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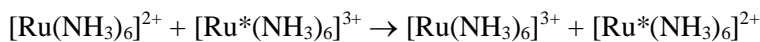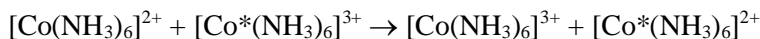@Madchem Classes Chemistry
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1. According to crystal filed theory, Ni^{2+} can have two unpaired electrons in   **[NET JUNE 2011]**

   (a) Octahedral geometry only   (b) Square–planar geometry only

   (c) Tetrahedral geometry only   (d) Both octhahedral and tetrahedral geometry.

2. The correct order of stability if difluorides is :   **[NET JUNE 2011]**

   (a) $GeF_2 > SiF_2 > CF_2$ (b) $CF_2 > SiF_2 > GeF_2$

   (c) $SiF_2 > GeF_2 > CF_2$ (d) $CF_2 > GeF_2 > SiF_2$

3. The number of possible isomers for $[Ru(bpy)_2Cl_2]$ is (bpy = 2,2'–bipyridine)   **[NET JUNE 2011]**

   (a) 2   (b) 3   (c) 4   (d) 5

4. Cis and trans complexes of the type $[PtA_2X_2]$ are distinguished by   **[NET JUNE 2011]**

   (a) Chromyl chloride test   (b) Carbylamine test

   (c) Kurnakov test   (d) Ring test

5. The correct order of LMCT energies is :   **[NET JUNE 2011]**

   (a) $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$ (b) $MnO_4^- > CrO_4^{2-} > VO_4^{3-}$

   (c) $MnO_4^- > CrO_4^{2-} < VO_4^{3-}$ (d) $MnO_4^- < CrO_4^{2-} > VO_4^{3-}$

6. Consider two redox pairs   **[NET JUNE 2011]**

   (1) Cr(II)/Ru(III)   (2) Cr(II)/Co(III)

   The rate of acceleration in going from a outer–sphere to a inner-sphere mechanism is lower for

   (1) relative to

   (2) Its correct explanation is :

   (a) HOMO/LUMI are σ* and σ* respectively

   (b) HOMO/LUMO are σ* and π* respectively

   (c) HOMO/LUMO are π* and σ* respectively

   (d) HOMO/LUMO are π* and π* respectively.

7. For the complexes   **[NET JUNE 2011]**

   (A) $[Ni(H_2O)_6]^{2+}$ (B) $[Mn(H_2O)_6]^{2+}$ (C) $[Cr(H_2O)_6]^{3+}$ (D)$[Ti(H_2O)_6]^{3+}$,

   the ideal octahedral geometry will not be observed in

   (a) (A) and (B)   (b) (C) and (D)   (c) (B) only   (d) (D) only

8. $Ni(CN_4)^{2-}$ and $Ni(Cl_4)^{2-}$ complex ions are: **[NET JUNE 2011]**

   (a) Both diamagnetic.

   (b) Both paramagnetic

   (c) Diamagnetic and paramagnetic respectively

   (d) Antiferromagnetic and diamagnetic respectively

9. The complex $[Mn(H_2O)_6]^{+2}$ has very light pink colour. The best reason for it is   **[NET JUNE 2011]**

   (a) The complex does not have a charge transfer transition.

   (b) d-d transitions here are orbital for bidden but spin allowed

(c) d-d transitions here are orbital allowed but spin forbidded.

(d) d-d transitions here are both orbital forbidden and spin forbidden.

10. The possible J values for ^3D term symbol are   **[NET JUNE 2011]**

(a) 2   (b) 3   (c) 4   (d) 5

11. The term symbol for the ground state of nitrogen atoms is   **[NET JUNE 2011]**

(a) $^3P_0$ (b) $^4P_{3/2}$ (c) $^1P_1$ (d) $^4S_{3/2}$

12. The complex that absorbs light of shortest wavelength is   **[NET DEC 2011]**

(a) $[CoF_6]^{3-}$ (b) $[Co(H_2O)_6]^{3+}$ (c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(ox)_3]^{3-}$ $(ox=C_2O_4^{2-})$

13. Observe the following electronic transition of a diatomic molecule.   **[NET DEC 2011]**

(a) $^1\Sigma + g \rightarrow {}^3\Sigma + g$ (b) $^1\Sigma + g \rightarrow {}^3\Sigma + g$ (c) $^1\Sigma + g \rightarrow {}^3\Sigma + g$ (d) $^1\Sigma + g \rightarrow {}^3\Sigma + g$

The allowed transitions are

(a) (A) and (c) only   (b) (B) and (D) only   (c) (A), (B) and (C) only   (d) (A), (C) and (D) only

14. The electronic spectrum of $[CrF_6]^{3-}$ shows three bands at 14, 900 cm^{-1}, 22400 cm^{-1} and 34,800 cm^{-1}. The value of Δ_o in this case is :   **[NET DEC 2011]**

(a) 5, 500 cm^{-1} (b) 14, 900 cm^{-1} (c) 22, 400 cm^{-1} (d) 34, 800 cm^{-1}

15. The actual magnetic moment shows a large deviation from the spin-only formula in the case of **[NET DEC 2011]**

(a) Ti^{3+} (b) V^{3+} (c) Gd^{3+} (d) Sm^{3+}

16. Green coloured Ni $(PPh_2Et)_2$ Br_2, has a magnetic moment of 3.20 B.M. The geometry and the number of isomers possible for the complex respectively, are   **[NET DEC 2011]**

(a) square planar and one   (b) tatrahedral and one

(c) Square planer and two   (d) tetrahedral and two

17. The correct order of acidity among the following species is   **[NET DEC 2011]**

(a) $[Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+}$

(b) $[Sc(H_2O)_6]^{3+} > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > [Na(H_2O)_6]^+$

(c) $[Mn(H_2O)_6]^{2+} > [Ni(H_2O)_6]^{2+} > [Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+$

(d) $[Sc(H_2O)_6]^{3+} > [Na(H_2O)_6]^+ > [Ni(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+}$

18. A true statement about base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ is :   **[NET DEC 2011]**

(a) It is a first order reaction

(b) The rate determining step involves the dissociation of chloride in $[Co(NH_3)_4(NH_2)Cl]^+$.

(c) The rate is independent of the concentration of the base

(d) The rate determining step involves the abstraction of a proton from $[Co(NH_3)_5Cl]^2$.

19. The correct order of d-orbital splitting in a trigonal bipyramidal geometry is :   **[NET DEC 2011]**

(a) $d_{z^2} > d_{xz} > d_{x^2-y^2}, d_{xy}$ (b) $d_{xz}, d_{yz} > d_{x^2-y^2}, d_{xy} > d_{z^2}$

(c) $d_{x^2-y^2}, d_{xy} > d_{z^2} > d_{xz}, d_{yz}$ (d) $d_{z^2} > d_{x^2-y^2}, > d_{xy} > d_{xz}, d_{yz}$

20. For the following outer sphere electron transfer reactions.   **[NET DEC 2011]**

$$[Co(NH_3)_6]^{2+} + [Co*(NH_3)_6]^{3+} \rightarrow [Co(NH_3)_6]^{3+} + [Co*(NH_3)_6]^{2+}$$

$$[Ru(NH_3)_6]^{2+} + [Ru*(NH_3)_6]^{3+} \rightarrow [Ru(NH_3)_6]^{3+} + [Ru*(NH_3)_6]^{2+}$$

the rate constants are 10^{-6} M^{-1} s^{-1} and 8.2×10^2 M^{-1} s^{-1} respectively. This difference in the rate constants is due to

(a) A change from high spin to low spin in Co* and high spin to low spin in Ru.

(b) A change from high spin to low spin in Co* and low spin to high spin Ru*

(c) A change from low spin to high spin in Co* and the low spin state remains unchanged in Ru.

(d) A change from low spin to high spin in Co* and high spin to low spin in Ru*

21. As a ligand Cl$^-$ is :   **[NET JUNE 2012]**

   (a) Only a σ – donor   (b) Only a π – donor

   (c) Both a σ–donor and a π–donor   (d) A σ–donor and a σ–acceptor

22. The number of microstates for d^5 electron configuration is :   **[NET JUNE 2012]**

   (a) 21×6^3 (b) 14×6^3 (c) 7×6^2 (d) 28×6^3

23. The correct d-electron configuration showing spin-orbit coupling is   **[NET JUNE 2012]**

   (a) $t_{2g}^4 \, e_g^2$ (b) $t_{2g}^6 \, e_g^0$ (c) $t_{2g}^4 \, e_g^0$ (d) $t_{2g}^3 \, e_g^2$

24. The number of spin-allowed ligand field transitions for octahedral Ni(II) complexes with $^3A_{2g}$, ground state is :

   [NET JUNE 2012]

   (a) Two   (b) Three   (c) One   (d) Four

25. The light pink color of $[Co(H_2O)_6]^{+2}$ and the deep blue color of $[Co(Cl_4]^{-2}$ are due to   **[NET DEC 2012]**

   (a) MLCT transition in the first and d-d transition in the second

   (b) LMCT transition in both

   (c) d-d transitions in both.

   (d) d-d transition in the first and MLCT transition in the secon.

26. The total number of Cu–O bonds present in the crystalline copper (II) acetate monohydrate is: **[NET DEC 2012]**

   (a) 10   (b) 6   (c) 8   (d) 4

27. The electric dipole allowed transition in a d2 atomic system is   **[NET DEC 2012]**

   (a) $^3F \rightarrow {}^1D$ (b) $^3F \rightarrow {}^1P$ (c) $^3F \rightarrow {}^3D$ (d) $^3F \rightarrow {}^3P$

28. Coordination number of "C" in Be$_2$C$_3$ whose structure is correlated with that of CaF$_2$ is : **[NET DEC 2012]**

   (a) 2   (b) 4   (c) 6   (d) 8

29. One of the excited states of Ti has the electric configuration [Ar] $4s_2$ $3d_1$ $4p_1$. The number of microstates with zero total spin (s)for this configuration is   **[NET DEC 2012]**

   (a) 9   (b) 15   (c) 27   (d) 60

30. The number of possible isomers of [Ru(PPh3)2(acac)2] (acac = acetylacetonate) is: **[NET DEC 2012]**

   (a) 2   (b)3   (c) 4   (d) 5

31. The correct spinel structure of Co$_3$O$_4$ is :   **[NET DEC 2012]**

   (a) $(Co^{2+})_t \, (2Co^{3+})_o O_4$ (b) $(Co^{2+})_t \, (2CO^{3+}Co^{3+})_o O_4$

(c) $(Co^{2+}Co^{3+})_t (Co^{3+})_oO_4$
(d) $(2Co^{3+})_t (Co^{2+})oO_4$

32. In the solid state, the $CuCl_5^{3-}$ ion has two types of bonds. These are **[NET DEC 2012]**

(a) Three long and two short
(b) Two long and three short

(c) One lone and four short
(d) Four long and one short

33. The platinum complex of NH_3 and Cl^- ligands is an anti-tumour agent. The correct isomeric formula of the complex and its precursor are **[NET DEC 2012]**

(a) cis-$Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$
(b) trans–$Pt(NH_3)_2Cl_2$ and $PtCl_4^{2-}$

(c) cis – $Pt(NH_3)_2Cl_2$ and $Pt(NH3)_4^{2+}$
(d) trans-pt $(NH_3)_2Cl_2$ and $Pt(NH_3)_4^{2-}$

34. Succesive addition of NaCl, H_3PO_4, KSCN and NaF to a solution of $Fe(NO_3)_3.9H_2O$ gives yellow, colourless, red and again colorless solutions due to the respective formation of : **[NET DEC 2012]**

(a) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_5F]^{2+}$

(b) $[Fe(H_2O)_4Cl(OH)]^+$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_5F]^{2+}$

(c) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[Fe(H_2O)_5(SNC)]^{2+}$, $[Fe(H_2O)_5]^{2+}$

(d) $[Fe(H_2O)_5Cl]^{2+}$, $[Fe(H_2O)_5(PO_4)]$, $[Fe(H_2O)_5(SCN)]^{2+}$, $[Fe(H_2O)_4(SCN)F]^+$

35. The rate of exchange of OH_2 present in the coordination sphere by $^{18}OH_2$ of , (i) $[Cu(OH)_2]_6]^{2+}$, (ii) $[Mn(OH_2)_6]^{2+}$, (iii) $Fe(OH_2)_6]^{2+}$, (iv) $[Ni(OH_2)_6]^{2+}$, follows an order. **[NET DEC 2012]**

(a) (i) > (ii) > (iii) > (iv)
(b) (i) > (iv) > (iii) > (ii)

(c) (ii) > (iii) > (iv) > (i)
(d) (iii) > (i) > (iv) > (ii)

36. For an electronic configuration of two non-equivalent π electronics $[\pi_1, \pi_1]$ which of the following terms is not possible ? **[NET JUNE 2013]**

(a) 1Σ (b) 3Σ (c) 3Δ (d) 3ϕ

37. The reaction of $[PtCl_4]^{2-}$ with two equivalents of NH_3 produces **[NET JUNE 2013]**

(a) cis–$[Pt(NH_3)_2Cl_2]$

(b) trans–$[Pt(NH_3)_2Cl_2]$

(c) boths cis – $[Pt(NH_3)_2Cl_2]$ and trans–$[Pt(NH_3)_2Cl_2]$

(d) cis–$[Pt(NH_3)Cl_4]^{2-}$

38. The electronic transition responsible for the color of the transition metal ions is **[NET JUNE 2013]**

(a) $d_\pi \to d_\sigma$ (b) $d_\pi \to d_{\sigma^*}$ (c) $d_\pi \to d_{\pi^*}$ (d) $d_\sigma \to d_{\pi^*}$

39. The Mulliken symbols for the spectroscopic states arising from the free-ion term F are **[NET JUNE 2013]**

(a) $T_{2g} + E_g$ (b) $T_{1g} + T_{2g} + T_{1u}$ (c) $T_{1g} + T_{2g} + A_{2g}$ (d) $A_{1g} + T_{2g} + T_{1g}$

40 The orders of reactivity of ligands, NMe_3, PMe_3 and CO with complexes $MeTiCl_3$ and $(CO)_5 Mo(thf)$ are

[NET JUNE 2013]

(a) CO > PMe_3 > NMe_3 and CO> NMe_3 > PMe_3
(b) PMe_3 > CO > NMe_3 and NMe_3 > CO > PMe_3

(c) NMe_3 > PMe_3 > CO and CO > PMe_3 > NMe_3
(d) NMe_3 > CO > PMe_3 and PMe_3 > NMe_3 > CO

41. Silica gel contains $[CoCl_4]^{2-}$ as an indicator. When activated, silica gel becomes dark blue while upon absorption of moisture, its colour changes to pale pink. This is because, **[NET JUNE 2013]**

    (a) Co(II) changes its coordination from tetrahedral to octahedral.

    (b) Co(II) changes its oxidation state to Co(III)

    (c) Tetrahedral crystal field splitting is NOT equal to octahedral crystal field splitting.

    (d) Co(II) forms kinetically labile while Co(III) forms kinetically inert complexes.

42. Intense band at 15000 cm^{-1} in the UV-visible spectrum of $[Bu_4N]_2Re_2Cl_8$ is due to the transition

    [NET JUNE 2013]

    (a) $\pi - \pi^*$ (b) $\delta - \delta^*$ (c) $\delta - \pi^*$ (d) $\pi - \delta^*$

43. Identify the order representing increasing π–acidity of the following ligands C_2F_4, NEt, CO and C_2H_4

    [NET JUNE 2013]

    (a) $CO < C_2F_4 < C_2H_4 < NEt_3$ (b) $C_2F_4 < C_2H_4 < NEt_3 < CO$

    (c) $C_2H_4 < NEt_3 < CO < C_2F_4$ (d) $NEt_3 < C_2H_4 < C_2F_4 < CO$

44. Three bands in the electronic spectrum of $[Cr(NH_3)_6]^{3+}$ are due to the following transitions

    [NET JUNE 2013]

    (A) $^4A_{2g} \rightarrow {}^4T_{1g}$ (B) $^4A_{2g} \rightarrow {}^4T_{2g}$ (c) $^4A_{2g} \rightarrow {}^2E_g$

    Identify the correct statement about them

    (a) Intensity of (A) is lowest   (b) Intensity of (C) is lowest

    (c) Intensitites of (A), (B) and (C) similar   (d) Intensities (B) and (C) are similar

45. The Δt of the following complexes   **[NET JUNE 2013]**

    (A) $[CoCl_4]^{2-}$ (B) $[CoBr_4]^{2-}$ (C) $[Co(NCS)_4]^{2-}$ follows the order

    (a) C > A > B   (b) A > B > C   (c) B > A > C   (d) C > B > A

46. The raeaction of $FeCl_3.6H_2O$ with $SOCl_2$ yields.   **[NET DEC 2013]**

    (a) $FeCl_2(s)$, $SO_2(g)$ and HCl(g)   (b) $FeCl_3(s)$, $SO_2(g)$ and HCl(l)

    (c) $FeCl_2(s)$, $SO_3(s)$ and HCl(g)   (d) $FeCl_3(s)$, $SO_2(g)$ and HCl(g)

47. Among the following the correct acid strength trend is represented by   **[NET DEC 2013]**

    (a) $[Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{2+}$

    (b) $[Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{2+}$

    (c) $[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)]^{3+}$

    (d) $[Fe(H_2O)_6]^{2+} < [Al(H_2O)_6]^{3+} < [Fe(H_2O)_6]^{3+}$

48. An octahedral metal ion M^{2+} has magnetic moment of 4.0 B.M. The correct combination of metal ion and d-electron configuration is given by   **[NET DEC 2013]**

    (a) Co^{2+}, $t_{2g}^5 e_g^2$ (b) Cr^{2+}, $t_{2g}^4 e_g^2$ (c) Mn^{2+}, $t_{2g}^3 e_g^1$ (d) Fe^{2+}, $t_{2g}^4 e_g^2$

49. Oxidised form of enzyme catalase (Structure A); prepared by the reaction of $[Fe(P)]^+$ (P = porphyrin) with H_2O_2, has green color because   **[NET DEC 2013]**
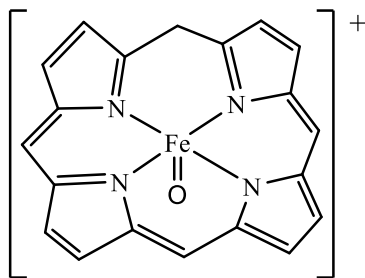
A(substitutents on ring are removed for clarity)

(a) Oxidation state of iron changed from Fe^{III} to Fe^{IV}.

(b) Porphyrin ring is oxidized by one electron

(c) $\pi–\pi^*$ transition appears in the visible region

(d) Fe^{IV} is coordinated with anionic tyrosinate ligand in axial position.

50. $MnCr_2O_4$ is likely to have a normal spinel structure because   **[NET DEC 2013]**

(a) Mn^{2+} will have a LFSE in the octahedral site whereas the Cr^{3+} will not

(b) Mn is +2 oxidation state and both the Cr are in +3 oxidation state.

(c) Mn is +3 oxidation state and 1 Cr is in +2 and the other is in +3 state.

(d) Cr^{3+} will have a LFSE in the octahedral site whereas the Mn^{2+} ion will not.

51.   Compounds $K_2Ba[Cu(NO_2)_6]$ (A) and $Cs_2Ba[Cu(NO_2)_6$(B) exhibit tetragonal elongation and tetragonal compression, respectively. The unpaired electron in A and   B are found respectively, in orbitals,

[NET DEC 2013]

(a) d_{z^2} and $d_{x^2-y^2}$ (b) $d_{x^2-y^2}$ and d_{z^2} (c) d_{z^2} and d_{z^2} (d) $d_{x^2-y^2}$ and $d_{x^2-y^2}$

52.   The most appropriate structure for the complex $[Pt_2(NH_3)_2(NCS)_2(PPh_3)_2]$ is   **[NET DEC 2013]**

53.   In bis (dimethylglyoximato) nickel(II), the number of Ni-N, Ni–O and intramolecular hydrogen bond(s) respectively are   **[NET JUNE 2014]**

(a) 4, 0 and 2   (b) 2, 2 and 2   (c) 2, 2 and 0   (d) 4, 0 and 1

54.   If L is a neutral mono-dentate ligand, the species, $[AgL_4]^{2+}$, $[AgL_6]^{2+}$ and $[AgL_4]^{3+}$ respectively are

[NET JUNE 2014]

(a) Paramagnetic, paramagnetic and diamagnetic

(b) Paramagnetic, diamagnetic and paramagnetic

(c) Diamagnetic, paramagnetic and diamagnetic

(d) Paramagnetic, diamagnetic and diamagnetic

55. The term symbol that is NOT allowed for the np2 configuration is   **[NET JUNE 2014]**

(a) 1D   (b) 3P   (c) 1S   (d) 3D

56. A1:2 mixture of $Me_2NCH_2CH_2PPh_2$ and KSCN with $K_2[PdCl_4]$ gives a square planar complex A. Identify the correct pairs of donor atoms trans to each other in complex A from the following combinations.

[NET JUNE 2014]

(a) P,N   (b) N, S   (c) P, S   (d) N, N

57. $NiBr_2$ reacts with (Et) (Ph_2) P at $-78°C$ in CS_2 to give red compound 'A', which upon standing at room temperature turns green to give compound, 'B' of the same formula. The measured magnetic moments of 'A' and 'B' are 0.0 and 3.2 BM, respectively. The geometries of 'A' and 'B' are   **[NET JUNE 2014]**

(a) square planar and tetrahedral   (b) tetrahedral and square planar

(c) square planar and octahedral   (d) tetrahedral and octahedral

58. $[CoL_6]^{3+}$ is red in colour whereas $[CoL'_6]^{3+}$ is green. L and L' respectively corresponds to: **[NET JUNE 2014]**

(a) NH_3 and H_2O (b) NH_3 and 1, 10-phenanthroline

(c) NH_3 and 1, 10- phenanthroline   (d) H_2O and NH_3

59. The maximum bond order obtained from the molecular orbitals of a transition metal dimer, formed as linear combination of d-orbitals alone, is   **[NET JUNE 2014]**

(a) 3   (b) 4   (c) 5   (d) 6

60. Reaction of $[Ru(NH_3)_5(isonicotinamide)]^{3+}$. with $[Cr(H_2O)_6]^{2+}$. occurs by inner sphere mechanism and rate of the reaction is determined by dissociation of the successor complex. It is due to the   **[NET JUNE 2014]**

(a) Inert ruthenium bridged to inert chromium centre

(b) Inert ruthenium bridged to labile chromium centre

(c) Labile ruthenium bridged to inert chromium centre

(d) Labile ruthenium bridged to labile chromium centre

61. Consider the second order rate constants for the following outer-sphere electron transfer reactions :

[NET JUNE 2014]

$[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}$ 4.0 M^{-1} sec^{-1}

$[Fe(phen)_3]^{3+}/[Fe(phen)_3]^{2+}$ 3.0×10^7 M^{-1}

(phen = 1, 10-phenanthroline)

The enhanced rate constant for the second reaction is due to the fact that

(a) The 'phen' is a π-acceptro ligand that allows mixing of electron donor and acceptor orbitals that enhances the rate of electron transfer

(b) The 'Phen' is a π–donor ligand that enhances the rate of electron transfer

(c) The 'phen' forms charge transfer complex with iron and facilitates the electron transfer

(d) The 'phen' forms kinetically labile complex with iron and facilitates the electron transfer.

62.   In its electronic spectrum, $[V(H_2O)_6]^{3+}$ exihibits two absorption bands, one at 17, 800 (v_1) and the second at 25, 700 (v_2) cm^{-1}. The correct assignment of these bands, respectively, is   **[NET JUNE 2014]**

(a) $v_1 = {}^3T_{1g}$ (F) $\rightarrow {}^3T_{2g}$ (F), $v_2 = {}^3T_{1g}$ (F) $\rightarrow {}^3T_{1g}$ (P)

(b) $v_1 = {}^3T_{1g}$ (F) $\rightarrow {}^3T_{1g}$ (F), $v_2 = {}^3T_{1g}$ (F) $\rightarrow {}^3T_{2g}$ (P)

(c) $v_1 = {}^3A_{2g} \rightarrow {}^3T_{1g}$ (F), $v_2 = {}^3A_{2g} \rightarrow {}^3T_{2g}$ (F)

(d) $v_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$ (F), $v_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}$ (F)

63.   identify the correct statement about $[Ni(H_2O_6)]^{2+}$ and $[CuCH_2O)_6]^{2+}$ **[NET JUNE 2014]**

(a) All Ni-O and Cu-O bond lengths of individual species are equal.

