cu(NH_3)_4]^{2+}$, $[Ni(Gly)_2]$ have dsp^2 hybridization .

22. $[Pt(NO_2)_2(en)]^{2+}$

→ E.A.N. = 78 – 4 + 12 = 86 ($_{86}$Rn)

→ Co-ordination number of Pt = 6

$[Cr(\pi\text{-}C_6H_6)(NO)_2]$

→ E.A.N. = 24 + 6 + 2 x 3 = 36 ($_{36}$Kr)

→ Synergic bonding is present hence, bond order of M – L bond > 1.0 and bond order of ligand decreases.

→ Co-ordination number for central metal not applicable.

$[Ir(SCN)(SO_4)(NH_3)_4]$

→ E.A.N. = 77 – 3 + 12 = 86 ($_{86}$Rn)

→ SCN^- : Ambidentate ligand

→ Co-ordination number of central metal = 6

$[Cr(C_2H_4)(CO)_5]$

→ E.A.N. = 24 + 2 + 10 = 36($_{36}$Kr)

→ Synergic bonding is present hence, bond order of M – L bond > 1.0 and bond order of ligand decrease.

→ Co-ordination number of central metal = 6

23. Sodium nitroprusside – $Na_2[Fe(CN)_5NO]$

Hyb^n. – d^2sp^3; $\mu = 0$; octahedral, NO^+ ligand

Brown ring $[Fe(H_2O)_5NO]^{2+}$

Hyb^n. – sp^3d^2; octahedral, m = 3.89 BM, NO^+ ligand

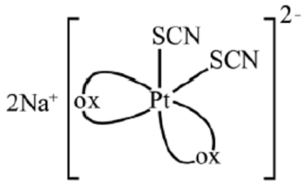
Complex formed during extraction of Ag is $[Ag(CN)_2]^-$

Hyb^n – sp; linear, $\mu = 0$

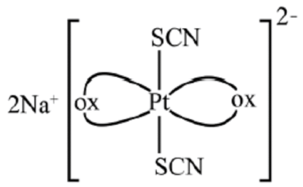
Potassium ferrocyanide – $K_4[Fe(CN)_6]$

Hyb^n – d^2sp^3; octahedral, $\mu = 0$

24. (A) SCN^- is ambidentate ligand, therefore it shows linkage isomerism



cis-form



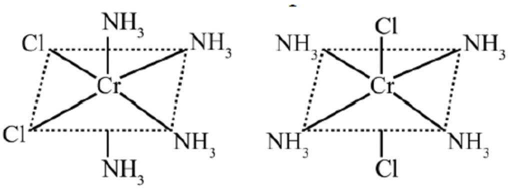
trans-form

cis form is optically active.

(B) $[CrCl_2(NH_3)_4]NO_3$

$[Cr(Cl)(NO_3)(NH_3)_4]Cl$

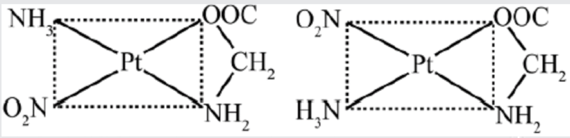
Ionization isomer of complex



cis-form trans-form

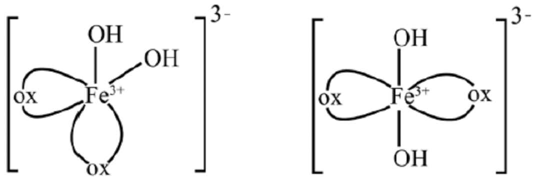
Both cis and trans-form are optically inactive

(C)



NO_2^- is ambidentate ligand so it also shows linkage isomerism. It is optically inactive square planar complex.

(D) $K_3[Fe(OH)_2(C_2O_4)_2]$



cis-form Optically active

trans-form Optically active

25. (i) $H_2O_6Cl_3Cr$

A should be $[Cr(H_2O)_6]Cl_3$ because it is not reacting with H_2SO_4. If there would have some moles of water outside the coordination sphere, then it will be reacting with H_2SO_4

(B) weight of $H_{12}O_6Cl_3Cr = 266.5$

$$266.5 \times \frac{6.73}{100} = 17.96 \approx 18(H_2O\,\text{weight})$$

It means one mole of H_2O in B complex outside the coordination sphere

$B = [Cr[H_2O]_5Cl]Cl_2.H_2O$

(C) $266.5 \times \frac{13.5}{100} \approx 36(2H_2O\,\text{weight})$

It means $C = [Cr(H_2O)_4Cl_2]Cl.2H_2O$

(ii) $A = [Cr(H_2O)_6]Cl_3$; $B = [Cr(H_2O)_5Cl]Cl_2.H_2O$; $C = [Cr(H_2O]_4Cl_2]Cl.2H_2O$

(iii) EAN = 33

(iv) C – 1 mole AgCl ppt; B – 2 mole AgCl ppt; A – 3 mole AgCl ppt