(b) Ni-O (equatorial) and Cu-O(equatorial) bond lengths are shorter than Ni-O(axial) and Cu-O(axial) ones respectively.

(c) All Ni-O bond lengths are equal whereas Cu-O(equatorial) bonds are shorter than Cu-O(axial)bonds:

(d) All Cu-O bond lengths are equal whereas Ni-O(equatorial) bonds are shorter than Ni-O(axial)bonds.

64.   In the following reaction $[PtCl_4]^{2-} + NO_2^- \rightarrow A \xrightarrow{NH_3}$ B, compound B is   **[NET DEC 2014]**

(a) trans–$[PtCl_2(NO_2)(NH_3)]^-$ (b) cis–$[PtCl_2(NO_2)(NH_3)]^-$

(c) trans–$[PtCl_2(NH_3)_2]$ (d) cis-$[PtCl_2(NO_2)_2]^{2-}$

65.   The number of stereoisomers of trans–$[CoCl_2(triethylenetetraamine)]$ Br is   **[NET DEC 2014]**

(a) One   (b) Two   (c) Three   (d) Four

66.   An aqueous solution of $[Mn(H_2O)_6]^{2+}$ complex is pale pink in colour. The probable reasons for it are

    [NET DEC 2014]

(A) presence of ${}^6A_{1g}$ ground state   (B) Disallowed transition by spin selection rule

(C) Presence of ${}^2T_{2g}$ ground state   (D) Charge transfer transition

The correct answer is

(a) A and B   (b) A and C   (c) B and C   (d) C and D

67.   Base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ is an second order reaction, whereas that of $[Co(CN)_6]^{3-}$ is of first order. The rates depend in both cases solely on the   concentrations of the cobalt complex. This may be due to

    [NET DEC 2014]

(A) Presence of ionizable proton in $[CoCl(NH_3)_5]^{2+}$ but not in $[Co(CN)_6]^{3-}$

(B) S_N1_{CB} mechanism in the case of $[CoCl(NH_3)_5]^{2+}$ only

(C) S_N1_{CB} mechanism in the case of $[Co(CN)_6]^{3-}$ only

(D) S_N1_{CB} mechanism in both the complexes

Correct explanation (s) is/are

(a) A and B   (b) A and C   (c) B only   (d) A and D

68. The spin–only magnetic moment and the spectroscopic ground state term symbol of manganese center in $[MnF_6]^{3-}$ ion respectively, are **[NET DEC 2014]**

    (a) 4.9 BM and ^5D (b) 4.9 BM and ^4F (c) 3.9 BM and ^3D (d) 4.9 BM and ^3F

69. The spin–only (μ_s) and spin plus orbital (μ_{s+I}) magnetic moments of $[CrCl_6]^{3-}$ are **[NET DEC 2014]**

    (a) 3.87 BM and 5.20 BM   (b) 2.84 BM and 5.20 BM

    (c) 3.87 BM and 6.34 BM   (d) 2.84 BM and 6.34 BM

70. The S and L values for ^{15}N atom respectively, are **[NET DEC 2014]**

    (a) 1/2 and 1   (b) 1/2 and 0   (c) 1 and 0   (d) 3/2 and 0

71. The configuration [Ne] $2p^1 3p^1$ has a ^3D term. Its levels are **[NET DEC 2014]**

    (a) $^3D_{3/2}, ^3D_{1/2}$ (b) $^3D_{5/2}, ^3D_{3/2}, ^3D_{1/2}$ (c) $^3D_3, ^3D_2, ^3D_1$ (d) $^3D_3, ^3D_2, ^3D_1, ^3D_0$

72. The three dimensional structure of compound $[Co(Co(NH_3)_4(OH)_2)_3] Br_6$, has **[NET DEC 2014]**

    (a) Twelve Co-O and twelve Co-B bonds   (b) Ten Co-O and ten Co-N bonds

    (c) Fourteen Co-O and ten Co-N bonds   (d) Twelve Co-O and ten Co-N bonds

73. The electric-dipole allowed transition among the following is **[NET JUNE 2015]**

    (a) $^3S \rightarrow ^3D$ (b) $^3S \rightarrow ^3P$ (c) $^3S \rightarrow ^1D$ (d) $^3S \rightarrow ^1F$

74. The lowest energy-state of an atom with electronic configuration $ns^1 np^1$ has the term symbol **[NET JUNE 2015]**

    (a) $^3P_1$ (b) $^1P_1$ (c) $^3P_2$ (d) $^3P_0$

75. Match the complexes given in column I with the electronic transitions (mainly responsible for their colours) listed in column II **[NET JUNE 2015]**

Column –I	Column –II
(I) Fe(II)-protoporphyrin IX	(A) $\pi \rightarrow \pi^*$
(II) $[Mn(H_2O)_6]Cl_2$	(B) spin allowed d-d
(III) $[Co(H_2O)_6]Cl_2$	(C) spin forbidden $d \rightarrow d$
	(D) M $\rightarrow$ L charge transfer

    The correct answer is :

    (a) I–A, II–C and III–B   (b) I–D, II–B and III–C

    (c) I–A, II–C and III–D   (d) I–A, II–B and III–C

76. Among the complexes, **[NET JUNE 2015]**

    (A) $K_4[Cr(CN)_6]$,   (B) $K_4[Fe(CN)_6]$,   (C) $K_3[Co(CN)_6]$,   (D) $K_4[Mn(CN)_6]$

    Jahn–Teller distortion is expected in

    (a) A, B and C   (b) B, C and D   (c) A and D   (d) B and C

77. Hence, complex will show Jahn-Teller Distortion. **[NET DEC 2015]**

(a) $^3S_1$ (b) $^3S_0$ (c) $^1S_0$ (d) $^2S_{1/2}$

78. Chelate effect is   **[NET DEC 2015]**

(a) predominantly due to enthalpy change

(b) predominantly due to entropy change

(c) Independent of ring size

(d) due to equal contribution of entropy and enthalpy change

79. Possible term symbol(s) of the excited states of Na atom with the electronic configuration $[1s^2\, 2s^2\, 2p^6\, 3p^1]$ is/are

     [NET DEC 2015]

(a) $^2S_{1/2}$ (b) $^2P_{3/2}$ and $^2P_{1/2}$ (c) $^1S_0$ and $^1P_1$ (d) $^3P_0$ and $^3P_1$

80. The symmetry-allowed atomic transition among the following is   **[NET DEC 2015]**

(a) $^3F \rightarrow {}^1D$ (b) $^3F \rightarrow {}^3D$ (c) $^3F \rightarrow {}^1P$ (d) $^3F \rightarrow {}^3P$

81. The term symbol for the first excited state of Be with the electronic configuration $1s^2\, 2s^1\, 3s^1$ is.

     [NET DEC 2015]

(a) $^3S_1$ (b) $^3S_0$ (c) $^1S_0$ (d) $^2S_{1/2}$

82. Chelate effect is   **[NET DEC 2015]**

(a) predominantly due to enthalpy change

(b) predominantly due to entropy change

(c) Independent of ring size

(d) due to equal contribution of entropy and enthalpy change

83. Possible term symbol(s) of the excited states of Na atom with the electronic configuration $[1s^2\, 2s^2\, 2p^6\, 3p^1]$ is/are

     [NET DEC 2015]

(a) $^2S_{1/2}$ (b) $^2P_{3/2}$ and $^2P_{1/2}$ (c) $^1S_0$ and $^1P_1$ (d) $^3P_0$ and $^3P_1$

84. The symmetry-allowed atomic transition among the following is   **[NET DEC 2015]**

(a) $^3F \rightarrow {}^1D$ (b) $^3F \rightarrow {}^3D$ (c) $^3F \rightarrow {}^1P$ (d) $^3F \rightarrow {}^3P$

85. The oxidizing, power of $[CrO_4]^{2-}$, $[MnO_4]^{2-}$, and $[FeO_4]^{2-}$ follows the order   **[NET DEC 2015]**

(a) $[CrO_4]^{2-} < [MnO_4]^{2-} < [FeO_4]^{2-}$ (b) $[FeO_4]^{2-} < [MnO_4]^{2-} < [CrO_4]^{2-}$

(c) $[MnO_4]^{2-} < [FeO_4]^{2-} < [CrO_4]^{2-}$ (d) $[CrO_4]^{2-} < [FeO_4]^{2-} < [MnO_4]^{2-}$

86. Using crystal field theory, identify from the following complex ions that shows same μ_{eff} (spin only) values

     [NET DEC 2015]

(A) $[CoF_6]^{3-}$ (B) $[IrCl_6]^{3-}$ (C) $[Fe(H_2O)_6]^{2+}$

(a) A and B   (b) B and C   (c) A and C   (d) A, B and C

87. The correct statement for Mn–O bond lengths in $[Mn(H_2O)_6]^{2+}$ is   **[NET DEC 2015]**

(a) All bonds are equal   (b) Four bonds are longer than two others

(c) Two bonds are longer than four others (d) they are shorter than then Mn–O bond in $[MnO_4]^{-}$

88. Spin motion of which of the following gives magnetic moment   **[NET DEC 2015]**

(A) electron,   (B) proton   (C) neutron

Correct answer is

(a) A and B   (b) B and C   (c) A and C   (d) A, B and C

89. $[MnO_4]^-$ is deep purple in color whereas $[ReO_4]^-$ is colorless. The is due to greater energy required for

[NET DEC 2015]

(a) d–d transitions in the Re compound compared to the Mn compound

(b) d–d transitions in the Mn compound compared to the Re compound

(c) Charge transfer from O to Re compared to O to Mn

(d) Charge transfer from O to Mn compared to O to Re

90. The correct statement about the substitution reaction of $[Co(CN_5Cl]^{3-}$ with OH^- to give **[NET DEC 2015]**

$[Co(CN)_5(OH)]^{3-}$ is ,

(a) it obeys first order kinetics

(b) Its rate is proportional to the concentration of both the reactions

(c) It follows the S_N1 CB mechanism

(d) Its rate is dependent only on the concentration of $[OH]^-$

91. Aqueous Cr^{2+} effects one electron redudction of $[Co(NH_3)_5Cl]^{2+}$ giving compound Y. Compound Y

undergoes rapid hydrolysis . Y is,   **[NET DEC 2015]**

(a) $[Co(NH_3)_5]^{2+}$ (b) $[Co(NH_3)_5(OH)]^+$

(c) $[Co(NH_3)_4(OH)_2]$ (d) $[Cr(H_2O)_5Cl]^{2+}$

92. Choose the correct statements about Tanabe-Sugano diagrams   **[NET DEC 2015]**

(A) E/B is plotted against $\Delta 0/B$

(B) The zero energy is taken as that of the lowest term

(C) Terms of the same symmetry cross each other

(D) Two terms of the same symmetry upon increases of ligand field strength bend apart from

Correct answer is

(a) A and B   (b) A and C   (c) A, B and D   (d) A, B , C and D

93. Three electronic transitions at 14900, 22700 and 34400 cm^{-1} are observed in the absorption spectrum of

$[CrF_6]^{3-}$. The Δ_0 value (in cm^{-1}) and the corresponding transition are   **[NET DEC 2015]**

(a) 7800 and $^4A_{2g} \rightarrow {}^4T_{2g}$ (b) 14900 and $^4A_{2g} \rightarrow {}^4T_{2g}$

(c) 14900 and $^4T_{2g} \rightarrow {}^4T_{1g}(F)$ (d) 7800 and $^4T_{2g} \rightarrow {}^4T_{1g}(F)$

94. $[Ni^{II}L_6]^{n+ \text{ or } n-}$ shows absorption bands at 8500, 15400, and 26000 cm^{-1} whereas $[Ni^{II}L'_6]^{n+}$ or $n-$, at 10750,

17500 and 28200 cm^{-1}. L and L' are respectively   **[NET JUNE 2016]**

(a) OH^- and N   (b) Cl^- and I^- (c) NCS^- and RCO   (d) H_2O and NH_3

95. The number of microstates present in 3F term is   **[NET JUNE 2016]**

(a) 3   (b) 21   (c) 9   (d) 28

96. The lowest energy term for the d6 configuration is **[NET JUNE 2016]**

    (a) ^2D (b) ^5D (c) ^1P (d) ^1D

97. Complex $[Cr(bipyridyl)_3]^{3+}$, shows red phosphorescence due to transition   **[NET JUNE 2016]**

    (a) $^4T_{2g} \leftarrow ^4A_{2g}$ (b) $^4T_{1g} \leftarrow ^4A_{2g}$ (c) $^4A_{2g} \leftarrow ^2E_g$ (d) $^2E_g \leftarrow ^4A_{2g}$

98. The complex that shows orbital contribution to the magnetic moment, is   **[NET JUNE 2016]**

    (a) $[Cu(H_2O)_6]^{2+}$ (b) $[Ni(H_2O)_6]^{2+}$ (c) $[Co(H_2O)_6]^{2+}$ (d) $[Cr(H_2O)_6]^{2+}$

99. Paramagnetic susceptibility of the order of 10^{-6} cm^3 mol^{-1} observed for $KMnO_4$ is due to

    [NET JUNE 2016]

    (a) random spin alignment   (b) antiferromagnetic exchange interaction

    (c) paramagnetic impurity   (d) temperature independent paramagnetism

100. The room temperature magnetic moment (μeff in BM) for a monomeric Cu(II) complex is greater than 1.73.

    This may be explained using the expression :   **[NET JUNE 2016]**

    (a) $\mu_{eff} = \mu_s \left(1 - \frac{\alpha\lambda}{\Delta} \right)$ (b) $\mu_{eff} = \sqrt{n(n+2)}$

    (c) $\mu_{eff} = \sqrt{4s(s+1) + L(L+1)}$ (d) $\mu_{eff} = g\sqrt{J(J+1)}$

101. Consider the following statements for $[FeO_4]^{-4}$ **[NET DEC 2016]**

    A. It is paramagnetic

    B. It has Td symmetry

    C. Adopts distorted square planar geometry

    D. Shows approximately D_2d symmetry The correct answer is

    (a) A, B and C   (b) A, C and D   (c) A and D   (d) A and B

102. The HOMO (highest occupied molecular orbital) to LUMO (lowest unoccupied molecular orbital) electronic

    transition responsible for the observed colours of halogen molecules (gas) is   **[NET DEC 2016]**

    (a) $\pi^* \rightarrow \sigma^*$ (b) $\pi^* \rightarrow \pi^*$ (c) $\sigma \rightarrow \sigma^*$ (d) $\pi \rightarrow \sigma^*$

103. In the hydrolysis of trans–$[Co(en)_2 Cl(A)]^+$, if the leaving group is chloride, the formation of cis product is the

    least, when A is   **[NET DEC 2016]**

    (a) NO_2^- (b) NCS^- (c) Cl^- (d) OH^-

104. The nephelauxetic parameter β is highest for   **[NET DEC 2016]**

    (a) Br^- (b) Cl^- (c) CN^- (d) F^-

105. The $^2E_g \leftarrow ^4A_{2g}$ transition in the electronic spectrum of $[Cr(NH_3)_6]^{3+}$ occurs nearly at   **[NET DEC 2016]**

    (a) 650 nm   (b) 450 nm   (c) 350 nm   (d) 200 nm

106. The spectroscopic ground state term symbols for the octahedral aqua complexes of Mn(II), Cr(III) and

    Cu(II), respectively, are   **[NET DEC 2016]**

    (a) ^2H, ^4F and ^2D (b) ^6S, ^4F and ^2D (c) ^2H, ^2H and ^2D (d) ^6S, ^4F and ^2P
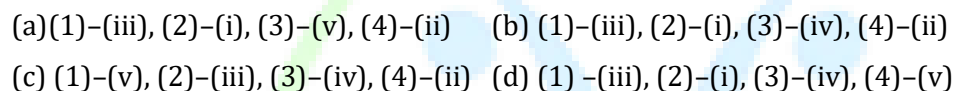
107. For OH⁻ catalysed S_N1 conjugate base mechanism of $[Co(NH_3)_5Cl]^{2+}$, the species obtained in the first step of the reaction is / are **[NET DEC 2016]**

(a) $[Co(NH_3)_5(OH)]^{2+} + Cl^-$

(b) $[Co(NH_3)_4(NH_2)Cl]^+ + H_2O$

(c) $[Co(NH_3)_4(NH_2)]^{2+} + Cl^-$

(d) $[Co(NH_3)_5Cl(OH)]^+$ only

108. Match the species in column X with their properties in column Y **[NET DEC 2016]**

Column –X

(1) Heme A

(2) Water splitting enzyme

(3) $[Mn(H_2O)_6]^{2+}$

(4) $[Cr(H_2O)_6]^{2+}$

Column – Y

(i) Oxo– bridged, Mn4 cluster

(ii) Tetragonal elongation

(iii) Predominantly $\pi \to \pi^*$, electronic transitions

(iv) $d \to d$ spin-forbidden transitions

(v) Tetragonal compression

The correct answer is

(a)(1)–(iii), (2)–(i), (3)–(v), (4)–(ii)

(b) (1)–(iii), (2)–(i), (3)–(iv), (4)–(ii)

(c) (1)–(v), (2)–(iii), (3)–(iv), (4)–(ii)

(d) (1) –(iii), (2)–(i), (3)–(iv), (4)–(v)

109. In the following redox reaction with an equilibrium constant $K = 2.0 \times 10^8$, **[NET DEC 2016]**

$[Ru(NH_3)_6]^{2+} + [Fe(H_2O)_6]^{3+} \rightleftharpoons [Ru(NH_3)_6]^{3+} + [Fe(H_2O)_6]^{2+}$
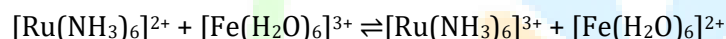
the self exchange rates for oxidant and recutant are $5.0 \, M^{-1} s^{-1}$ and $4.0 \times 10^3 \, M^{-1} s^{-1}$, respectively. The approximate rate constant $(M^{-1}s^{-1})$ for the reaction is

(a) 3.16×10^6

(b) 2.0×10^6

(c) 6.32×10^6

(d) 3.16×10^4
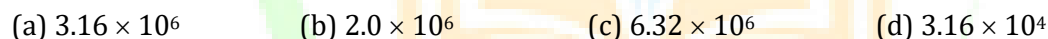
110. Consider the following sulfur donor atom bearing bidentate ligand where X and name of ligands are given in following columns **[NET JUNE 2017]**
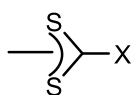
X	Ligand Name
A. NR_2	I. Dithiocarbonate
B. OR	II. Dithicarbamet
C. O^-	III. Xanthate
D. SR	IV. Thioxanthate

Correct match of entries given in two columns is

(a) A–II, B–III, C–I, D–IV

(b) A–I, B–II, C–III, D–IV

(c) A–III, B–II, C–IV, D–I

(d) A–IV, B–I, C–II, D–III

111. A copper (II) complex having distorted octahedral geometry shows an absorption band at 625 nm. Given spin-orbit coupling of the complex as $625 \, cm^{-1}$, the μ_{eff} (in B.M.) is **[NET JUNE 2017]**

(a) 1.73

(b) 1.81

(c) 1.63

(d) 1.93

112. CdS, HgS and BiI_3, are coloured due to **[NET JUNE 2017]**

(a) L → M charge transfer transitions

(b) d → d electronic transitions

(c) M → L charge transfer transitions

(d) combination of L → M charge transfer and d → d electronic transitions

113. The relative rates of water exchange for the hydrated complexes of (1) Ni^{2+}, (2) V^{2+} and (3) Cr^{3+} ions follows the trend **[NET JUNE 2017]**

(a) (1) > (2) > (3)　　　(b) (1) < (2) < (3)　　　(c) (1) > (2) < (3)　　　(d) (1) < (2) > (3)

114. Consider the following statements for octahedral complexes, (a) $[CrF_6]^{3-}$, (b) $[Cr(ox)_3]^{3-}$ and (c) $[Cr(en)_3]^{3+}$: **[NET JUNE 2017]**

A. their d → d transitions are at 14900, 17500, and 21800 cm^{-1}, respectively

B. Their spin-only magnetic moments are same

C. Two of them have optical isomers

D. All of them show Jahn-Teller distortion

The correct statements are

(a) A, B and C　　　(b) A, C, and D　　　(c) B, C, and D　　　(d) B and D

115. The μ_{eff} of $[Fe(S_2CNEt_2)_3]$ changes with temperature with the involvement of two electronic states. The states are **[NET JUNE 2017]**

(a) Low spin $^2T_{2g}$ and high-spin $^6A_{1g}$

(b) low spin $^1A_{1g}$ and high–spin $^3T_{2g}$

(c) low spin ^2E_g and high – spin $^6A_{1g}$

(d) low spin $^2T_{2g}$ and high-spin $^4T_{1g}$

116. Match the items in the three columns. **[NET JUNE 2017]**

Complex (column 1)	Color (column 2)	Absorption max (λmax, nm) (column 3)
A. $[Ni(H_2O)_6]$ $(NO_3)_2$	I. Blue	X. 675
B. $[Ni(NH_3)_6]$ $(NO_3)_2$	II. Green	Y. 565
C. $[Ni(en)_3]$ $(NO_3)_2$	III. Violet	Z. 615

The correct answer is

(a) A–II–X; B–I–Z; C–III-Y　　　　(b) A–I–X; B–II–Y; C–III-Z

(c) A–III-Y; B-I-Z; C-II-X　　　　(d) A-I–X; B-II-Z; C-III-Y

117. Br^2 with propanone forms a charge transfer complex and l^2 forms triiodide anion with l-. This implies that **[NET DEC 2017]**

(a) Both Br^2 and l^2 act as bases　　　(b) both Br^2 and l^2 act as acids

(c) Br^2 acts as an acid and l^2 acts as a base　　　(d) Br^2 acts as a base and 1^2 acts an acid

118. For the following complexes, the increasing order of magnetic moment (spin only value) is

[NET DEC 2017]

A. $[TiF_6]^{3-}$ B. $[CrF_6]^{3-}$ C. $[MnF_6]^{3-}$ D. $[CoF_6]^{3-}$

(a) D < A < B < C   (b) C < A < D < B   (c) B ≈ A < D < C   (d) A < B < C ≈ D

119. In trigonal prismatic ligand field, the most stabilized d orbital is   **[NET DEC 2017]**

(a) d_z^2 (b) d_{xy} (c) d_{xz} (d) d_{yz}

120. Mismatch among the following is   **[NET DEC 2017]**

(a) Sharp transition and fluorescence in lanthanides

(b) Broad bands and d-d transitions

(c) Very high spin-orbit coupling and transition elements

(d) Charge transfer and molar absorptivity of the order of 10^4 L mol^{-1} cm^{-1}

121. For high spin and low spin d^6 octahedral complexes (ML_6), the generally observed spin allowed

transitions, respectively, are   **[NET DEC 2017]**

(a) two and one   (b) one and two   (c) zero and one   (d) two and two

122. The geometry around Cu and its spin state for K_3CuF_6 and $KCuL_2$, [$H_2L = H_2NCONHCONH_2$], respectively are

:   **[NET DEC 2017]**

(a) (Octahedral, high-spin) and (square planar, low-spin)

(b) (Octahedral , low-spin) and (square planar, low-spin)

(c) (trigonal prismatic, high-spin) and (tetrahedral, high-spin)

(d) (trigonal prismatic, low-spin) and (tetrahedral, high-spin)

123. Consider the following statements with respect to the base hydrolysis of $[CoCl(NH_3)_5]^{2+}$ to

$[Co(NH_3)_5(OH)^{2+}$.   **[NET DEC 2017]**

A. One of the ammonia ligands acts as a Bronsted acid.

B. The entering group is water.

C. A heptacoordinated Co^{3+} species is an intermediate.

The correct statement(s) is/are

(a) A and B   (b) A and C   (c) B and C   (d) C only

124. The total degeneracy of the ground term of Co11 (high spin) in octahedral geometry is   **[NET JUNE 2018]**

(a) 18   (b) 12   (c) 28   (d) 9

125. The lowest energy state of a $1s^1 2s^1$ electronic configuration, according to hund's rule, is   **[NET JUNE 2018]**

(a) $^3S_0$ (b) $^1S_0$ (c) $^3S_1$ (d) $^1S_1$

126. The allowed electronic transition in fluorine molecule is   **[NET JUNE 2018]**

(a) $\Sigma_g^+ \to \Sigma_g^+$ (b) $\Sigma_g^+ \to \Sigma_g^+$ (c) $\Sigma_g^+ \to \pi_u$ (d) $\Sigma_g^+ \to \Delta_u$

127. For magnesium complex of $EDTA^{2-}$, the number of N-donor and O-donor centers respectively are

[NET JUNE 2018]

(a) Two and four   (b) Two and two   (c) two and six   (d) Two and eight

128. High spin complex of a 3d metal ion M has a magnetic moment of 2.9 B.M. in octahedral coordination environment and 4.1 B.M. in tetrahedral environment. The M ion is   **[NET JUNE 2018]**

(a) Co^{III} (b) Ni^{II} (c) Cu^{II} (d) Co^{II}

129. For electronic spectra of K_2CrO_4(A) and K_2MoO_4(B) the correct combination is   **[NET JUNE 2018]**

(a) Transition is d-d and λmax for A < B

(b) transition is LMCT and λmax for A < B

(c) Transition is LMCT and λmax for A > B

(d) transition in MLCT and λmax for A > B

130. Choose the correct set of statements for cis/platin.   **[NET JUNE 2018]**

(A) It can be prepared from $K_2[PtCl_4]$

(B) It can be prepared from $[Pt(NH_3)_4]Cl_2$

(C) In its preparation, the observed trans effect for Cl^- is greater than that of NH_3.

(D) In blood it stays in equilibrium with cis–$[Pt(NH_3)_2Cl(H_2O)]^+$

(E) In DNA strand, it bonds to two adjacent cytosine bases

The correct set is

(a) A, C and D   (b) A, C , D and E   (c) B, C and D   (d) B, C, D and E

131. Consider the following statements   **[NET JUNE 2018]**

(A) Cr^{2+} is easier to oxidise than V^{2+} in the

(B) Cr^{2+} (aq) is a more powerful reducing agent than V^{2+}(aq)

(C) The rate of water exchange for Cr^{2+} (aq) is much faster than for V^{2+}(aq)

The correct statements are

(a) A and B   (b) A and C   (c) B and C   (d) A, B and C

132. Consider the statements A–D regarding equation I–III: **[NET JUNE 2018]**

(I) $[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \rightarrow [Fe(CN)_6]^{4-} + [Co(CN)_5]^{2-}$

(II) $[Co(bipy)_3]^{2+} + [Co^*(bipy)_3]^{3+} \rightarrow [Ci(bipy)_3]^{3+} + [Co^*(bipy)_3]^{2+}$

(III) $[Co(NH_3)_5F]^{2+} [Cr(H_2O)_6]^{2+} \rightarrow [Co(NH_3)_5(H_2O)]^{2+} + [Cr(H_2O)_5F]^{2+}$

(A) Marcus equation is applicable to I and II

(B) Marcus equation is applicable to II only

(C) Equation I and II involve inner sphere electron transfer

(D) Equations I and III involve inner sphere electron transfer

(a) A and B   (b) B and C   (c) B and D   (d) C and D

133. The intermediate $[Fe(SCN)(H_2O)_5]^{2+}$ is detected in the reaction of $[Co(NCS)(NH_3)_5]^{2+}$ with $[Fe(H_2O)_6]^{2+}$ in aqueous medium to produce $[Co(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ **[NET DEC 2018]**

The mechanism of the reaction is

(a) Interchange dissociative   (b) Interchange associative

(c) Inner sphere electron transfer   (d) Outer sphere electron transfer

134. The correct set of electronic configuration for metal ions in octahedral coordination geometry for strong Jahn-Teller distortion is   **[NET DEC 2018]**

(a) $t_{2g}^6\ e_g^1, t_{2g}^3\ e_g^1, t_{2g}^6\ e_g^3$ (b) $t_{2g}^1, t_{2g}^3\ e_g^1,\ t_{2g}^6, e_g^1$

(c) $t_{2g}^3, t_{2g}^3\ e_g^1, t_{2g}^3\ e_g^2$ (d) $t_{2g}^3\ e_g^2, t_{2g}^6\ e_g^2, t_{2g}^6\ e_g^3$

135. The correct order of intensity of the d-d transitions in the complexes of a 3d- transition metal ion M^{2+} is   **[NET DEC 2018]**

(a) cis – $[M(H_2O)_4Cl_2]$ > trans – $[M(H_2O)_4Cl_2]$ > $[M(H_2O)_6]^{2+}$

(b) $[M(H_2O)_6]^{2+}$ > cis–$[M(H_2O)_4Cl_2]$ > trans–$[M(H_2O)_4Cl_2]$

(c) trans–$[M(H_2O)_4Cl_2]$ > cis – $[M(H_2O)_4Cl_2]$ > $[M(H_2O)_6]^{2+}$

(d) $[M(H_2O)_6]^{2+}$> cis – $[M(H_2O)_4Cl_2]$ $\approx$ trans – $[M(H_2O)_4Cl_2]$

136.

(A)   (B)
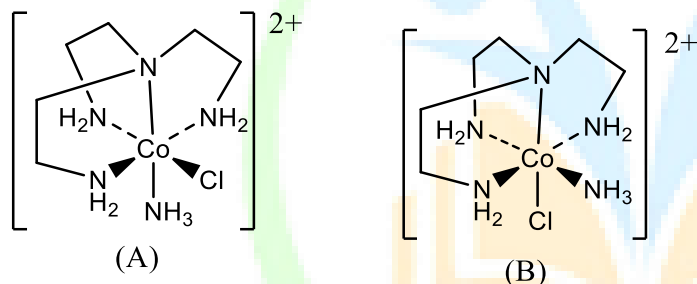
The isomers A and B undergo base hydrolysis by forming a trigonal bipyramidal intermediate. The correct statement is   **[NET DEC 2018]**

(a) A reacts faster than B and both results in a mixture of products

(b) B reacts faster than A and both results in a mixture of products

(c) A reacts faster than B and B results in a mixture of products

(d) B reacts faster than A and A results in a mixture of products.

137. Consider the two sets of molecules.   **[NET DEC 2018]**

Set A : $[AlF_6]^{3-}$, $[PF_6]^-$, $[SF_6]$ and $[SiF_6]^{2-}$

Set B: $[Ba(H_2O)_6]^{2+}$, $[Ca(H_2O)_6]^{2+}$, $[Mg(H_2O)_6]^{2+}$, $[Sr(H_2O)_6]^{2+}$

The slowest ligand exchange rate in Set A and Set B are, respectively

(a) $[AlF_6]^{3-}$ and $[Sr(H_2O)_6]^{2+}$ (b) $[SF_6]$ and $[Mg(H_2O)_6]^{2+}$

(c) $[SiF_6]^{2-}$ and $[Ca(H_2O)_6]^{2+}$ (d) $[PF_6]^-$ and $[Ca(H_2O)_6]^{2+}$

138. Consider the following reaction :   **[NET JUNE 2019]**

$Hg^{+2}(aq) + X^-(aq) = [HgX]^+ (aq)$
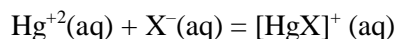
The stability constants for $[HgX]^+$ (aq) for X = F, Cl and Br follow the order

(a) F < Cl < Br   (b) Br < Cl < F   (c) Cl < Br < F   (d) Br < F < Cl

139. An aqueous solution of metal ion (A) gives a blood-red colored product (B) upon reaction with KSCN. Upon dropwise addition of NaF, the complex turns to a colorless compound (C), Identify A, B and C

[NET JUNE 2019]

(a) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and $[Fe(H_2O)_6]^{+2}$

(b) aq. Fe(III), $[Fe(SCN)(H_2O)_5]^{+2}$ and $[FeF_6]^{+3}$

(c) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and FeF_3

(d) aq. Fe(III), $[Fe(SCN)_3(H_2O)_3]^+$ and FeF_3

140. Self –exchange electron transfer is fastest in **[NET JUNE 2019]**

(a) $[Ru(NH_3)_6]^{2+/3+}$ (b) $[Co(NH_3)_6]^{2+/3+}$ (c) $[Cr(OH_2)_6]^{2+/3+}$ (d) $[Fe(OH_2)_6]^{2+/3+}$

141. The allowed transition in an atomic system is **[NET JUNE 2019]**

(a) $^3F_4 \rightarrow {}^3D_3$ (b) $^3F_4 \rightarrow {}^1D_3$ (c) $^3F_4 \rightarrow {}^3P_4$ (d) $^3F_4 \rightarrow {}^3D_2$

142. The correct set of information is **[NET JUNE 2019]**

(a) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} = \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Paramagnetic

(b) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} > \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Diamagnetic

(c) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} = \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Diamagnetic

(d) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} > \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Paramagnetic

143. Consider the following statements regarding electronic spectra of high spin complexes **[NET JUNE 2019]**

(A) Ti^{3+} complexes exhibit one sharp band.

(B) Co^{2+} and Cr^{3+} complexes exhibit two broad bands.

(C) Mn^{2+} complexes exhibit a series of very weak and sharp bands.

(D) Ni^{2+} complexes exhibit three broad bands.

The correct statements are.

(a) A and C (b) A, C and D (c) C and D (d) B, C and D

144. Hydrolysis of trans–$[CoLCl(en)_2]^+$ (L = NO_2^-, NCS$^-$, OH$^-$, Cl$^-$) results in a product (A). The tendency to form cis-isomer of the product (A) follows the order. **[NET JUNE 2019]**

(a) L = NO_2^- < NCS$^-$ < OH$^-$ < Cl– (b) L = NO_2^- < Cl$^-$ < NCS$^-$ < OH$^-$

(c) L = OH$^-$ < Cl$^-$ < NO_2^- < NCS$^-$ (d) L = OH$^-$ < NCS$^-$ < Cl$^-$ < NO_2^-

145. An aqueous solution of metal ion (A) gives a blood-red colored product (B) upon reaction with KSCN. Upon dropwise addition of NaF, the complex turns to a colorless compound (C). Identify A, B and C

[NET JUNE 2019]

(a) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and $[Fe(H_2O)_6]^{2+}$

(b) aq. Fe(III), $[Fe(SCN)(H_2O)_5]^+$ and $[FeF_6]^{3+}$

(c) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and FeF_3

(d) aq. Fe(III), $[Fe(SCN)_3(H_2O)_3]^+$ and FeF_3

146. Considering σ–bonding only, in the MO diagram of a metal complex with trigonal bipyramidal (TBP) geometry, the d-orbitals which remain non-bonding are   **[NET JUNE 2019]**

(a) d_{z^2} and d_{xz} (b) d_{xz} and d_{yz} (c) $d_{x^2-y^2}$ and d_{xy} (d) d_{z^2} and d_{yz}

147. In the electronic spectrum of $[IrBr_6]^{2-}$, the number of charge transfer band (s) and their origin are respectively

                                                                      [NET DEC 2019]

(a) Two ligand → metal ($6\Delta t_{2g}$ and $6 \to a_{1g}*$)

(b) One ligand → metal ($6 \to e_g$)

(c) Two ligand → metal ($6 \to t_{2g}$ and $6 \to e_g$)

(d) One ligand → metal ($6 \to t_{2g}$)

148. Correct order of molar extinction coefficient values of the visible absorption bands for the following species is

                                                                      [NET DEC 2019]

(a) $[Cr(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+} > Chlorophyll > [NiCl_4]^{2-}$

(b) $Chlorophyll > [NiCl_4]^{2-} > [Cr(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+}$

(c) $[NiCl_4]^{2-} > Chlorophyll > [Cr(H_2O)_6]^{2+} > [Mn(H_2O)_6]^{2+}$

(d) $Chlorophyll > [Cr(H_2O)_6]^{2+} > [NiCl_4]^{2-} > [Mn(H_2O)_6]^{2+}$

149. For an octahedral Cu^{2+} complex depicting axial EPR spectrum ($g_{||} > g\perp$), the geometry of Cu^{2+} and the orbital containing the unpaired electron are, respectively.   **[NET DEC 2019]**

(a) Tetragonally elongated, $d_{x^2-y^2}$ (b) Tetragonally compressed, d_{z^2}

(c) Tetragonally elongated, d_{z^2} (d) Tetragonally compressed, $d_{x^2-y^2}$

150. The most stable vandium species in aqueous medium is   **[NET DEC 2019]**

(a) $[V(H_2O)_5(OH)]^{2+}$ (b) $[VO(H_2O)_5]^{2+}$ (c) $[VO(H_2O)_3]^{+}$ (d) $[V(H_2O)_4(OH)_2]^{2+}$

151. In the electronic spectrum of $[IrBr_6]^{2-}$ the number of charge transfer band (s) and their origin are, respectively:

                                                                      [NET DEC 2019]

(a) Two, ligand → metal ($\sigma \to t_{2g}$, and $\sigma \to a_{1g}*$)

(b) One, ligand → metal ($\sigma \to e_g$)

(c) Two, ligand → metal ($\sigma \to t_{2g}$ and $\sigma \to e_g$)

(d) One, ligand → metal ($\sigma \to t_{2g}$)

152. $FeCr_2O_4$ and $NiGa_2O_4$ have normal and inverse spinel structures, respectively. The correct statement is :

                                                                     [NET DEC 2019]

(1) Fe(II) and Ni(II) occupy octahedral sites

(2) Fe(II) and Ni(II) occupy tetrahedral and octahedral sites, respectively

(3) Cr(III) and Ga(III) occupy only octahedral sites

(4) Cr(III) and Ga(III) occupy tetrahedral and octahedral sites, respectively

153. The correct match of spin–only magnetic moment for the complexes cis-$[Fe(phen)_2(NCS-N)_2]$**[NET DEC 2019]**

(A) and $[Fe(phen)_3] Cl_2$ (B) at 300 K is (phen) = 1, 10–phenanthroline)

(a) 4.89 BM for both A and B

(b) 0 BM for both A and B

(c) 4.89 BM for A and 0 BM for B

(d) 0 BM for A and 4.89 BM for B

154. The correct statement about base hydrolysis of $[Co(py)_1Cl_2]^+$ (py = pyridine) is **[NET DEC 2019]**

(a) rate expression is , Rate = $k[Co(py)_4Cl_2][OH^-]$

(b) reaction does not depend on hydroxide ion concenration

(c) reaction proceeds through S_N1 CB mechanism

(d) intermediate involved in this reaction is $[Co(py)1Cl_2(OH)]$

155. Consider the following statements : **[NET DEC 2019]**

(A) The highest oxidation state of Group 3 elements is more readily shown in their oxides than in fluorides.

(B) Fe can exist in –2 formal oxidation state also.

(C) Mn, Tc and Re easily form M (II) compounds.

The correct statement(s) is / are:

(a) A and B   (b) A and C   (c) B and C   (d) C only

156. Self –exchange electron transfer is fastest in **[NET DEC 2019]**

(a) $[Ru(NH_3)_6]^{2+/3+}$ (b) $[Co(NH_3)_6]^{2+/3+}$ (c) $[Cr(OH_2)_6]^{2+/3+}$ (d) $[Fe(OH_2)_6]^{2+/3+}$

157. The allowed transition in an atomic system is **[NET DEC 2019]**

(a) $^3F_4 \rightarrow {}^3D_3$ (b) $^3F_4 \rightarrow {}^1D_3$ (c) $^3F_4 \rightarrow {}^3P_4$ (d) $^3F_4 \rightarrow {}^3D_2$

158. The correct set of information is **[NET DEC 2019]**

(a) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} = \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Paramagnetic

(b) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} > \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Diamagnetic

(c) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} = \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Diamagnetic

(d) $[Mn(H_2O)_6]^{2+}$: $\mu_{observed} > \mu_{spin}$; $[Co(H_2O)_6]^{3+}$: Paramagnetic

159. Consider the following statements regarding electronic spectra of high spin complexes **[NET DEC 2019]**

(A) Ti^{3+} complexes exhibit one sharp band.

(B) Co^{2+} and Cr^{3+} complexes exhibit two broad bands.

(C) Mn^{2+} complexes exhibit a series of very weak and sharp bands.

(D) Ni^{2+} complexes exhibit three broad bands.

The correct statements are

(b) A and C   (b) A, C and D   (c) C and D   (d) B, C and D

160. Hydrolysis of trans–$[CoLCl(en)_2]^+$ (L = NO_2^-, NCS-, OH-, Cl-) results in a product (A).The tendency to form

cis-isomer of the product (A) follows the order. **[NET DEC 2019]**

(a) L = NO_2^- < NCS- < OH- < Cl– (b) L = NO_2^- < Cl- < NCS- < OH-

(c) L = OH- < Cl- < NO_2^- < NCS- (d) L = OH- < NCS- < Cl- < NO_2^-

161. An aqueous solution of metal ion (A) gives a blood-red colored product (B) upon reaction with KSCN. Upon dropwise addition of NaF, the complex turns to a colorless compound (C). Identify A, B and C

[NET DEC 2019]

(a) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and $[Fe(H_2O)_6]^{2+}$

(b) aq. Fe(III), $[Fe(SCN)(H_2O)_5]^+$ and $[FeF_6]^{3+}$

(c) aq. Fe(II), $[Fe(SCN)(H_2O)_5]^+$ and FeF_3

(d) aq. Fe(III), $[Fe(SCN)_3(H_2O)_3]^+$ and FeF_3

162. Considering σ–bonding only, in the MO diagram of a metal complex with trigonal bipyramidal (TBP) geometry, the d-orbitals which remain non-bonding are **[NET DEC 2019]**

(a) d_{z^2} and d_{xz} (b) d_{xz} and d_{yz} (c) $d_{x^2-y^2}$ and d_{xy} (d) d_{z^2} and d_{yz}

163. I_2 is violet in the solid as well as in gas phase. However in acetone or ethanol, it turns brown. Choose the correct statement(s) for this colour change: **[NET NOV 2020]**

(a) Dissociation of I_2 in atomic state

(b) Interaction of low-lying 6*–orbital of iodine with lone pair of O (solvent)

(c) Formation of a charge-transfer complex

164. For the d^3 electron configuration, the ground state term symbol is **[NET NOV 2020]**

(a) $^4F_{1/2}$ (b) $^4F_{3/2}$ (c) $^4F_{7/2}$ (d) $^4F_{9/2}$

165. The products A and B for the given reaction **[NET NOV 2020]**

$[Co(NH_3)_5Cl]^{+2} + [Cr(OH_2)_6]^{+2} + 5H_3O^+ \rightarrow A+B$

are respectively,

(a) $[Co(OH_2)_5Cl]^+$, $[Cr(OH_2)_6]^{+3}$ (b) $[Co(NH_3)_5(OH_2)_5Cl]^{+2}$

(c) $[Co(OH_2)_6]^{+2}$, $[Cr(OH_2)_5Cl]^{+2}$ (d) $[Co(NH_3)_5Cl]^+$, $[Cr(OH_2)_6]^{+3}$

166. The number of expected electronic transitions in $[Cr(en)_3]^{+3}$ and trans $- [Cr(en)_2F]^+$ at 4 K is, respectively (en = ethylenediamine) **[NET NOV 2020]**

(a) 3 and 3 (b) 3 and 4 (c) 3 and 5 (d) 3 and 6

167. The products A and B for the given reaction **[NET NOV 2020]**

$[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} + 5H_3O^+ \rightarrow A + B$

are, respectively

(a) $[Co(OH_2)_5Cl]^+$, $[Cr(OH_2)_6]^{3+}$ (b) $[Co(NH_3)_5(OH_2)]^{2+}$, $[Cr(OH_2)_5Cl]^{2+}$

(c) $[Co(OH_2)_6]^{2+}$, $[Cr(OH_2)_5Cl]^{2+}$ (d) $[Co(NH_3)_5Cl]^+$, $[Cr(OH_2)_6]^{3+}$

168. The number of expected electronic transitions in $[Cr(en)_3]^{3+}$ and trans-$[Cr(en)_2F_2]^+$ at 4 K is, respectively (en = ethylenediamine) **[NET NOV 2020]**

(a) 3 and 3 (b) 3 and 4 (c) 3 and 5 (d) 3 and 6

169. The value of magnetic moment will be independent of temperature for **[NET NOV 2020]**

(acac = acetylacetonato: OAc = acetate : o-phen = o-phenathroline. Pz = pyrazolyl)

(a) [Fe(acac)₃] → $[Fe(acac)_3]$

(a) $[Fe(acac)_3]$ (b) $[Cu_2(OAc)_4(H_2O)_2]$

(c) $[Fe(o\text{-phen})_2)(NCS)_2]$ (d) $[Fe\{HC(3.5\text{-Me2Pz})_3\}_2]^{2+}$

170. The correct electronic configuration of frontier MO's of **[NET NOV 2020]**

$Mn(\eta^5\text{–}C_5Me_5)_2$ is

(a) $e_{2g}^2 a_{1g}^1 e_{1g}^2$ (b) $e_{2g}^4 a_{1g}^1$ (c) $e_{2g}^3 a_{1g}^2$ (d) $a_{1g}^2 e_{2g}^3$

171. For the given reaction **[NET NOV 2020]**

$[*Co(L)_n]^{2+} + [Co(L)_n]^{3+} \rightarrow [*Co(L)_n]^{3+} + [Co(L)_n]^{2+}$

the correct statement with respect to the rate of electron transfer process is

o-phen = o-phenanthroline; *Co is labeled atom

(a) fast electron transfer ; L = NH_3; n = 6

(b) slow electron transfer ; L = o-phen; n = 3

(c) Very slow electron transfer; L = NH_3 ; n = 6

(d) Very slow electron transfer; L = o-phen ; n = 3

172. The pair of compounds in which both members show LMCT band in their electronic spectra is

[NET NOV 2020]

(a) $[FeCl_4]^{2-}$ and $[Fe(bpy)_3]^{2+}$ (b) $[FeBr_4]^{2-}$ and $[TcO_4]^-$

(c) $[ReO_4]^-$ and $[Ru(bpy)_3]^{2+}$ (d) $[Fe(phen)_3]^{2+}$ and $[FeCl_4]^{2-}$

173. The number of geometrical isomers of the complex $[RhH(C{\equiv}CR)_2(PMe_3)_3]$ is **[NET NOV 2020]**

(a) 2 (b) 3 (c) 4 (d) 1

174. Of the following statements regarding dissociative substitution in an octahedral transition metal complex,

(a) High steric hindrance between in the metal complex favors fast dissociation of ligand.

[NET FEB 2022]

(b) Increased charge on the metal complex fast dissociation of ligand.

(c) A pentacoordinated intermediate is observed.

(d) Nature of the entering ligand significantly influences the reaction.

Which are correct ?

(a) a and d (b) a and c (c) a, c and d (d) a, b, c and d

175. Consider an octahedral complex Ma_2b_2cd, where a, b, c and d are monodentate ligands, The number of enantiomeric pairs for the complex is **[NET FEB 2022]**

(a) One (b) two (c) three (d) Four

176. For the ligand-to-metal charge-transfer (LMCT) transitions in the oxo-anion given below, the wavelength of the order **[NET FEB 2022]**

(a) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-} \; CrO_4^{2-}$

(b) $VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} > MoO_4^{2-} \; CrO_4^{2-}$

(c) $VO_4^{3-} > CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-} \; CrO_4^{2-}$

(d) $VO_4^{3-} > CrO_4^{2-} < MnO_4^{-}$ and $WO_4^{2-} > MoO_4^{2-} CrO_4^{2-}$
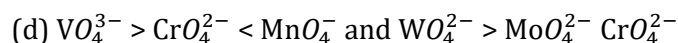
177. Consider t he following statements for the self-exchange electron transfer reaction in $[Cr(H_2O)_6]^{2+/3+}$ **[NET FEB 2022]**

(a) σ* orbitals are only involved in electron transfer

(b) It involves large inner-sphere reorganization energy

(c) It involves no change in M-L bond lengths

(d) Rate of self-exchange electron transfer is fast

The correct statements are

(a) a, b and d   (b) a and b   (c) a and c   (d) b and d

178. Consider the following statements regarding EPR spectra : **[NET FEB 2022]**

(a) For allowed transitions, $\Delta Ms = \pm 1$ and $\Delta M1 = 0$

(b) For allowed transitions, $\Delta Ms = 0$ and $\Delta M1 = \pm 1$.

(c) Tetragonally elongated Cu(II) complexes have $g_{||} > g_{\perp}$.

(d) The orbital considered as ground state for tetragonally compressed Cu(II) complexes is $d_{x^2-y^2}$.

The correct statements are

(a) (a), (c) and (d)   (b) (b), (c) and (d)   (c) (a) and (c) only   (d) (b) and (d) only

179. For trigonal bipyramidal coordination complex (ML5) the correct point group symmetry and the relative order of the energies of the 3d orbitals in that crystal field, respectively are **[NET FEB 2022]**

(a) D_{3h}; $d_{x^2-y^2} > dz^2, > d_{xz}, d_{yz}$ (b) D_{3d}, $d_{z^2} > d_{x^2-y^2}, d_{xz} > d_{xy}, d_{yz}$

(c) D_{3d}; $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz}, d_{yz}$ (d) D_{3h}; $d_{z^2} > d_{x^2-y^2}, d_{xy} > d_{xz}, d_{yz}$

180. The number of CO bands for isomers from sets (i) and (ii) in their IR spectra **[NET FEB 2022]**

Set(i): Trigonal bipyramidal isomers, axial-Fe(CO)₄L(A) and equatorial –Fe(CO)₄L(B)

Set(ii): Octahedral isomers, fac-Mo(CO)₃L₃(C) and mer-Mo(CO)₃L₃(D) are

(a) A, 4 and B, 3; C, 3 and D, 2   (b) A, 4 and B, 3; C, 2 and D, 3

(c) A, 3 and B, 4; C, 3 and D, 2   (d) A, 3 and B, 4; C, 2 and D, 3

181. Tge absorption spectrum of $[Cr(NH_3)_6]^{3+}$ in water shows two bands around 475 and 365 nm. The ground term and the spin-allowed transitions, respectively, are **[NET FEB 2022]**

(a) ⁴F; $^4T_{1g}(F) \to {}^4T_{2g}$ and $^4T_{1g} \to {}^4A_{2g}$ (b) ⁴F; $^4A_{2g} \to {}^4T_{2g}$ and $^4A_{2g} \to {}^4T_{1g}(F)$

(c) ²G; $^2E_g \to {}^2T_{1g}$ and $^2E_g \to {}^2T_{2g}$ (d) ²F; $^2A_{2g} \to {}^2T_{2g}$ and $^2A_{2g} \to {}^2T_{1g}(F)$

182. Consider the following molecules/ions **[NET SEP 2022]**

A. $[Mn(H_2O)_6]^{3+}$ B. $[Ni(H_2O)_6]^{2+}$ C. VCl₄

The Jahn-Teller effect is expected for

(a) A and C only   (b) A only   (c) C only   (d) A and B only

183. The electronic spectrum of an aqueous solution of $[Ni(H_2O)_6]^{2+}$ shows three distinct bands: A (~ 400nm), B (~ 690 nm) and C (~ 1070 nm). The transitions assigned to A, B and C. **[NET SEP 2022]**

(a) $T_{1g}(P) \leftarrow A_{2g}$, $T_{2g} \leftarrow A_{2g}$, and $T_{1g} \leftarrow A_{2g}$

(b) $T_{1g}(P) \leftarrow A_{2g}$, $T_{1g} \leftarrow A_{2g}$, and $T_{2g} \leftarrow A_{2g}$

(c) $T_{2g} \leftarrow A_{2g}$, $T_{1g} \leftarrow A_{2g}$, and $T_{1g}(P) \leftarrow A_{2g}$

(d) $T_{1g} \leftarrow A_{2g}$, $T_{2g} \leftarrow A_{2g}$, and $T_{1g}(P) \leftarrow A_{2g}$

184. The Second order rate constants for the outer sphere self-exchange electron transfer reactions for $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+}/[Co(NH_3)_6]^{3+}$ are 9.2×10^2 M^{-1} Sec^{-1} and $\leq 10^{-9}$ M^{-1} Sec^{-1}, respectively. The Correct rationale for teh above data is : **[NET SEP 2022]**

(a) The change in the number of σ^*–electrons in Co(II)/Co(III) system.

(b) The change in the number of π^*–electrons in Co(II)/Co(III) system.

(c) The change in the number of both σ^* and π^*–electrons in Co(II)/Co(III) system.

(d) The change in the number of σ^*–electrons in Ru(II)/Ru(III) system.

185. An octahedral d^6 complex has a single spin-allowed absorption band. The spin-only magnetic moment (B.M) and the electronic transition for this complex, respectively, are **[NET SEP 2022]**

(a) 0 and $^1T_{1g} \leftarrow {}^1A_{1g}$ (b) 4.9 and $^5T_{2g} \leftarrow {}^5E_g$ (c) 4.9 and $^5E_g \leftarrow {}^5T_{2g}$ (d) 0 and $^1T_{2g} \leftarrow {}^1A_{1g}$

186. In the following electron transfer reactions, the one in which the bridging ligand comes from the reductant is **[NET SEP 2022]**

(a) $[IrCl_6]^{2-} + [Cr(OH_2)_6]^{2+} \rightarrow$ Products

(b) $[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} \rightarrow$ Products

(c) $[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow$ Products

(d) $[CrO_4]^{2-} + [Fe(CN)_6]^{4-} \rightarrow$ Products

187. In the following electron transfer reactions, the one in which the bridging ligand comes from the reductant is **[NET SEP 2022]**

(a) $[IrCl_6]^{2-} + [Cr(OH_2)_6]^{2+} \rightarrow$ Products

(b) $[Co(NH_3)_5Cl]^{2+} + [Cr(OH_2)_6]^{2+} \rightarrow$ Products

(c) $[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow$ Products

(d) $[CrO_4]^{2-} + [Fe(CN)_6]^{4-} \rightarrow$ Products

188. The electronic spectrum of an aqueous solution of $[Ni(H_2O)_6]^{2+}$ shows three distinct bands: A (~ 400nm), B(~ 690nm) and C(~ 1070nm). The transitions assigned to A, B and C , respectively, are **[NET SEP 2022]**

(a) $T_{1g}(P) \leftarrow A_{2g}$, $T_{2g} \leftarrow A_{2g}$, and $T_{1g} \leftarrow A_{2g}$

(b) $T_{1g}(P) \leftarrow A_{2g}$, $T_{1g} \leftarrow A_{2g}$, and $T_{2g} \leftarrow A_{2g}$

(c) $T_{2g} \leftarrow A_{2g}$, $T_{1g} \leftarrow A_{2g}$, and $T_{1g}(P) \leftarrow A_{2g}$

(d) $T_{1g} \leftarrow A_{2g}$, $T_{2g} \leftarrow A_{2g}$, and $T_{1g}(P) \leftarrow A_{2g}$

189. Consider the following molecules/ions **[NET SEP 2022]**

A. $[Mn(H_2O)_6]^{3+}$ B. $[Ni(H_2O)_6]^{2+}$ C. VCl_4

The Jahn-Teller effect is expected for

(a) A and C only   (b) A only   (c) C only   (d) A and B only

190. The Second order rate constants for the outer sphere self-exchange electron transfer reactions for $[Ru(NH_3)_6]^{2+}/[Ru(NH_3)_6]^{3+}$ and $[Co(NH_3)_6]^{2+} / [Co(NH_3)_6]^{3+}$ are 9.2×10^2 M^{-1}Sec^{-1} and $\leq 10^{-9}$ M^{-1}Sec^{-1}, respectively. The Correct rationale for the above data is: **[NET SEP 2022]**

    (a) The change in the number of σ* -electrons in Co(II)/Co(III) system.

    (b) The change in the number of π*-electrons in Co(II)/Co(III) system.

    (c) The change in the number of both σ* and π* – Co(II)/Co(III)system.

    (d) The change in the number of σ*-electrons in Ru(II)/Ru(III) system.

191. Hydrolysis of the purple isomer of the complex $[Co(tren)(NH_3)Cl]^{2+}$ [tren = Tris(2-aminoethyl) amine] under basic conditions results in two products. The geometry of the intermediate involved in this reaction is **[NET SEP 2022]**

    (a) Trigonalbipyramidal   (b) Square pyramidal

    (c) Pentagonal planar   (d) Tetrahedral

192. An octahedral d^6 complex has a single spin-allowed absorption band. The spin-only magnetic moment (B.M.) and the electronic transition for this complex, respectively, are **[NET SEP 2022]**

    (a) 0 and $^1T_{1g} \leftarrow ^1A_{1g}$ (b) 4.9 and $^5T_{2g} \leftarrow ^5E_g$ (c) 4.9 and $^5E_g \leftarrow ^5T_{2g}$ (d) 0 and $^1T_{2g} \leftarrow ^1A_{1g}$

ANSWER KEY

1. D	2. B	3. B	4. C	5. A	6. B	7. D	8. C	9. D	10. B
11. D	12. C	13. B	14. B	15. D	16. B	17. B	18. B	19. D	20. C
21. C	22. C	23. C	24. B	25. C	26. A	27. C	28. D	29. B	30. B
31. A	32. A	33. A	34. A	35. A	36. D	37. A	38. B	39. C	40. C
41. A	42. B	43. D	44. B	45. A	46. D	47. C	48. A	49. A	50. D
51. B	52. C	53. A	54. A	55. D	56. A	57. A	58. A	59. C	60. A
61. A	62. A	63. C	64. A	65. C	66. A	67. A	68. A	69. A	70. D
71. A	72. A	73. B	74. D	75. A	76. C	77. A	78. B	79. B	80. B
81. A	82. B	83. B	84. B	85. A	86. C	87. A	88. D	89. C	90. A
91. A	92. C	93. B	94. D	95. B	96. B	97. C	98. C	99. D	100. A
101. C	102. A	103. A	104. D	105. A	106. B	107. B	108. B	109. B	110. A
111. B	112. A	113. A	114. A	115. A	116. A	117. B	118. D	119. B	120. C
121. B	122. A	123. A	124. C	125. C	126. C	127. A	128. B	129. C	130. A
131. C	132. D	133. C	134. A	135. A	136. C	137. B	138. A	139. B	140. A
141. A	142. C	143. C	144. B	145. B	146. B	147. C	148. B	149. A	150. B
151. B	152. B	153. B	154. C	155. B	156. A	157. A	158. C	159. C	160. B
161. B	162. B	163. B	164. B	165. C	166. D	167. C	168. D	169. A	170. B
171. C	172. B	173. B	174. B	175. B	176. A	177. A&B	178. C	179. D	180. C
181. C	182. C	183. B	184. A	185. C	186. D	187. D	188. C	189. A	190. A
191. A	192. C								

SOLUTION

1.
Ans. **(d)**
Sol.

$\text{Ni}^{+2} \equiv\!\equiv\!\equiv [\text{Ar}]\ 3d^8\ 4s^0 \equiv\!\equiv\!\equiv$

$\underset{\text{3d}}{\qquad} \quad \underset{\text{4s}}{\square} \quad \underset{\text{4p}}{\square} \quad \underset{\text{4d}}{\square\square\square}$
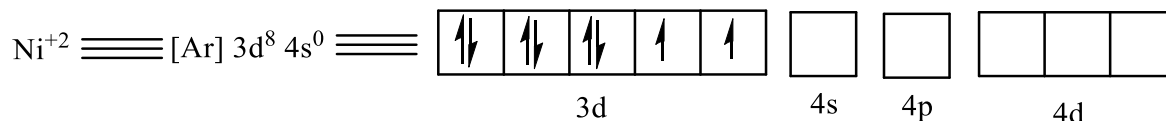
Geometry	Possible hybridisation	No. of unpaired electrons
Octahedral	sp^3d^2	2
Square planar	$d\,sp^2$	0
Tetrahedral	sp^3	2

2.
Ans. **(b)**
Sol.
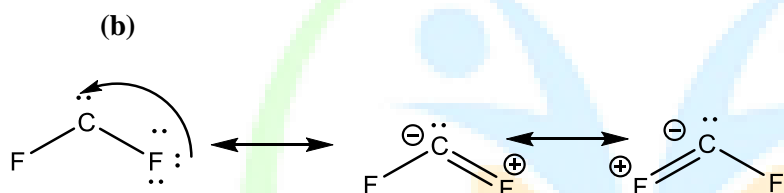
Stabilisation via back-bonding Due to innert pair effect stability of +2 oxidation state increases down the group.

3.
Ans. **(b)**
Sol. Isomers of $[\text{Ru(bpy)}_2\text{Cl}_2]$ can be represented as

trans-form   (II)   (III)
(Optically inactive)   d-cir-form   l-cis-form
(I)
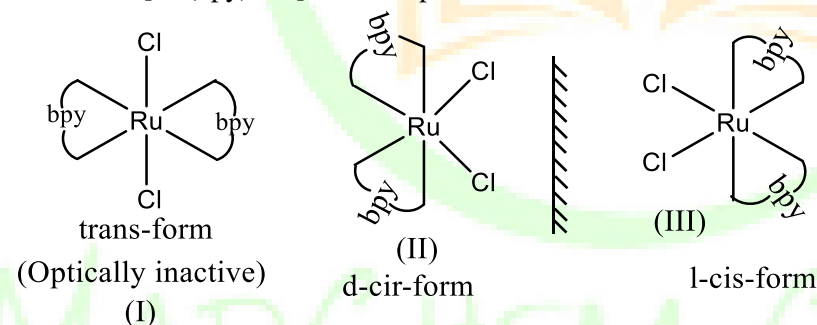
II and III are enantiomers.

4.
Ans. **(c)**
Sol. Kurnakov test is used to distinguish between cisplatin and transplatin, by using thiourea as a reagent.
Cisplatin + Aqueous thiourea → deep yellow solution

$\downarrow$ Crystallisation

yellow needle shape crystal
or tetrakis (thiourea) platinum (II)
chloride

Transplatin + Aqueous thiourea →Colourless solution

$\downarrow$ Crystallisation

white needle shape crystal of
trans-bis (thiourea) diaammine
platinum (II) chloride

5.

Ans.　　　**(a)**

Sol.　In the given case ligand in same, so higher the formal oxidation state of the metal, lower will be LMCT, So, order is $MnO_4^- < CrO_4^{2-} < VO_4^{3-}$

6.

Ans.　　　**(b)**

Sol.
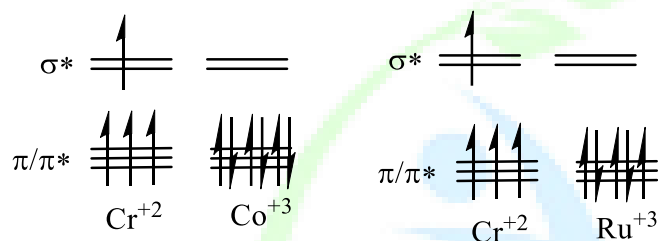
Large reorganisation for Co^{+3}　Reorganisation of Ru^{+3} less

outer sphere, so inner sphere　than CO^{+2}, So, slower tendency to go

mush faster　　　　　　　　　inner sphere

　　　HOMO = σ*(of Cr^{+2})　HOMO = σ* (of Cr^{+2})

　　　LUMO = σ* (of Co^{+3})　LUMO = π/π* (of Ru^{+3})

Acce;eration IS/OS = 10^{10}　Acceleration IS/ OS = 10^2

Inner sphere mechanism is favorable for σ* to σ* transition only

As Cr^{+2}/Ru^{+3} has σ* to π* transition which is responsible for its slower acceleration in going from　　outer sphere mechanism to inner sphere mechanis.

7.

Ans.　　　**(d)**

Sol.　Due to Jahn-Teller distrortion.

8.

Ans.　　　**(c)**

Sol.　In, Ni(CN$_4$)$^{2-}$ oxidation state of Ni is +2 & its valence shell electronic configuration is 3d^8. Since CN$^-$ is a strong ligand, therefore these ligands cause to pair up two unpaired electron, resulting in vacant 3d orbital. Hybridization: dsp^2 geometry: Square planar.
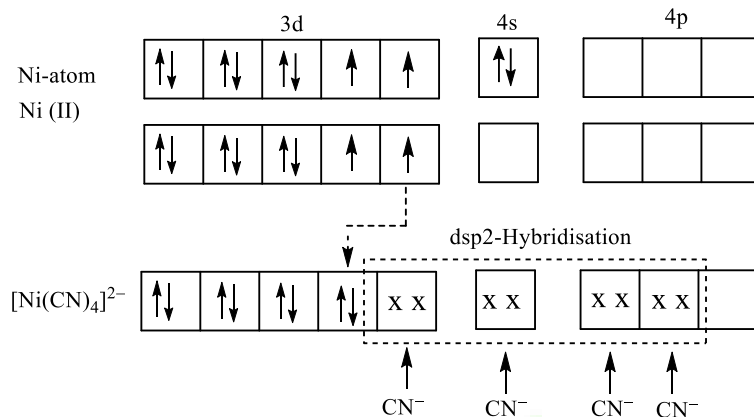
In $Ni(CL)_4$ oxidation state of Ni is +2 & its valence shell electronic configuration is 3d" Since Cl is a week ligand, no pairing, none of the 3d orbital is vacant. Hybridization: Sp^3 Gemoetry: tetrahedral
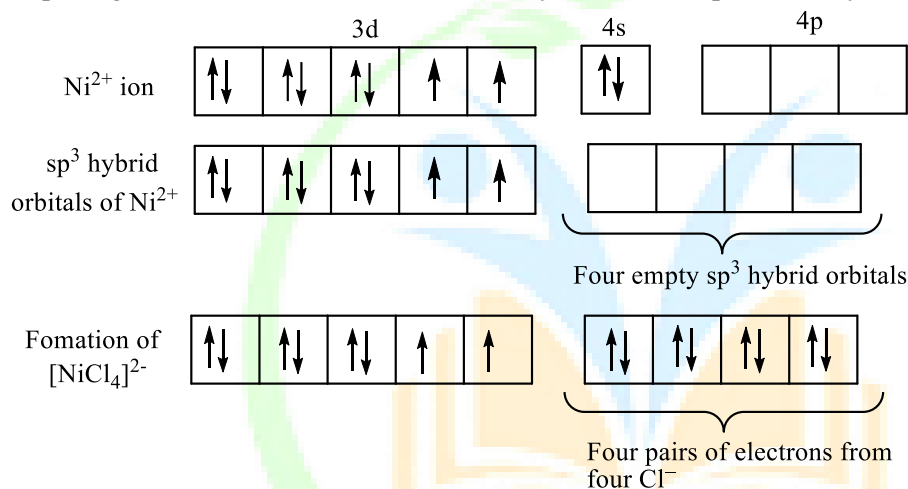
9.

Ans.   **(d)**

Sol.   For a d5 octahedral complex $[Mn(H_2O)_6]^{+2}$ all transitions are Laporte forbidden (orbital forbidden) as well as spin forbidden. Absorptions associated with doubly forbidden transitions are extremely weak, so it is very lightly coloured.

10.

Ans.   **(b)**

Sol. $2S + 1 = 3, 2S = 2, S = 1$

$S = 1, L = 2$

For term ,   S, P , D, F

Value of $L = 0, 1, 2, 3$

J can have values from [L+S] ... [L–S]

|2 +1|....|2–1|

3   2   1

Possible J values are : 3

11.

Ans.   **(d)**

Sol. $N \rightarrow 1s^1\ 2s^2\ 2p^3$

$L = 1 + 0 -1 = 0$

$s = 3/2$

$2s + 1 = 2 \times 3/2 + 1 = 4$

$J = (L+S) .... (L–S)$

$= |0+3/2|....|0–3/2| = 3/2$

Therefore, Ground state term = S

Term symbol = $^4S_{3/2}$

12.

Ans.   **(c)**

Sol. $[Co(NH_3)_6]^{3+}$ highest value of Δ_0

Highest energy (v) or lowest value of wavelength is absorbed

13.

Ans.   **(b)**

Sol.   For allowed transition : a) Spin multiplicity should be same or $\Delta S = 0$

Therefore (a) is not allowed as $\Delta S \neq 0$

b) $\Delta L = 0, \pm 1$, for allowed transition

Therefore (c) is not allowed as $\Delta L \neq 0, \pm 1$

c) u $\rightarrow$ g (allowed)

g $\rightarrow$ g (not allowed)

Therefore (b) is correct option.

14.

Ans.   **(b)**

Sol.   For d^3 and d^8, the lowest transition gives the value of Δo

Correlation of spectra for $[CrF_6]^3$ (in cm^{-1})
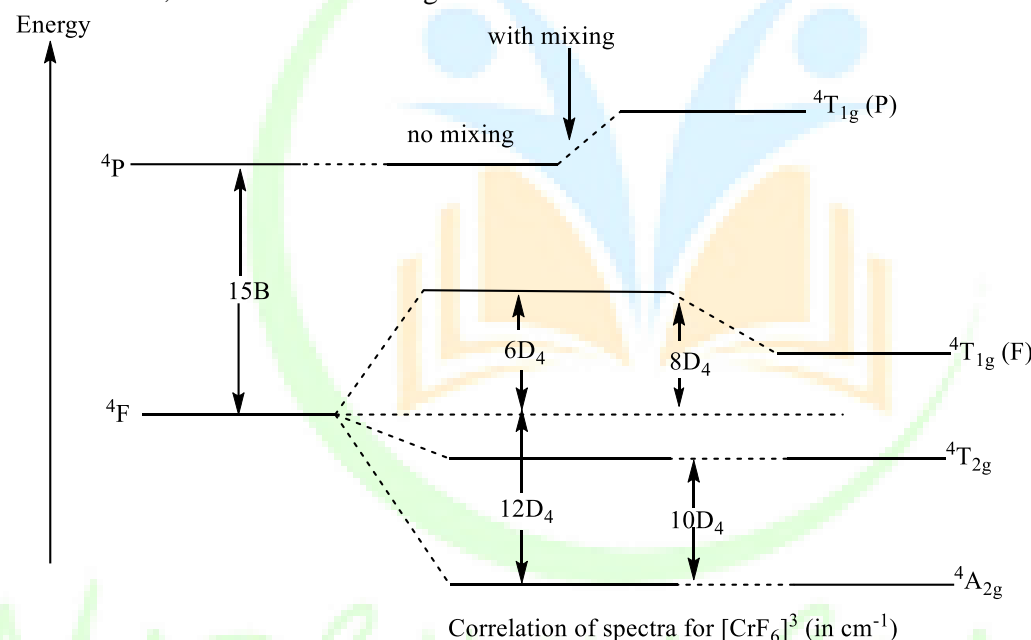
	Observed spectra	Predicted
$^4A_{2g} \rightarrow {}^4T_{1g}(P)$ v_3	34, 400	30, 700 (12D$_4$ +15B)
$^4A_{2g} \rightarrow {}^4T_{1g}$ (F) v_2	22 700	26, 800 (18 D$_4$)
$^4A_{2g} \rightarrow {}^4T_{2g}$ v_1	14, 900	14, 900 (10 D$_4$)

15.

Ans.   **(d)**

Sol. $Sm^{3+} \rightarrow$ due to spin-orbital coupling

16.

Ans.   **(b)**

Sol. $Ni(PPh_2Et)_2Br_2$; $\mu = 3.20$

Number of unpaired electrons = 2

Thus this complex is tetrahedral. Tetrahedral complexes show only one isomer.

Magnetic moment corresponding to two unpaired electrons = 2.9 B.M. The hesh values

3.20 BM is due to spin-orbit coupling.

17.

Ans. (b)

Sol. Higher the charge and smaller size of the central metal cation increases the acidic strength of hydrated complex because it polarizes O–H band of H_2O easily.

In $[Sc(H_2O)_6]^{3+}$, Sc is in +3 oxidation state and has smallest size.

Therefore, in size of dipositive ions increase in the order $Ni^{2+} < Mn^{2+}$. Na^+ has lowest oxidation state and largest size.

18.

Ans. (b)

Sol. Substitution nucleophilic unimolecular conjugate base mechanism.

(i) $[Co(NH_3)_5Cl]^{+2} + OH- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$
      acid   conjugate base

(ii) $[Co(NH_3)_4(NH_2)Cl]^+ \xrightarrow[\text{rate determining step}]{\text{slow step}} [Co(NH_3)_4(NH_2)]^{+2} + Cl^-$

(iii) $[Co(NH_3)_4(NH_2)]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH)]^{+2}$

19.

Ans. (d)

Sol.

20.

Ans. (c)

Sol. $[Co*(NH_3)_6]^{2+} \rightarrow HS$;

$[Co*(NH_3)_6]^{3+} \rightarrow$ Low spin

$[Ru(NH_3)_6]^{2+} \rightarrow$ Low spin; $[Ru*(NH_3)_6]^{3+} \rightarrow$ Low spin

21.

Ans. (c)

Sol. Ligand Cl^- is both σ–donor $\rightarrow$ and π donor $\rightarrow$

According to LFT, each ligand is always σ–donor some ligands like: NH3 which has only one lone pair of electrons is only σ–donor. Some ligands like F^-, Cl^-, OH^- etc which hence two or more lone pair of electrons are σ–as well as π donors Some ligands like CO, CN^-, SH_4 bpy, phen etc how vacant π^*– orbitals so these are σ–donor but π–acceptors.

22.

Ans. (c)

Sol. We know that number of microstates $= \frac{n!}{r!(n-r)!}$

For d^5, $r = 5$, $l = 2$

Therefore, $n = 2(2l+1) = 2(2 \times 2+1) = 10$

Number of microstates $= \frac{10!}{5!5!} = 252 = 7 \times 6^2$

23.

Ans. (c)

Sol. Spin-orbit coupling of d-electrons takes place in which t_{2g} orbitals are unsymmetrically filled.

24.

Ans. **(b)**
Sol. For Ni^{+2} ion in free state, the thus having same spin multiplicity as ^3F and ^3P. In octahedral field, 3F splits into $^3A_{2g}$, $^3T_{2g}$ and $^3T_{1g}$ terms but ^3P does not split but it transforms into $^3T_{1g}(P)$. Therefore orgel diagram is.
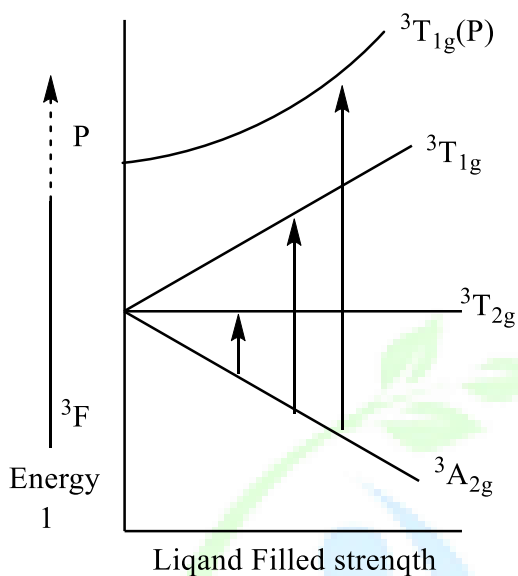
Three electronic transitions are $^3T_{2g} \leftarrow {}^3A_{2g}$, $^3T_{1g} \leftarrow {}^3A_{2g}$, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$

25.
Ans. **(c)**
Sol. $[Co(H_2O)_6]^{+2} \rightarrow t_{2g}^5 \, e_g^2$
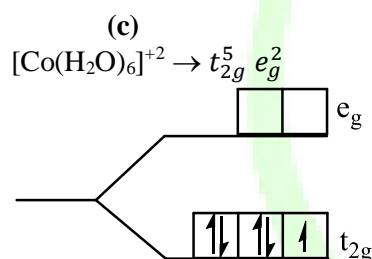
In this electron transition from $t_{2g}^5 \rightarrow e_g^2$, therefore d-d transition.
$[CoCl_4]^{-2} \rightarrow t_{2g}^5 \, e_g^2$
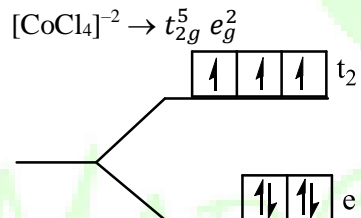
Electron transfer from e to t_2, therefore d-d transition.

26.
Ans. **(a)**
Sol.

10 Cu--O bonds
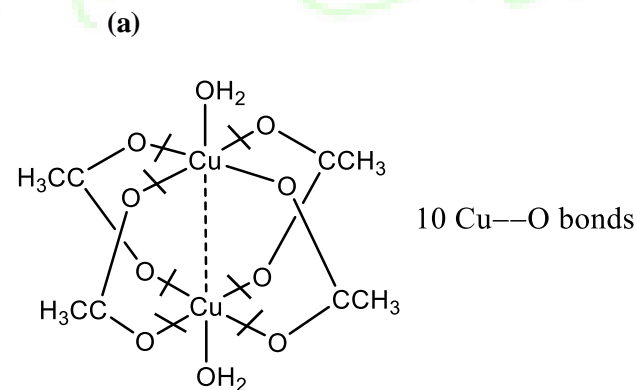
27.
Ans. **(c)**

Sol. Electric dipole allowed transition in d^2

For electronic transition selection rule, spin multiplicity $\Delta S = 0$; $\Delta 1 = \pm 1$, $\Delta J = 0, \pm 1$

$^3F \rightarrow {}^3D$ is allowed transition because $\Delta S = 0$, $\Delta 1 = -1$

28.

Ans. **(d)**

Sol. C_3^{-2} = In FCC arrangement (Lattice point at corner + at each face centre)

Therefore, coordination number of $Be^+ = 4$

And coordination number of $C_3^{-2} = 8$

In Be_2C_3, Be^+ = In tetrahedral voids

$Be^+ = \bullet$

$C_3^{--} = \bigcirc$

29.

Ans. **(b)**

Sol.

30.

Ans. **(b)**

Sol.

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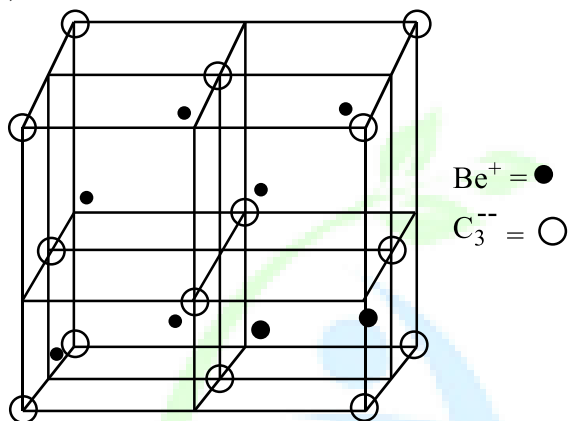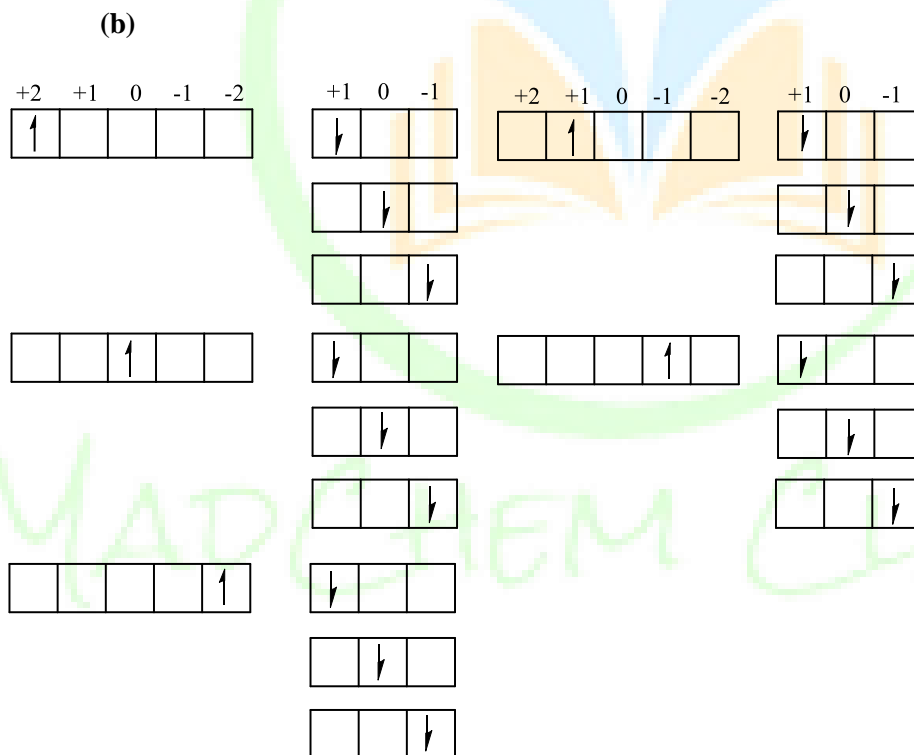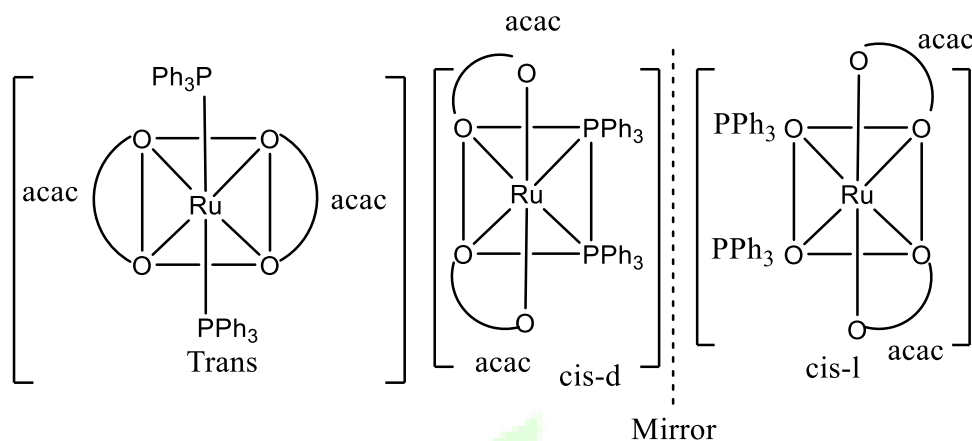
31.

Ans.   (a)

Sol. Co_3O_4 is a normal spinel. In normal spinel the Co^{2+} ions occupy tetrahedral voids and Co^{3+} ions occupy octahedral voids. Therefore, spinel structure of Co_3O_4 is $(Co^{2+})_t(2Co^{3+})_oO_{4-}$

32.

Ans.   (a)

Sol.   In trigonal bipyramidal complexes, the two ligands lie on z-axis and the three in xy plane somewhere in between the axes. In xy plane, there are four electrons and on z-axis there is only one electron in d_z^2 orbital (Electronic Configuration, $d_{xz}^2 = d_{yz}^2 < d_{xy}^2 = d_{x^2-y^2}^2 < d_{z^2}^1$)

33.

Ans.   (a)

Sol.   Trans effect of $Cl- > NH_3$ Anti-tumour agent is $cis–[Pt(NH_3)_2Cl]$
The precursor of this complex is $[PtCl_4]^{2-}$
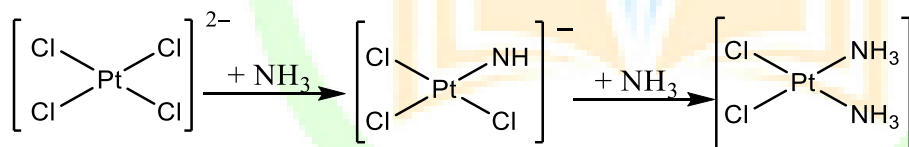
34.

Ans.   (a)

Sol.   When $Fe(NO_3)_3. 9H_2O$ is dissolved in water, the complex ion $[Fe(H_2O)_6]^{3+}$ is formed.
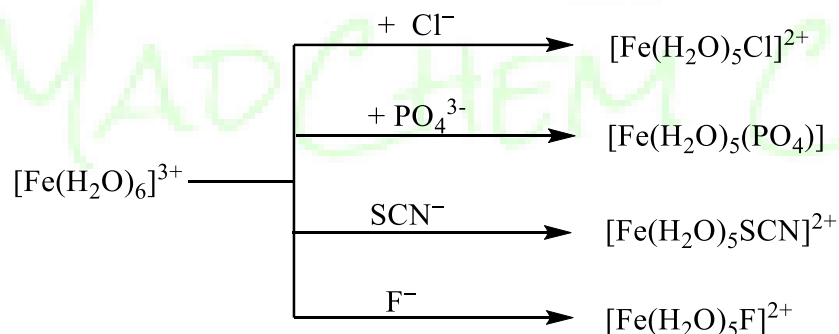
35.

Ans.   (a)

Sol.   The rate of water exchange in $[Cu(H_2O)_6]^{2+}$ is fastest due to Jahn-Teller distortion. For other three complexes of 3d–series dipositive metal cation. The rate of water exchange decreases with   increase in effective nuclear charge and decrease in size.

36.

Ans.   (d)

Sol. For two non- equivalent π-electrons $[\pi^1, \pi^1]$,

If we consider the following arrangement

m_L H -1

$L = 0 \to \Sigma$

$S = 1$

$2S + 1 = 3$

term $\to {}^1\Sigma$

m_L $+1$ -1

$L = 0 \to \Sigma$

$S = 0$

$2S + 1 = 1$

term $\to {}^1\Sigma$

H -1 $+1$ -1

$L = 2 \to 0$

$S = 1$

$2S + 1 = 3$

term $\to {}^3\Delta$
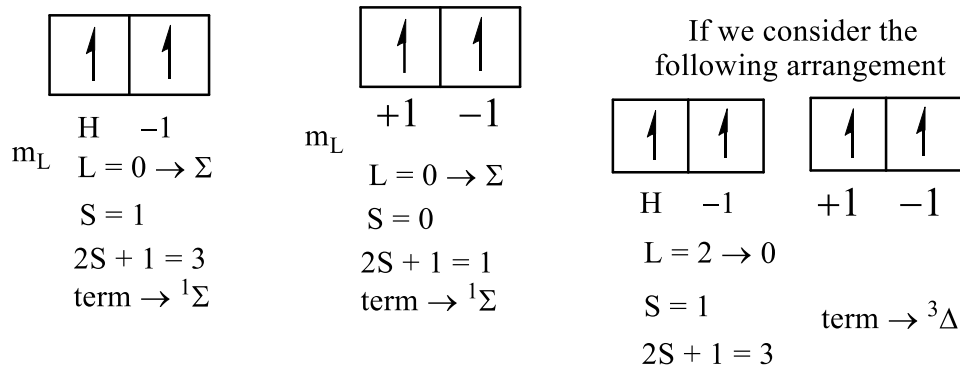
${}^3\phi$ is not possible.

37.

Ans.   (a)

Sol. Trans effect Cl^- has larger trans effect than NH_3.

$$\begin{bmatrix} Cl & Cl \\ & Pt & \\ Cl & Cl \end{bmatrix}^{-2} \xrightarrow[-Cl]{+ NH_3} \begin{bmatrix} Cl & Cl \\ & Pt & \\ Cl & NH_3 \end{bmatrix}^{-1} \xrightarrow[-Cl]{+ NH_3} \begin{bmatrix} Cl & NH_3 \\ & Pt & \\ Cl & NH_3 \end{bmatrix}$$
cis
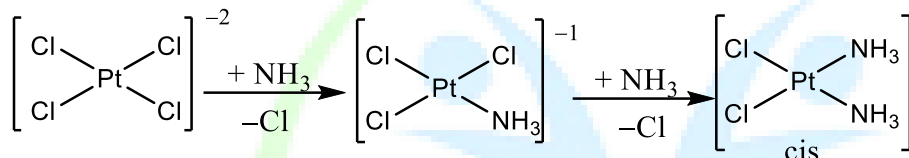
38.

Ans.   (b)

Sol. The electronic transition responsible for the colour of the transition metal ions is $d_\pi \to d_\sigma^*$ which   is in according to LFT.
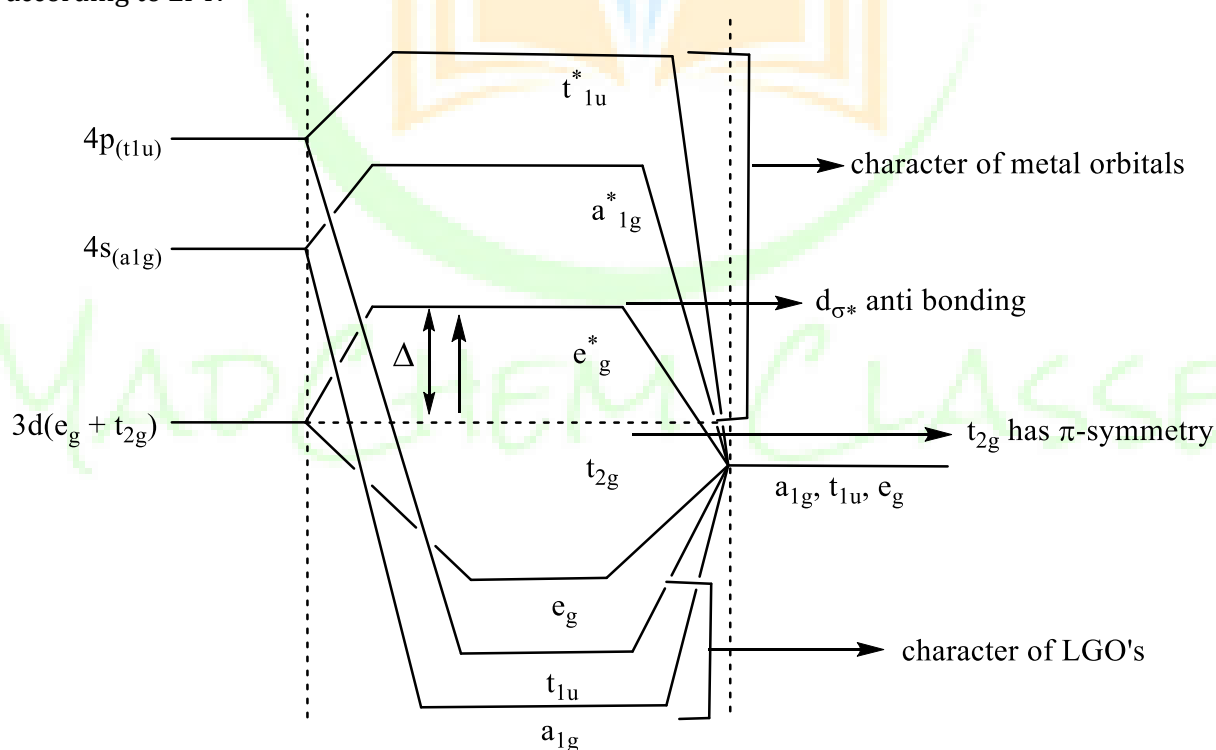
39.

Ans.   (c)

Sol. The mulliken symbols for the spectroscopic state arising from free ion term F are

$T_{1g} + T_{2g} + A_{2g}$

40.

Ans. (c)

Sol.

$$\begin{array}{c} +4 \\ \text{Me} \diagdown \quad \diagup \text{Cl} \\ \text{Ti} \\ \text{Cl} \diagup \quad \diagdown \text{Cl} \end{array}$$
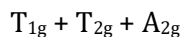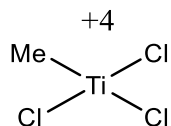
In the first complex titanium in high oxidation state +4. So react faster with σ–donor ligand.

Correct order $NMe_3 > PMe_3 > CO$

Where as in the second complex

$$\begin{array}{c} \text{THF} \\ \text{OC} \diagdown \quad | \quad \diagup \text{CO} \\ \quad \text{Mo} \\ \text{OC} \diagup \quad \diagdown \text{CO} \\ \quad \text{CO} \end{array}$$
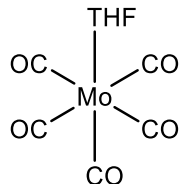
Mo in low oxidation state. So, reactivity order is $CO > PMe_3 > NMe_3$

41.

Ans. (a)

Sol. $[CoCl_4]^{2-} + 6H_2O \rightleftharpoons [Co(H_2O)_6]^{2+} + 4Cl^-$
(blue)   (Light pink)

42.

Ans. (b)

Sol. $[Bu_4N]_2 Re_2Cl_8$

$$2[Bu_4N]^+ + [Re_2Cl_8]^{-2} \quad \begin{bmatrix} \begin{array}{c} \text{Cl} \qquad \text{Cl} \\ \text{Cl} \diagdown \quad \diagup \text{Cl} \\ \text{Cl} - \text{Re} \equiv \text{Re} - \text{Cl} \\ \text{Cl} \diagup \quad \diagdown \text{Cl} \\ \text{Cl} \qquad \text{Cl} \end{array} \end{bmatrix}^{-2}$$

$$\text{ABMO} \begin{bmatrix} \underline{\quad} & \overline{\quad} \; \sigma^* \\ & \underline{\quad} \; \pi^* \\ & \underline{\quad} \; \delta^* \text{[LUMO]} \end{bmatrix}$$

HOMO

$$\text{BMO} \begin{bmatrix} & \underline{\uparrow\downarrow} \; \delta \\ \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} \; \pi \\ & \underline{\uparrow\downarrow} \; \sigma \end{bmatrix}$$

$\delta - \delta^*$ transition
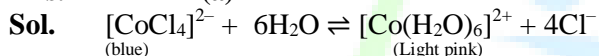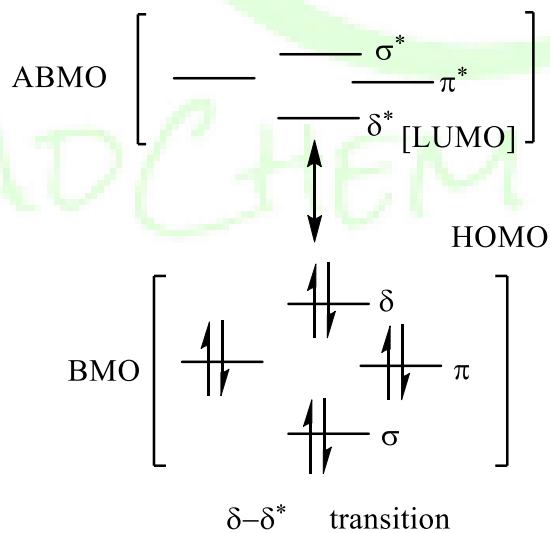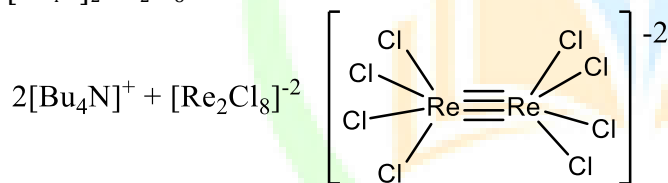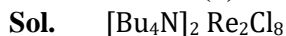
43.

Ans. (d)

Sol. Increasing π–acidity
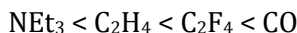
$$NEt_3 < C_2H_4 < C_2F_4 < CO$$

Where, NEt_3 = Neither π–donor nor π–acceptor

$C_2H_4 < C_2F_4 < CO$ = Increasing order of π–acceptor ability (on the bases of LET)

44.
Ans.　　　**(b)**
Sol.　Intensity of $C(^4A_{2g} \rightarrow -E_g)$ is lowest, since it is spin forbidden.

45.
Ans.　　　**(a)**
Sol.　From spectro chemical series order, $Br^- < Cl^- < NCS^-$
　　Order of Δ_t

$$[Co(NCS)_4]^{-2} > [CoCl_4]^{-2} > [CO(Br_4)]^{-2}$$

46.
Ans.　　　**(d)**
Sol.　+3　　　−3　　　　　　+4−2−2+3 −3　　　+4 −4　　　+1 −1
　　$FeCl_3 \cdot 6H_2O +$ 　　　　$SOCl_2$ $\longrightarrow$ $FeCl_3(s) + SO_2(g) + HCl(g)$
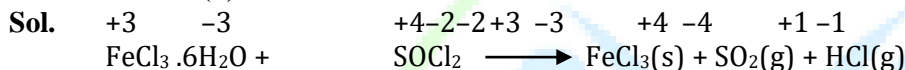
47.
Ans.　　　**(c)**
Sol.　$[Fe(H_2O)_6]^{2+} < [Fe(H_2O)_6]^{3+} < [Al(H_2O)_6]^{3+}$
　　Reference – Shriver Atkin (P.No. 123 $\rightarrow$ Bronsted acid base concept)

48.
Ans.　　　**(a)**
Sol.　$Co^{2+} \rightarrow t_{2g}^5 \, e_g^2$ 　　　　$\mu = 3.89$ B.M.
　　$Cr^{2+} \rightarrow t_{2g}^4 \, e_g^2$ 　　　　$\mu = 4.9$ B.M.
　　$Mr^{2+} \rightarrow t_{2g}^3 \, e_g^1$ 　　　　$\mu = 4.9$ B.M.
　　$Fe^{2+} \rightarrow t_{2g}^4 \, e_g^2$ 　　　　$\mu = 4.9$ B.M.
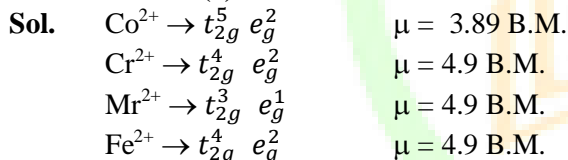
49.
Ans.　　　**(a)**
Sol.　Catalase is a tetramer of four polypeptide chains covering 500 amino acids.
　　It works as $H_2O_2 + Fe(III) - E \rightarrow H_2O + O = Fe(IV) - E^{+0}$
　　$H_2O_2 + O = Fe(IV) - E^+ \rightarrow H_2O + Fe(III) - E + O_2$
　　The colour arises as Fe(III) changes into Fe(IV)
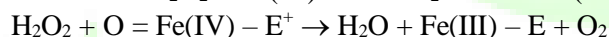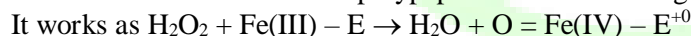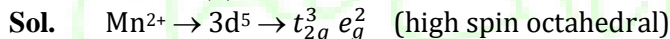
50.
Ans.　　　**(d)**
Sol.　$Mn^{2+} \rightarrow 3d^5 \rightarrow t_{2g}^3 \, e_g^2$ 　(high spin octahedral)
　　CFSE in Oh field = $(-0.4 \times 3 + 0.6 \times 2) = 0$

　　$Cr^{3+} \rightarrow 3d^3 \rightarrow t_{2g}^3 \, e_g^0$ 　　　　(octahedral)
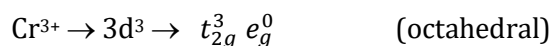
　　CFSE in octahedral field. = $-0.4 \times 3\Delta_0 = -(0.4 \times 3) \Delta_0 = -1.2 \Delta_0$

51.
Ans.　　　**(b)**
Sol.

In tetragonal elongation

In tetragonal compression

52.
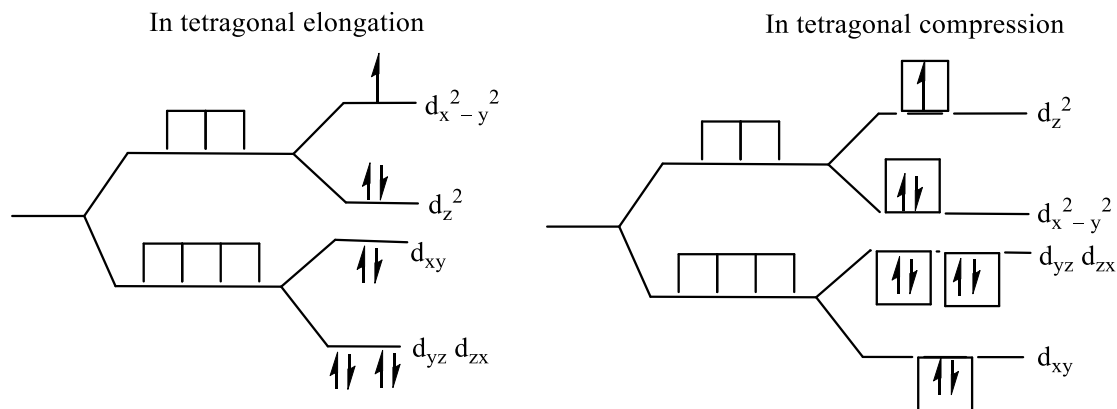
Ans. (c)

Sol. Pt–S→ dπ–dπ bonding in weaker than that of Pt–P bonding. When Pt–S and Pt–P bond are trans to each other then Pt–S become weaker therefore in such a situation SCN ligand tends to form bonding through M atoms of ligand as M do not form dπ–pπ bonding. Hence, the most probable structure will be
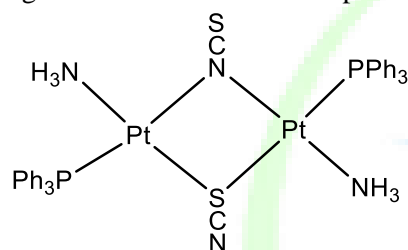
53.

Ans. (a)

Sol. Ni^{2+} is tested by dmg

Ni^{2+} + 2dmg → $[Ni(dmg)_2]$ (Tschygaeff test)

The structure of complex is
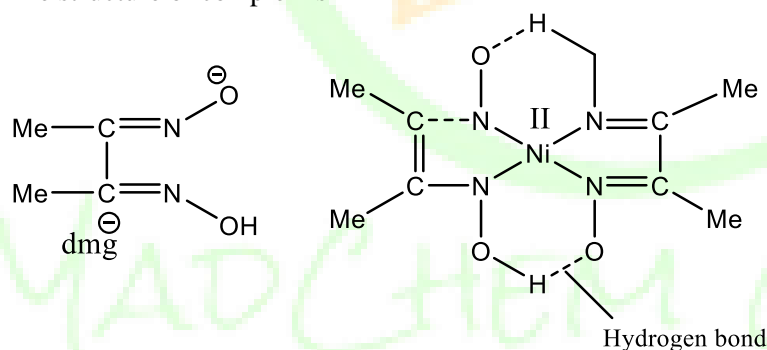
Hydrogen bond

Therefore

Ni–N bonds = 4

Ni–O = 0

Hydrogen bonds = 2

54.

Ans. (a)

Sol. In $[AgL_4]^{2+}$ and $[AgL_6]^{2+}$, Ag^{2+} has d^9 configuration, hence have unpaired electron. Hence paramagnetic.

$[AgL_4]^{3+}$, Ag^{3+} has d^8 configuration and dsp^2 hybridization (square planar so pairing of electron).

Hence, dimagentic in nature.

55.

Ans. (d)

Sol. For np^2 configurations (microstates)

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		L	M	S
(I) $l = +1$ 0 -1	^1D	2	1	0
(II)	^3P	1	3	1
(III)	^1S	0	1	0
(IV)	^3D	1	3	1

The configuration (IV) violets the Pauli's Principle, Hence term symbol ^3D is not possible.

56.

Ans.   **(a)**

Sol. S and p both form π-bonding with complex and π-bonding capacity of sulphur is greater than phosphorus due to smaller size of d-orbital of sulphur. Hence, in presence of sulphur trans to phosphours donor atom phosphours – metal bond will be weak hence they do not lie trans to each other in the complex. As nitrogen does not involment in π-bonding with complex hence when nitrogen atom is trans to phosphours, phosphorus become able to form efficient π-bond with metal hence become stable thats why P and N are trans to each other

57.
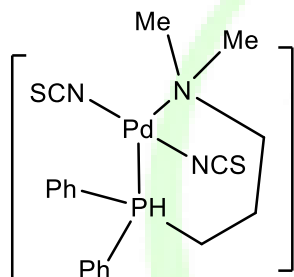
Ans.   **(a)**

Sol. $NiBr_2 \xrightarrow[-78°/CS_2]{Et.Ph_2P} (A) \rightarrow (B)$

$\qquad\qquad$ (Red)$\quad$(Green)

$\qquad\qquad$ $\vec{\mu} = 0 BM \qquad \vec{\mu} = 3.2$ BM

n = unpaired $\quad \therefore$ n = 0 $\qquad \vec{\mu} = \sqrt{n(n+2)}$ $\qquad$ n = near about two.

$\quad$ electrons

$Ni^{++} = 3d^8\, 4s^0\, 4p^0 =$
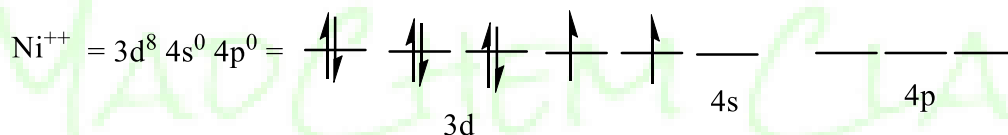
Hence, (A) will be square planar.

For(B), $Ni^{++} =$

dsp^2 hybridisation

For(B), $Ni^{++} =$

sp^3 hybridisation
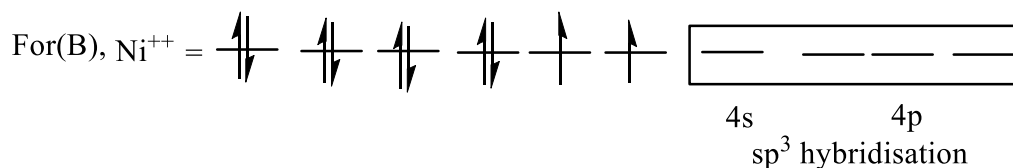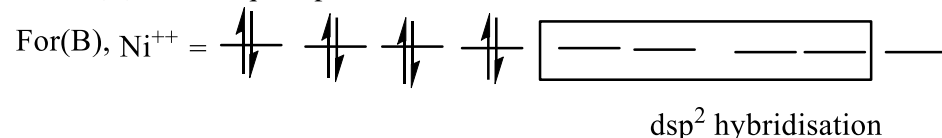
Hence, (B) will be tetrahedral.

Therefore, $NiBr_2$ $\xrightarrow{\text{2 EtPh}_2\text{P}}$

Square Planar
(A)

Tetrahedral
(B)
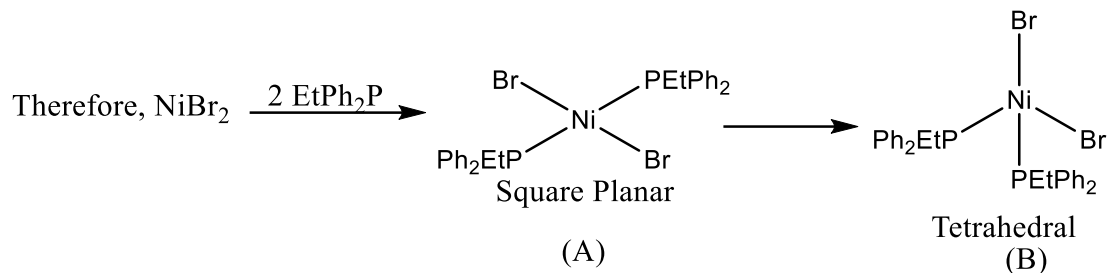
(A) and (B) are polytopal isomers.

58.
Ans.   **(a)**
Sol. $[CoL_6]^{3+} \rightarrow$ red colour $\rightarrow$ absorbs green radiations.
$[CoL'_6]^{3+} \rightarrow$ green colour $\rightarrow$ absorbs red radations.
Energy of green radiations > energy of red radiations.
Therefore, L will be stronger ligand and than L'. Thus, L and L' are NH_3 and H_2O respectively.

59.
Ans.   **(c)**
Sol.   A maximum five 'd' orbitals can from bonding with each other

$M \equiv M$ σ bonds $\Longrightarrow$ 1
π bonds $\Longrightarrow$ 2
δ bonds $\Longrightarrow$ 2
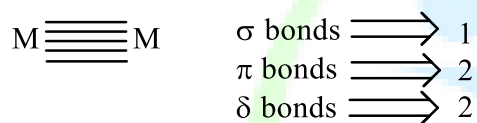
Firstly reported in 2007 in chromium complexes.

$\left[Ar - Cr \equiv Cr - Ar \right]$
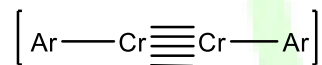
Ar = Substituted aromatic rings.

60.
Ans.   **(a)**
Sol.

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$$+ [Cr(H_2O)_6]^{2+}$$

Labile

Inert

$-H_2O$

Electron exchange
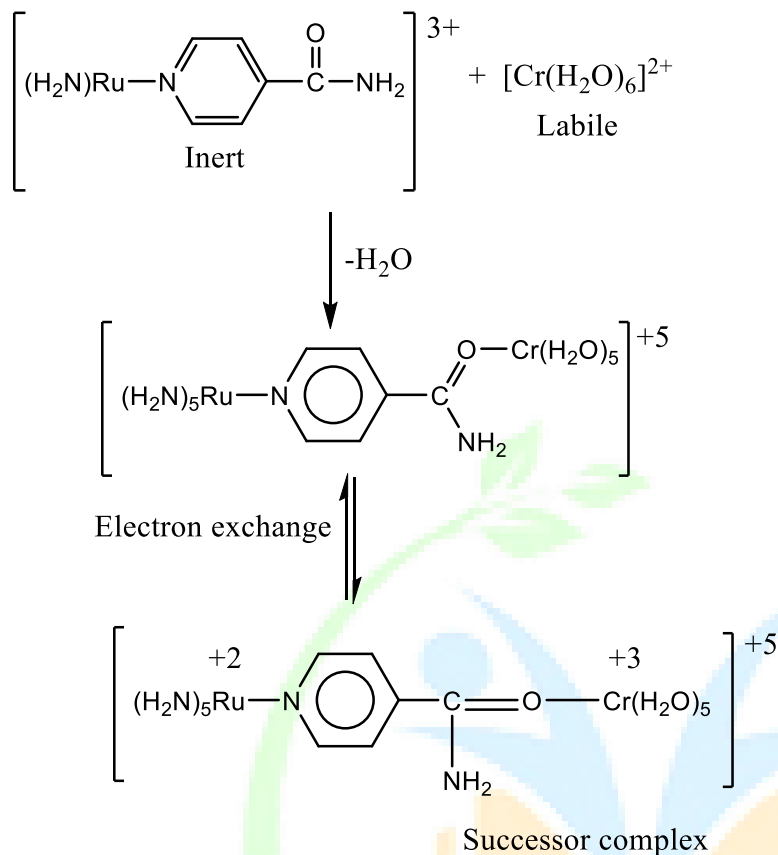
Successor complex

In the successor complex inert ruthenium bridged to inert chromium.

61.

Ans. (a)

Sol. (Phen) is an π-acceptor ligands hence there is mixing of donor and acceptor orbital having similar symmetry this leads to fast transfer of electron leading to enhance rate of reaction.

$[Fe(phen)_3]^{3+}$ $[Fe(Phen)_3]^{2+}$

$\downarrow$ $\downarrow$

$t_{2g}^2 \, e_g^0$ $t_{2g}^6 \, e_g^0$

$\pi^{*5} \, \sigma^{*0}$ $\pi^{*6} \, e_g^0$

62.

Ans. (a)

Sol. $[V(H_2O)_6]^{+3} \; V^{+3} \to 3d^2 \to t_{2g}^2 \, e_g^0$

Two transitions.

$V_1 = {}^3T_{1g}(F) \to {}^3T_{2g}(F); \; V_2 = {}^3T_{1g}(F) \to {}^3T_{1g}(P)$

$^3A_{2g}$

$^3T_{1g}(P)$

^3P

$^3T_{2g}$

^3F

$^3T_{1g}$

63.
Ans. (c)
Sol.

Ni^{2+}

e_g

t_{2g}

Symmetrical electronic environment so all bond length same

OH_2

equatorial bond short

Cu^{2+}

d_{z^2} $d_{x^2y^2}$

e_g

t_{2g}

There is large electron density at z-axis So, on z-axis increases

64.
Ans. (a)
Sol.
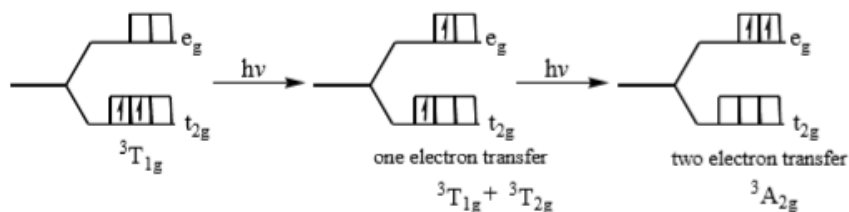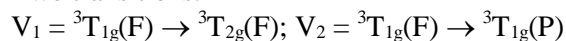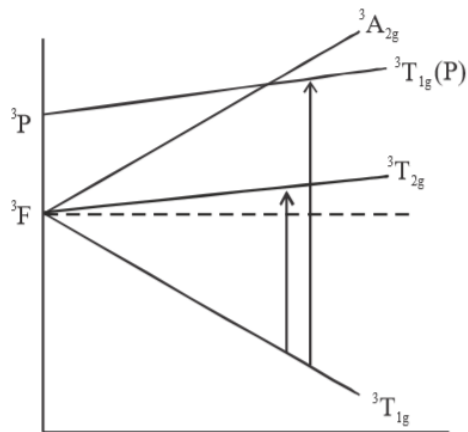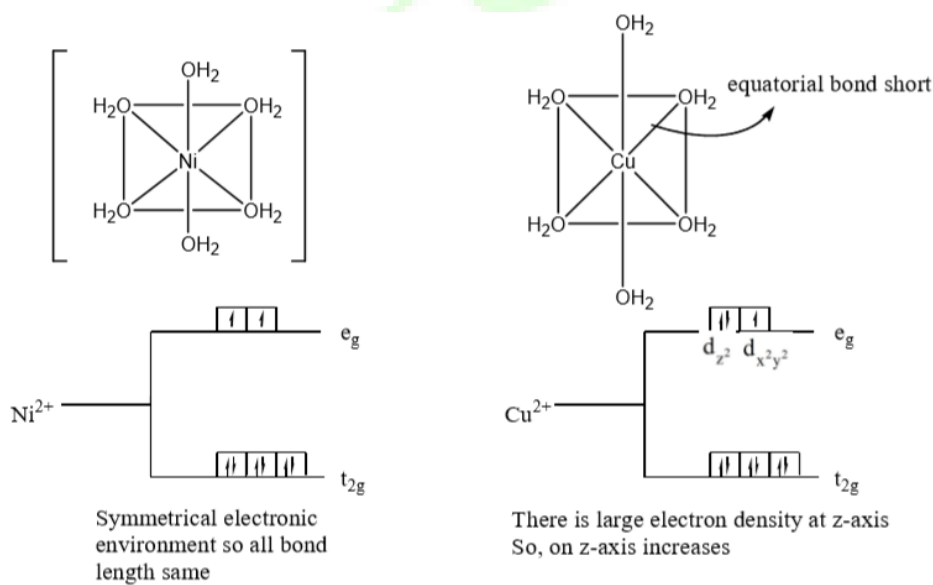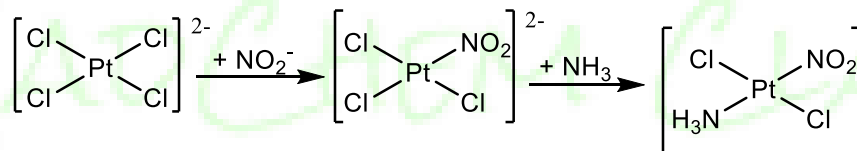
Trans effect $NO_2^- > Cl^- > NH_3$

65.
Ans. (c)
Sol.

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cis-d   cis-d   Trans optically inactive

66.
Ans.   **(a)**
Sol.

$[Mn(H_2O)_6]^{2+}$, Mn^{2+} ⟶ $3d^5$
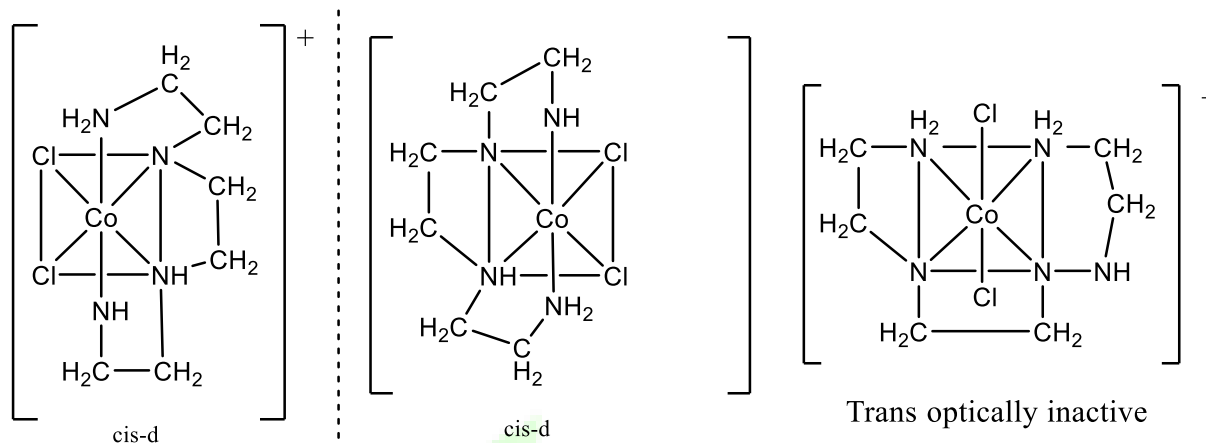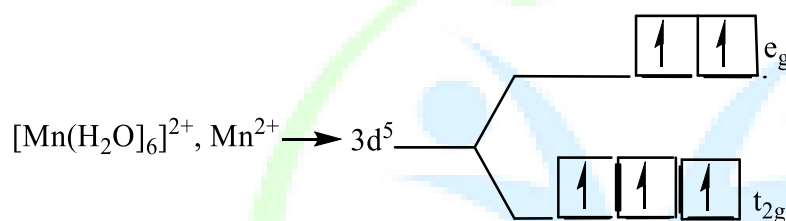
Ground state term for d^5 is ^6S which transform into $^6A_{1g}$ in octahedral field.
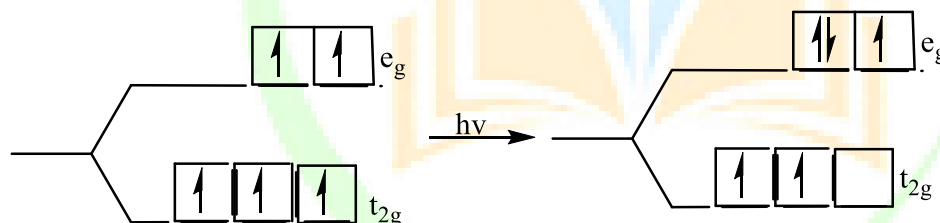
There is spin change during electron transition. Therefore, transition is spin disallowed.

67.
Ans.   **(a)**
Sol. $[Co(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O$
$[Co(NH_3)_4(NH_2)Cl]^+ \rightarrow [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$

$[Co(NH_3)_4(NH_2)]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+}$
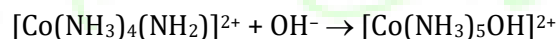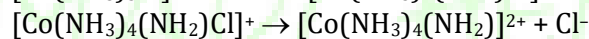
Base hydrolysis of $[Co(NH_3)_5Cl]^{2+}$ depends on the concentration of both $[Co(NH_3)_5Cl]^{2-}$ and base. In this reaction OH– abstract proton from coordinated NH_3.

The base hydrolysis of $[Co(CN)_6]^{3-}$ is independent of base because it has no ionizable proton.

68.
Ans.   **(a)**
Sol. $[MnF_6]^{3-}$, $Mn^{3+} \rightarrow 3d^4 \rightarrow t_{2g}^3 eg^1$
    (HS)

$\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.9$

d^4 | ↑ | ↑ | ↑ | ↑ | |
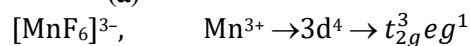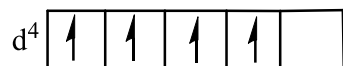
$s = 2 \Rightarrow 2s + 1 = 2 \times 2 + 1 = 5$

$L = 2 \rightarrow D$

Ground state term symbol $\rightarrow {}^5D$

69.
Ans. **(a)**
Sol. $[CrCl_6]^{3-}$ $\qquad$ $Cr^{3+} \rightarrow 3d^3$

$$\mu_s = \sqrt{3(3+2)} = 3.87 \; B.M.$$

$$\mu_{L+S} = \sqrt{n(n+2) + L(L+1)} \quad B.M.$$

↑	↑

-1 -2

d^3 | ↑ | ↑ | ↑ | ↑ | |

$m l$ +2   +1   0
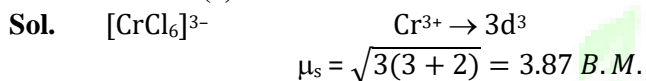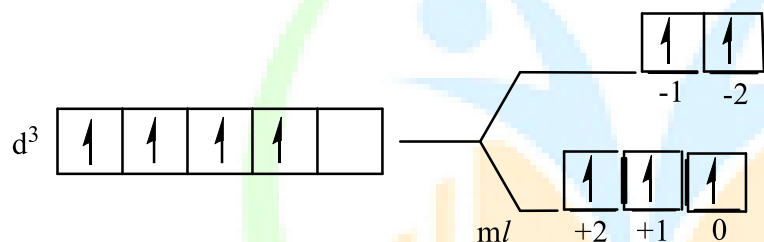
$L = 3$

$$\mu_{L+S} = \sqrt{3(3+2) + 3(3+1)} = \sqrt{15 + 12} = \sqrt{27} = 5.20 \; B.M.$$

70.
Ans. **(d)**
Sol.

$N = 1s \; 2s \; 2p$

$L = +1 \quad 0 \quad -1$

↑	↑	↑

$S = 1/2 + 1/2 + 1/2 = 3/2$
$L = +1 + 0 - 1 = 0$

71.
Ans. **(a)**
Sol. $[Ne]2p^1 \; 3p^1$
$2s + 1 = 3; \qquad 2s = 2; \quad s = 1$
For, D, L = 2
$J = |L+s|...|L-s| = |2+1|....|2-1| = 3, 2, 1$
Levels for ${}^3D$ are ${}^3D_3, {}^3D_2, {}^3D_1$

72.
Ans. **(a)**
Sol. It is first inorganic optically active compound discovered by Werner.
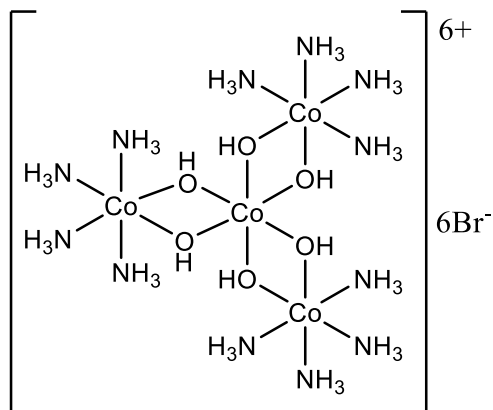
Number of Co–O bonds = 12
Number of Co–N bonds 12

73.
Ans.   **(b)**
Sol.   For allowed transition : a) Spin multiplicity should be same or $\Delta S = 0$
Option c and d (incorrect) as $\Delta S \neq 0$
b) $\Delta L = \pm 1$, for allowed transition
$\qquad$ $3S \rightarrow 3p$
$\qquad$ $\Delta S = 3-3=0$
$\qquad$ $\Delta L = 1-0=1$

74.
Ans.   **(d)**
Sol. $ns^1 \, np^1$
$L=1 \equiv P$
$S= 1$ hence, $2S + 1 = 3$
For J value, if orbital is less than half filled than
$J = |L–S| = |1–1| = 0$
Hence, $^3P_0$

75.
Ans.   **(a)**
Sol.   Fe (II) protoporphyrin $\rightarrow \pi \rightarrow \pi^*$ transition
$[Mn(H_2O)_6]Cl_2 \rightarrow Mn^{+2} \rightarrow d^5$ (high spin) spin forbidden (d-d) transition.
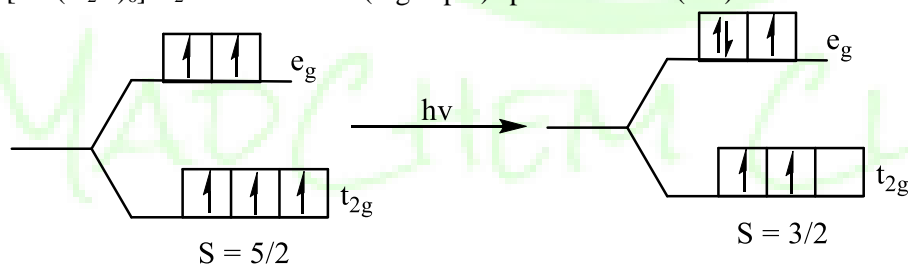
$\Delta S = 1$. Hence, not allowed.
$[Co(H_2O)_6] \, Cl_2 \rightarrow Co^{+2} \rightarrow d7$ (high spin) (d–d)
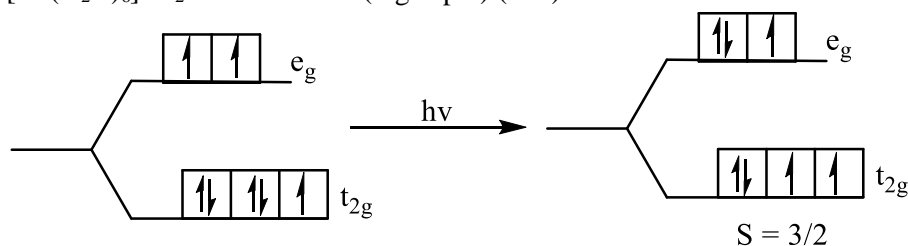
$\Delta S = O$. hence allowed

76.

Ans. **(c)**

Sol. $K_4[Cr(CN)_6] = Cr^{+2} \rightarrow d^4$ (low spin)

For a compound to show John Teller Distortion e_g or t_{2g} set should be electronically degenerate.

(1) $Cr^{+2} \rightarrow d^4$ (low spin)
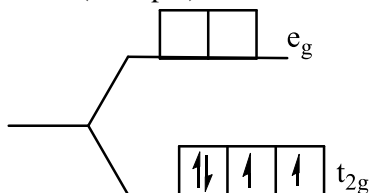
Electronically degenerate hence show John Teller Distortion.

(2) $K_4[Fe(CN)_6] = Fe^{+2}$ (low spin) $= d^6$ (low spin)
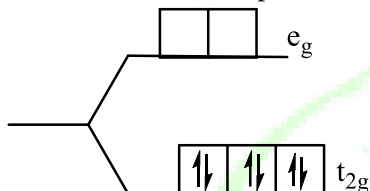
Electronically non-degenerate hence, no Jahn-Teller distortion

(3) $K_3[Co(CN)_6] = Co^{+3} \rightarrow d^6$ (low spin)

Same as above hence, no Jahn-Teller Distortion.

(4) $K_4(Mn(CN)_6] = Mn^{+2}$ (low spin)
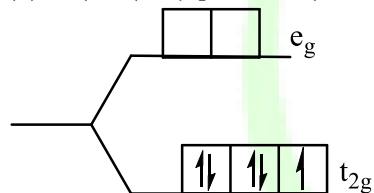
electronically degenerate

77.

Ans. **(a)**

Sol. Taking the valence shell configuration

Be $2s^1 3s^1$

$s = 1/2 + 1/2 = 1$

Multiplicity $= 2S + 1 = 2x\ 1 + 1 = 3$

$L = 0 + 0 = 0$, S term

$J = (L+S) = (0+1) = 1$

Hence, terms is $^3S_1$

78.

Ans. **(b)**

Sol. Chelate effect is predominately due to entropy change

$$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$$
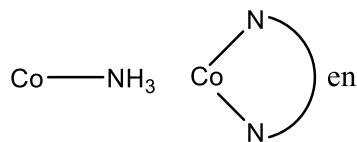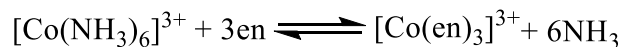
ΔH nearly same but entropy change is more.

79.

Ans. **(b)**

Sol. For $[1s^2\ 2s2p^6\ 3p^1]$

+1   0   −1

↑		

$s = \dfrac{1}{2}$
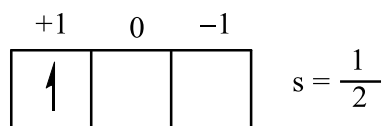
$2s + 1 = 2 \times \dfrac{1}{2} + 1 = 2$

$J = |1+s|....|1-s|$

$= |1+1/2|....|1-1/2|$

$= 3/2 \quad 1/2$

Term symbol $^2P_{3/2}$ $^2P_{1/2}$

80.

Ans.   **(b)**

Sol. $^3F \rightarrow {}^3D$

Since, for allowed transition (atomic), $\Delta S = 0$, $\Delta L = 0, \pm 1$

In option a and c spin multiplicity is not same therefore incorrect

In option d, $\Delta L = 2$ therefore incorrect.

81.

Ans.   **(a)**

Sol.   Taking the valence shell configuration

Be $2s^1 3s^1$

$s = 1/2 + 1/2 = 1$

Multiplicity $= 2S + 1 = 2 \times 1 + 1 = 3$

$L = 0 + 0 = 0$, S term

$J = (L+S) = (0+1) = 1$

Hence, terms is $^3S_1$

82.

Ans.   **(b)**

Sol.   Chelate effect is predominately due to entropy change

$[Co(NH_3)_6]^{3+} + 3en \rightleftharpoons [Co(en)_3]^{3+} + 6NH_3$

$Co{-\!-\!-}NH_3$ Co $\overset{N}{\underset{N}{\diagdown\!\diagup}}$ en
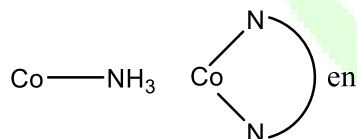
ΔH nearly same but entropy change is more.

83.

Ans.   **(b)**

Sol.   For $[1s^2\, 2s2p^6\, 3p^1]$

+1   0   −1

↑		

$s = \dfrac{1}{2}$
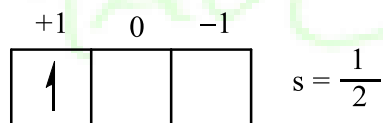
$2s + 1 = 2 \times \dfrac{1}{2} + 1 = 2$

$J = |1+s|....|1-s|$

$= |1+1/2|....|1-1/2|$

$= 3/2 \quad 1/2$

Term symbol $^2P_{3/2}$ $^2P_{1/2}$

84.

Ans.   (b)

Sol. $^3F \rightarrow {}^3D$

Since, for allowed transition (atomic), $\Delta S = 0$, $\Delta L = 0, \pm 1$

In option a and c spin multiplicity is not same therefore incorrect

In option d, $\Delta L = 2$ therefore incorrect.

85.
Ans. **(a)**
Sol. $CrO_4^{2-} < MnO_4^{2-} < FeO_4^{2-}$
All have +6 oxidation state but due to smaller size on going from Cr to Fe. Fe has very high charge density. Hence, it has very high tendency to accept electron. Hence, strongest oxidising agent.

86.
Ans. **(c)**
Sol.

	Number of unpaired electrons
(A) $[CoF_6]^{3-} \Rightarrow d^6$(high spin) $\approx t_{2g}^4 \, e_g^2$	4
(B) $[IrCl_6]^{3-} \Rightarrow d^6$ (low spin) $\approx t_{2g}^6 \, e_g^0$	0
(C) $[Fe(H_2O)_6]^{2+} \Rightarrow d^6$ (high spin) $\approx t_{2g}^4 \, e_g^2$	4

Since, A and C has same number of unpaired electron. Hence, they have same magnetic moment. As A and C are 3d-block metal with weak ligand. Hence, they are high spin while Ir being 5d-metal is low spin. Because 5d greater splitting power than 3d.

87.
Ans. **(a)**
Sol. $[Mn(H_2O)_6]^{2+} = d^5$ (H.S)
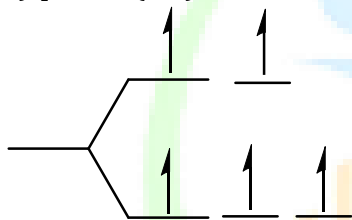
As all the levels are electronically non-degenerate. Hence, No Jahn–Teller distortion. Therefore, all the Mn–O bond length will be equal.

88.
Ans. **(d)**

89.
Ans. **(c)**
Sol.
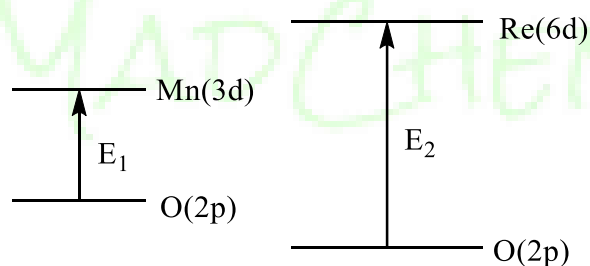
$E_2 > E_1$ hence, energy required for transfer of electron from oxygen to Re falls in UV region. Hence, ReO_4^- colourless while in MnO_4^- due to less energy difference it falls in visible region. Hence, MnO_4^- coloured. Also as Both Mn and Fe Have +7 oxidation state i.e. they have no d-electron hence. no d- d transition and colour arises due to LMCT.

90.
Ans. **(a)**
Sol. $[Co(CN)_5Cl]^{3-} + OH^- \rightarrow [Co(CN)_5(OH)]^{3-} + Cl^-$

The reaction proceed through dissociative pathway and rate is dependent only concentration of sub strates. As substate do not have acidic hydrogen. Hence, it does not undergo S_N1 CB mechanism.

$$[Co(CN)_5Cl]^{3-} \xrightarrow{slow} [Co(CN)_5]^{2-} + Cl^- \xrightarrow{OH^-} [Co(CN)_5OH]^{3-}$$

91.
Ans.   **(a)**
Sol. $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+}$ $\qquad$ (III) | (II)
$[(NH_3)_5Co---Cl---Cr(H_2O)_5]^{4+}$

Labile due to d^7(HS)

$[Co(NH_3)_5]^{2+} + [Cr(H_2O)_5Cl]^{3+} \longleftarrow [(NH_3)_5Co---Cl----Cr(H_2O)_5]^{4+}$ (III)

$\downarrow H_3O^+$ $\qquad$ (II)

$[Co(H_2O)_6]^{2+} + NH_4^+$ $\qquad$ d^3(inert)

inert due to stable (d^3 state)
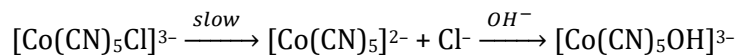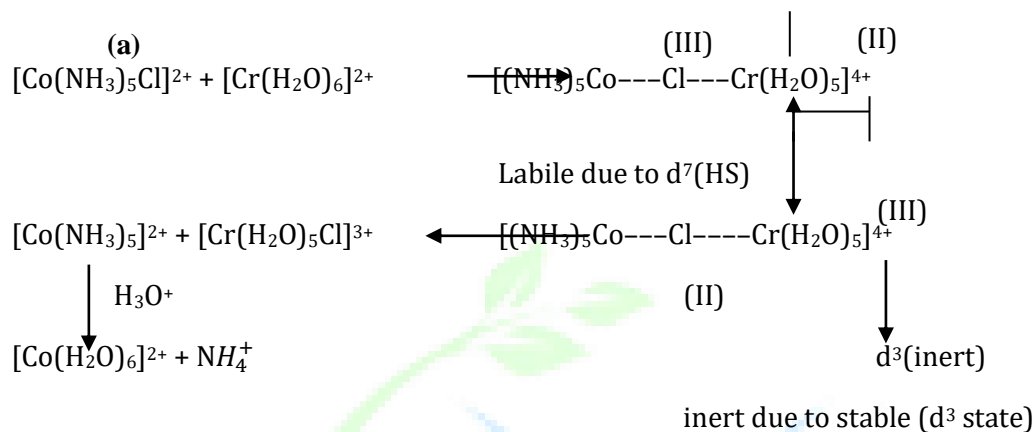
92.
Ans.   **(c)**
Sol.   Tanabe-Sugano are useful in interpretation of spectra of both high spin and low spin complexes of d^2–d^8 metal cation.

In Tanabe-Sugano, the energy of excited sate (expressed as E/B) are plotted against ligand field strength (expressed as (Δ_0/B).

Zero energy is taken for the lowest term and also two form of same symmetry never cross each other and they bent for apart from each other due to repulsion.

93.
Ans.   **(b)**
Sol. $[CrF_6]^{3-} \Rightarrow d^3$
Orgel diagram for d^3.
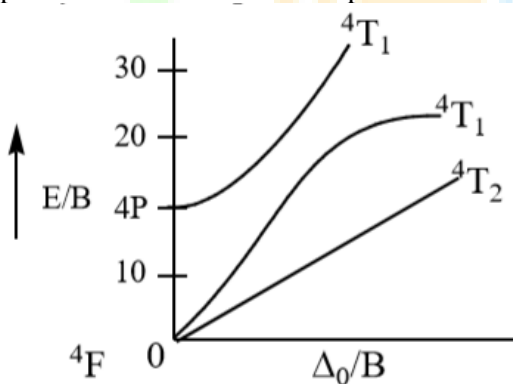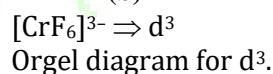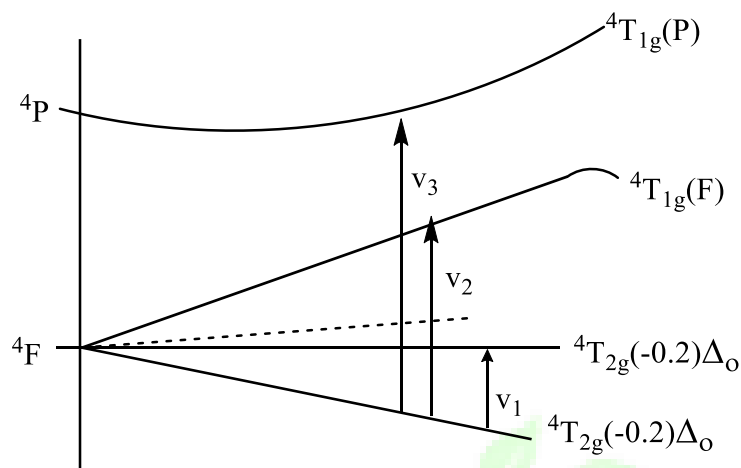
= ground state = ^4F

First exited state = ^4P
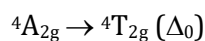
$^4A_{2g} \rightarrow {^4T_{2g}} (\Delta_0)$

$v_1 \approx 14900$ cm^{-1}; $v_2 = 22700$ cm^{-1} ; $v_3 = 34400$ cm^{-1}

Since, $^4T_{1g}(p)$ and $^4T_{1g}$ (F) have no fix energy therefore, they will not provide accurate value of Δ_0. Thus, energy difference between $^4A_{2g} \rightarrow {^4T_{2g}} \approx 14900$ cm^{-1} will be correspond to Δ_0.

94.
Ans.   **(d)**
Sol.

$\left[\begin{array}{c} II \\ Ni\ L_6 \end{array} \right]^{n^+\ or\ n^-}$ has absorption bonds at 8500, 15400, 26000 cm^{-1}.

$\left[\begin{array}{c} II \\ Ni\ L_6^1 \end{array} \right]^{n^+\ or\ n^-}$ at 10750, 17500 and 28200 cm^{-1}
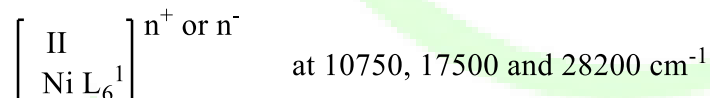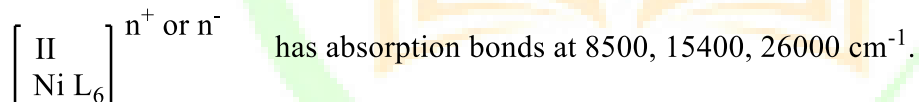
as for first complex absorptions bonds are at low energy i.e. it has weak splitting therefore, it has weak ligand and for IInd complex high energy absorption bonds corresponds to strong logand. thus, L is weak and L^1 strong ligand.

95.
Ans.   **(b)**
Sol.   Number of microstate in ^3F is calculated as (2S +1) (2L+1)
       For F, L = 3
       Hence, (3) (2 ×3+1) = 21

96.
Ans.   **(b)**
Sol.

$$d^6 = \begin{array}{|c|c|c|c|c|} \hline +2 & +1 & 0 & -1 & -2 \\ \hline \uparrow\downarrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline \end{array}$$
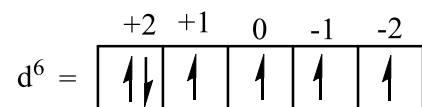
$L = \Sigma M_L = 5-3 = 2 = D$

$S = 2$ $2S + 1 = 5$

Hence, lowest energy form = ^5D

97.

Ans.   **(c)**

Sol.

$[Cr(bipyridyl)_3]^{3+} \longrightarrow d^3 = 4F$ (ground state term)

$^4A_{2g}$ $^4T_{1g}$ $^4T_{2g}$
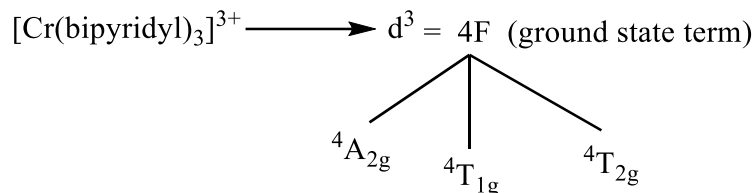
As Phosphorescence is spin-forbidden transition and also occurs when electron comes from excited to ground tstae. Hence, transition $^4A_{2g} \leftarrow ^2E_g$ is responsible for the phosphorescence.

98.

Ans.   **(c)**

Sol.   For orbital contribution the t_{2g} set should be unsymmetrically filled

$[Cu(H_2O)_6]^{2+} \rightarrow t_{2g}^6\ e_g^3 \rightarrow$ No contribution

$[Ni(H_2O)_6]^{2+} \rightarrow t_{2g}^6\ e_g^2 \rightarrow$ No contribution

$[Co(H_2O)_6]^{2+} \rightarrow t_{2g}^5\ e_g^2 \rightarrow$ Orbital contribution

$[Cr(H_2O)_6]^{2+} \rightarrow t_{2g}^3\ e_g^1 \rightarrow$ No contribution
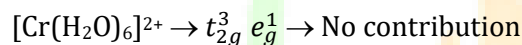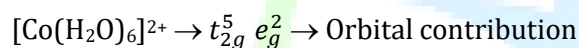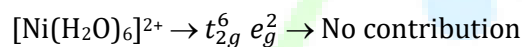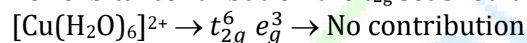
99.

Ans.   **(d)**

Sol.   In $KMnO_4$ all the electrons are paired. However, its paramagnetic susceptibility of the order of 10^{-6} cm³ mol⁻¹ is due to the temperature independent paramagnetism.

100.

Ans.   **(a)**

Sol.   The complexes having T ground state have orbital contribution to magnetic moment however for complex having A or E ground state some time μeff is slightly greater than μspin is due to mixing of first excited state T (having same spin multiplicity to ground state) mixes with A or E due to spin coupling and there μ_{eff} is calculated by

$$\mu_{eff} = \mu_{spin}\left(1 - \frac{\alpha\lambda}{\Delta}\right)$$

$Cu(II) - ^2D$

^2E_g

No orbital contribution

$\xrightarrow{h\nu}$

$^2E_{2g}$
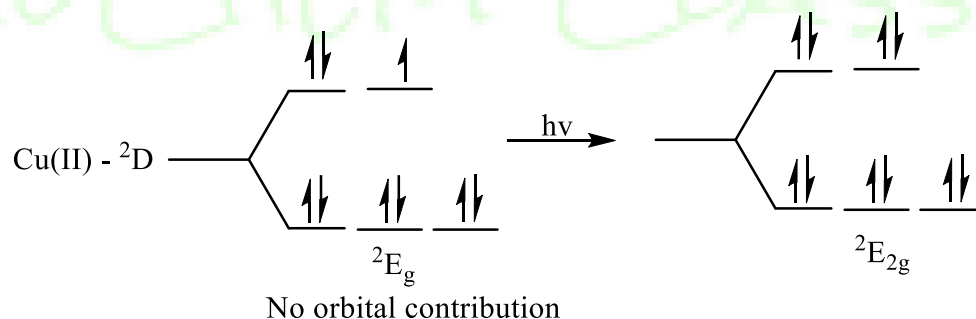
Hence, higher value of $\mu = \mu_{spin}\left(1 - \frac{\alpha\lambda}{\Delta}\right)$

101.

Ans. **(c)**

Sol. $[FeO_4]^{-4} \to$ Jahn –Teller distorted away from the ideal tetrahedral towards a flattered structure

$Fe^{4+} \longrightarrow$ | ↑ | ↑ | ↑ | ↑ | |

it is paramagnetic due to unpaired electron D_{2d} symmetry

102.

Ans. **(a)**

Sol. In halogen molecules, the $\pi^* \to \sigma^*$ transitions are responsible for their colours as evident from the following figure

103.
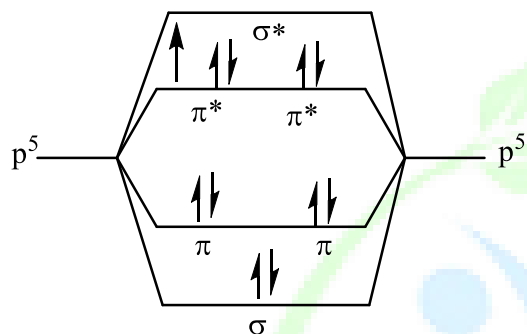
Ans. **(a)**

Sol. The π–donor ligands such as Cl^-, Br^-, I^-, N–bonded NCS^- etc stabilize the TBP intermediate and favour the stereochemical change. The trans-forms tendency to isomers in the order
$A = NO_2^- < Cl^- < NCS^- < OH^-$

104.

Ans. **(d)**

Sol. According to Nephelauxetic series
$F^- > H_2O > NH_3 > en > NCS^- > Cl^- \sim CN^- > Br^-$

The highest value of β is for F^-

105.

Ans. **(a)**

Sol. The $^2E_g \leftarrow {}^4A_{2g}$ transition in the electronic spectrum of $[Cr(NH_3)_6]^{3+}$ occurs nearly at 650 nm.

106.

Ans. **(b)**

Sol. $[Mn(H_2O)_6]^{2+} \to H_2O$ is a weak ligand, No pairing occurs.

$Mn^{2+} \longrightarrow$ | ↑ | ↑ | ↑ | ↑ | ↑ |

   +2   +1   **0**   -1   -2
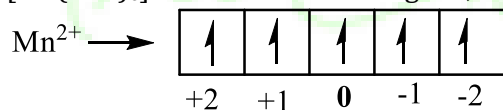
$S = 5$, $2S + 1 = 6$

$L = 0 \to 5$ Term

$\therefore$ Ground state term $\to$ 6S

$Cr^{3+} \longrightarrow$ | ↑ | ↑ | ↑ | 1 | |

   +2   +1   0   -1   -2
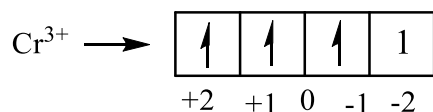
L = 3 → F Term

$S = \frac{3}{2}$ 2S + 1 = 2 × $\frac{3}{2}$ + 1 = 4

Ground state term → ^4F

Cu^{2+} ⟶

↑↓	↑↓	↑↓	↑↓	↑
+2	+1	0	-1	-2
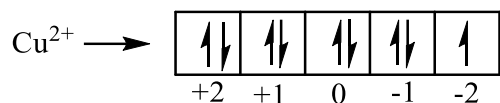
L = Σ|M_L| = 2 → D

$S = \frac{1}{2}$, 2S + 1 = 2

Ground state term → ^2D

107.
Ans.   **(b)**
Sol. $[CO(NH_3)_5Cl]^{2+} + OH^- \rightleftharpoons [CO(NH_3)_4(NH_2)Cl]^+ + H_2O$ .....(i)
$[CO(NH_3)_4(NH_2)Cl]^+ \rightarrow [CO(NH_3)_4(NH_2)]^{2+} + Cl^-$ ...(ii)
$[CO(NH_3)_4(NH_2)]^{2+}$ HOH → $[CO(NH_3)_5(OH)]^{2+}$
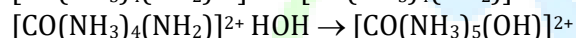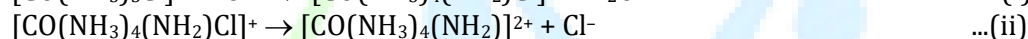
108.
Ans.   **(b)**
Sol.   Heme A → Iron porphyrin → Colour due to π−π* water splitting enzyme contains transition 0 × 0
bridged Mn_4 cluster

$[Mn(H_2O)_6]^{2+}$ ⟶ $3d^5$

| ↑ | ↑ | e_g

| ↑ | ↑ | ↑ | t_{2g}

Spin forbidden
transitions
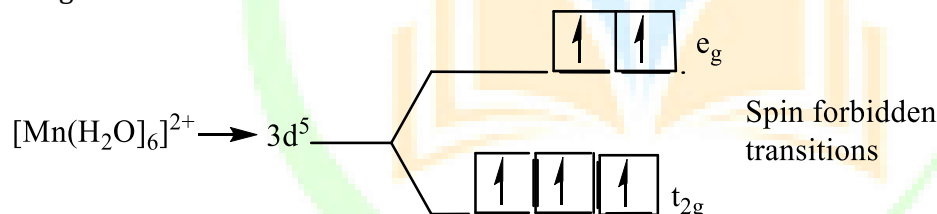
$[Cr(H_2O)_6]^{2+} \rightarrow t_{2g}^3$ eg^1 → Tetragonal elongation.

109.
Ans.   **(b)**
Sol. $k_{12} = (k_{11} K k_{22}f)^{1/2} = (5 \times 4 \times 10^3 \times 2 \times 10^8 \times 1.0)^{1/2} = 20 \times 10^5 = 2.0 \times 10^6$

110.
Ans.   **(a)**
Sol.   NR → Dithiocarbamate
OR → Xanthate
O → Dithiocarbonate
SR → Thioxanthate

111.
Ans.   **(b)**
Sol. μeff = μs $\left(1 - \frac{\lambda\alpha}{\Delta}\right)$
$\Delta = \frac{1}{\lambda} = \frac{1}{625} \times 10^{-7}$ cm = $\frac{10^{-7}}{625}$ cm^{-1}
For Cu^{+2} → Term is ^2D, hence, $\alpha = 2$, $\lambda = -625$ cm^{-1}
$\mu_{eff} = 1.73 \left(1 - \frac{2 \times 625 \times 625}{10^7}\right) = 1.73 \left(1 + \frac{2 \times 625 \times 625}{10^7}\right)$
$1.73 \left(1 + \frac{2 \times 625 \times 625}{10^7}\right) = 1.73 \{1 + 0.078\} = 1.73 \{1.078\} = 1.864$

$\mu_{eff} = 1.864$

112.
Ans.   (a)
Sol.   In CdS, HgS and BiI_3 colour is due to LMCT Cd^{2+} and Hg^{2+} has d^{10} configuration. Hence, no d-d transition. Also, MLCT as ligand is not π-acceptor. Hence, correct option (a).

113.
Ans.   (a)
Sol.   Change in CFSE on going for O_h to five coordinate intermediate for ions is as follows.
$V^2(d^3) = -2.00$

$Cr^{3+} (d^3) = -2.00$

$Ni^{2+} (d^8) = -2.00$

114.
Ans.   (a)
Sol. $[\bar{C}r(ox)_3]^{3-}$ and $[\bar{C}r(en)_3]^{3+}$ will show optical isomer. As t_{2g} level is electronically non-degenerate. Hence, there will be no Jahn-Teller distortion.

115.
Ans.   (a)
Sol.   In $[FeS_2CNEt_2)_3]$ oxidation state of Fe = +3
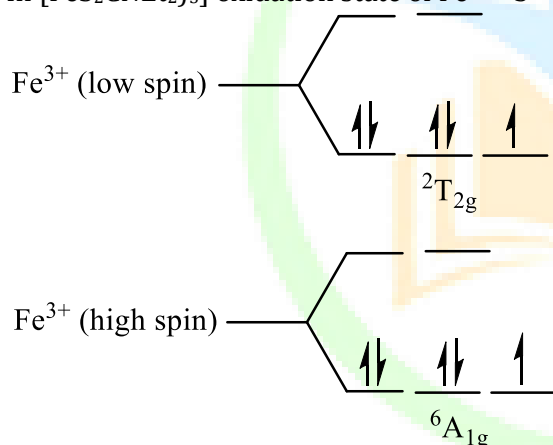
116.
Ans.   (a)
Sol. $\underline{(A)[Ni(H_2O)_6](NO_3)_2<(B)[Ni(NH_3)_6](NO_3)_2<(C)[Ni(en)_3](NO_3)_2}$
$\Delta_0 increases$

Thus , order for energy absorition is 675 (A) < 615 (B) < 565(C)

Complementary colour of blue $\rightarrow$ Orange, green $\rightarrow$ Red, Violet $\rightarrow$ Yellow

Energy order for absorbed light is, yellow > orange > red

Thus,   A absorbs red hence it is green
         B absorbs orange hence it is blue
         C absorbs yellow hence it is violet

Thus correct Option is (a)

117.
Ans.   (b)
Sol.   In I_3^- there is interaction between $\sigma*$ a of I_2 non-bonding electron of I^-. In case propanone and Br_2 there in interaction between $\sigma*$ of Br_2 and non-bonding electron of propanone. Thus, both I_2 and Br_2 behave as acid.

118.
Ans. (d)
Sol.

(A) $[TiF_6]^{3-}$

Ti $\Rightarrow 3d^2\ 4s^2$ d^1

$Ti^{3+} = 3d^1\ 4s^0$

e_g

t_{2g}

1 unpaired electron

(B) CrF_6^{3-}

Cr $\Rightarrow 3d^5\ 4s^1$ d^3

$Cr^{+3} \Rightarrow 3d^3\ 4s^2$

e_g

t_{2g}

3 unpaired electron

(C) $[MnF_6]^{3-}$

Mn $= 3d^5 4s^2$ d^4

$Mn^{+3} = 3d^4$

e_g

t_{2g}

4 unpaired electron

(D) $CoF_6{}^{3-}$

Co $= 3d^7\ 4s^2$ d^4

$Co^{3+} = 3d^6\ 4s^0$

e_g

t_{2g}

4 unpaired electron
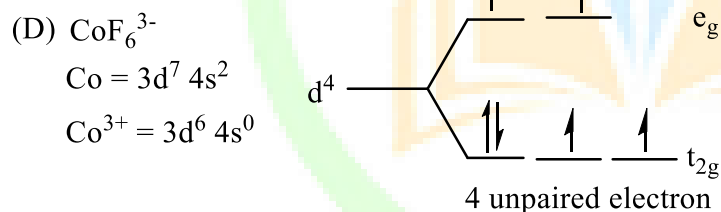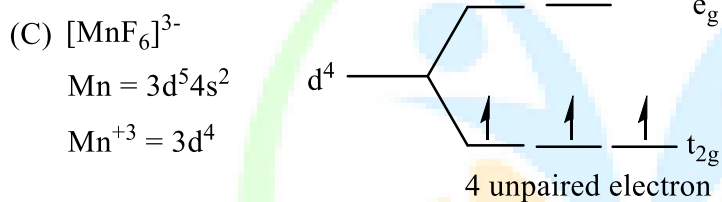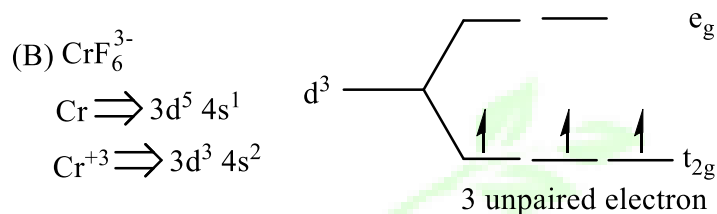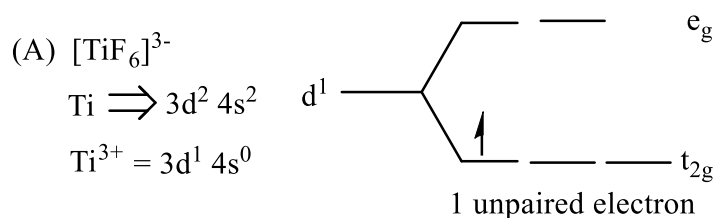
119.
Ans. (b)
Sol. In trigonal prismatic ligand field, energy of 'd' orbital is
$d_{yz} = d_{xz} > d_{z^2} > d_{x^2-y^2} = d_{xy}$
Hence, the most stabized 'd' orbital is d_{xy}

120.
Ans. (c)
Sol. Spin-orbit coupling is larger for the heavier atoms (Inner transition) and very small for lighter atoms.
121.
Ans. (b)
Sol. For d_6(high spin) there is one spin allowed transition from $^5T_{2g} \rightarrow {}^5E_g$
in case of d6 low spin commonly two spin allowed transition are observed.

$^1A_{1g} \rightarrow {}^1T_{1g}$

$^1A_{1g} \rightarrow {}^1T_{2g}$

there are additional spin allowed transitions at higher energy but they are marked by allowed transitions. Hence, are not observed.

122.
Ans.   (a)
Sol. $K_3CuF_6 \Rightarrow 3k^+ [CuF_6]^{3-}$, oxidation state of $Cu^{3+} = 3d^8$

Thus. Cu^{3+} d^8(Oh)
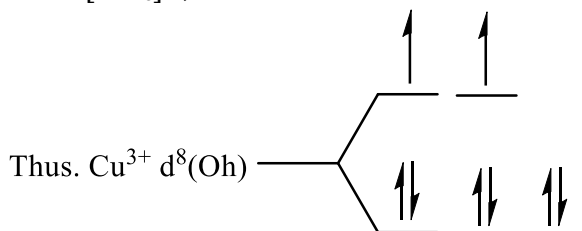
$KCuL_2 \Rightarrow$ oxidation state of Cu = 1 + x – 4 = 0 $\Rightarrow$ x = +3

Cu^{3+} (d^8)

Hence, square planar low spin
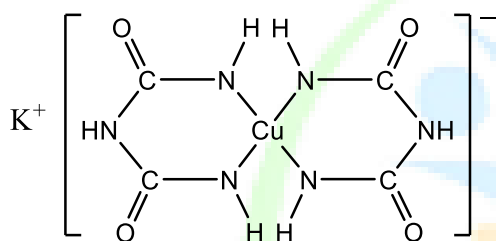
123.
Ans.   (a)
Sol.   Mechanism of base hydrolysis can be given as
$[Co(Cl)(NH_3)_5]^{2+} + OH^- \rightleftharpoons [Co(Cl)(NH_3)_4(NH_2)]^+$

$[Co(Cl)(NH_3)_4(NH_2)]^+ \xrightarrow[RDS]{slow} [Co(NH_3)_4(NH_2)]^{2+} + Cl^-$
                                                    intermediate (C.N. = 5)

$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \xrightarrow{fast} [Co(NH_3)_5(OH)]^{2+}$
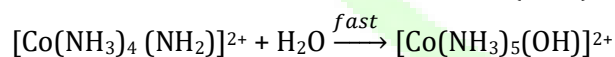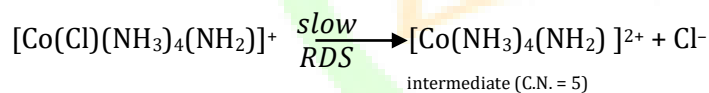
124.
Ans.   (c)
Sol. Co^{+3} (high spin) $\rightarrow 3d^7 4s^0$

d^7

↑	↑
-1	-2

↑↓	↑↓	↑
+2	+1	0
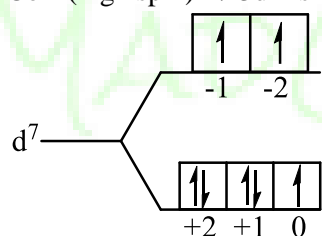
S = 1/2 + 1/2 + 1/2 = 3/2
L= 4+2–0–1–2
L = 3
Degeneracy for d-orbital = (2S+1) (2L+1) = (2 × 3/2 +1) (2×3+1) = 4×7 = 28

125.
Ans.   (c)
Sol.

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$1s^1$ $\quad$ $2s^1$
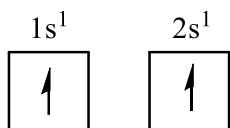
$S = 1/2 + 1/2 = 1$

$2S + 1 = 2 \times 1 + 1 = 3$

$J = |1 + s|...|1 - s| = |1+0|...|1-0| = 1$

$1 = 0 \rightarrow S$ (term)

$^3S_1$

126.

Ans. $\qquad$ **(c)**

Sol. For allowed transition: a) Spin multiplicity should be same or $\Delta S = 0$

b) $\Delta L = 0, \pm 1$, for allowed transition

Therefore (4) is not allowed as $\Delta L \neq 0, \pm 1$

c) u $\rightarrow$ g (allowed)

g $\rightarrow$ g (not allowed)

Therefore (1, 2) are not allowed

$[+ \rightarrow \bullet] \rightarrow$ forbidden so, therefore (1, 2) are not allowed

$[+ \rightarrow +] \rightarrow$ allowed

127.

Ans. $\qquad$ **(a)**

Sol.

128.

Ans. $\qquad$ **(b)**

Sol.

$Ni^{2+}(3d^8)$
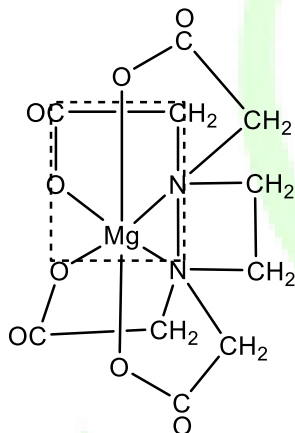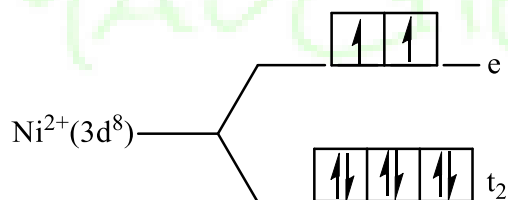
No. of unpaired electron = 2

$\mu_s = 2.9$ B.M.

No orbital contribution

$Ni^{2+}(Td)$
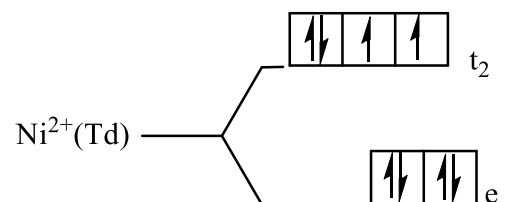
No. of unpaired electron = 2

$\mu_s = 4.1$ B.M.

High value (4.1 B.M.) is due to μ_{spin} + orbital contribution because t_2 is electronically degenerate.

129.
Ans. **(c)**
Sol. CrO_4^{2-} $\qquad\qquad$ MoO_4^{2-}
$Cr^{2-} \rightarrow 3d^0\ 4s^0$ $Mo^{6+} \rightarrow 4d^0\ 5s^0$

$O^{2-} \rightarrow 2s^2\ 2p^6$
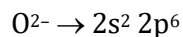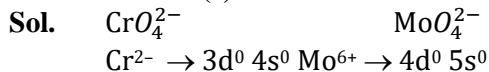
in both Cr^{6+} and Mo^{6+} ions, there is no d-electrons, therefore, there is no d-d transition, since in both the ions. Oxidation state is very high. there is LMCT in both cases. The energy gap between $2p^*(O^{2-})$ and $3d^0$ (Cr^{6+}) is less than that between $2p^6$ (O^{2-}) and $4d^0(Mo^{6+})$. Thus, LMCT energy in CrO_4^{2-} is less (high λ_{max}) than that of MoO_4^{2-} (low λ_{max}).

130.
Ans. **(a)**
Sol.
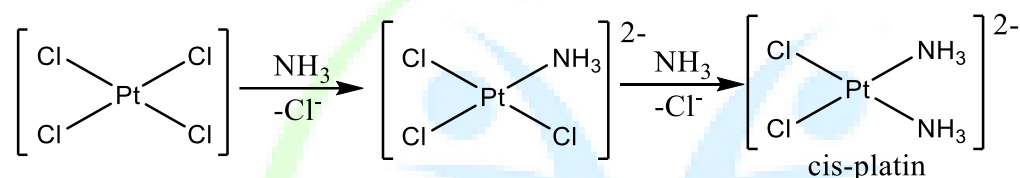
Trans effect of $Cl^- > NH_3$

In blood it stays in equilibrium with cis – $[Pt(NH_3)_2\ Cl(H_2O)]^+$
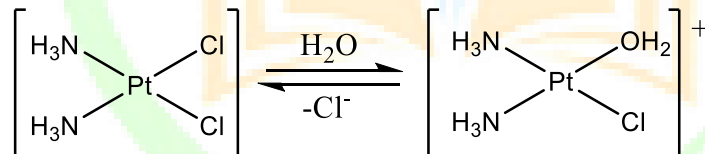
In DNA stand, cis – platin binds to two adjacent guanin bases [Not to cytosine bases]

131.
Ans. **(c)**
Sol. Electronic configuration of $_{24}Cr^{2+} = 3d^5\ 4s^1$
Electronic configuration of $Cr^{2+} = 3d^4$

Electronic configuration of $_{23}V^{2+} = 3d^3$

(A) Because of high nuclear charge of Cr is greater than that of V, Cr has higher. Thus ionization energy than V. Hence, Cr^{2+} is not easier to oxidized than V^{2+} in gas phase. Thus, option(a) is incorrect.

(B) Cr^{2+} (aq) $\rightarrow$ $[Cr(H_2O)_6]^{2+}$ $\rightarrow$ $[Cr(H_2O)_6]^{3+} + e^-$

$\boxed{\uparrow}\,\boxed{\uparrow}$ e_g $\boxed{}\,\boxed{}$ e_g

$\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}$ t_{2g} $\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}$ t_{2g}
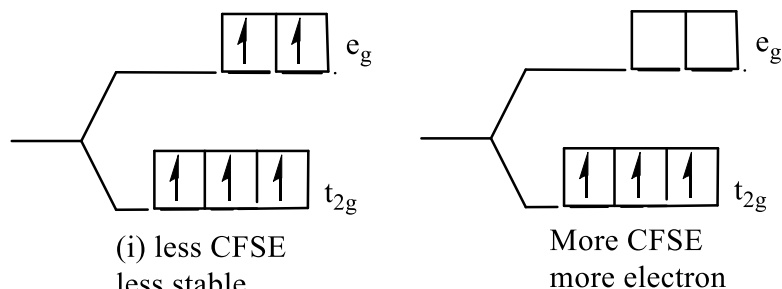
(i) less CFSE
less stable
(i) One electron in eg has high
energy and high energy and
can easily be resolved

        More CFSE
more electron

V^{2+} (aq) $\rightarrow$ V$[V(H_2O)_6]^{2+}$ $\rightarrow [V(H_2O)_6]^{3+}$ + e$^-$

$\boxed{}\,\boxed{}$ e_g $\boxed{}\,\boxed{}$ e_g

$\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{\uparrow}$ t_{2g} $\boxed{\uparrow}\,\boxed{\uparrow}\,\boxed{}$ t_{2g}

less CFSE
less stable

    less CFSE
    less stable
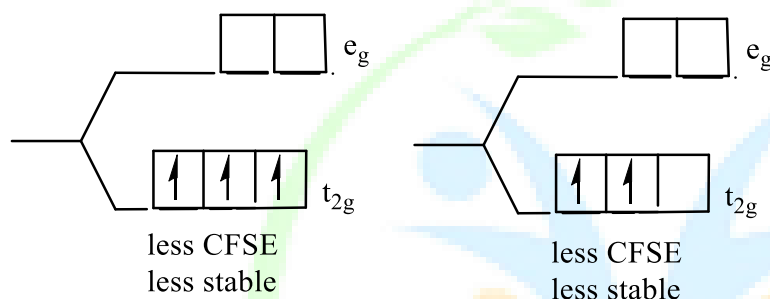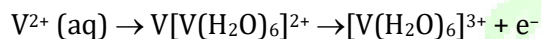
Thus V^{2+} (aq) does not easily oxidized

Thus, Cr^{2+}(aq) is more powerful reducing agent than V^{2+} (aq)

(C) Cr^{2+} (aq) is more labile than V2+ (aq). Also, Cr^{2+} belongs to class 1 metals and V^{2+} belongs to class 3 metals. Thus, the rate of water exchange in Cr^{2+} (aq) is faster than Cr^{2+} (aq)

132.
Ans.   **(d)**
Sol.   (I) $[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} \rightarrow [(NC)_5Fe-CN-Co(CN)_5]^{6-}$

$\xrightarrow{electron\ transfer}$ $[Fe(CN)_6]^{4-} + [Co(CN)_5(OH_2)]^{2-}$

(inner sphere mechanism)

(II) $[Co(bipy)_3]^{2+} + [Co(bipy)_3]^{3+} \rightarrow [Co(bipy)_3]^{3+} + [Co(bipy)_3]^{2+}$

(outer sphere mechanism)

(III) $[Co(NH_3)_5F]^{2+} + [Cr(H_2O)_6]^{2+} \xrightarrow{-H_2O} [H_3N]_5\overset{III}{Co}-F-\overset{II}{Cr}(OH_2)_5]^{4+} \underset{\rightleftharpoons}{E.T.}$

$[H_3N]_5\overset{II}{Co}-F-\overset{+3}{Cr}(OH_2)_5]^{4+} \xrightarrow{+H_2O} [Co(NH_3)_5(OH)_2]^{2+} + [Cr(OH_2)_5F]^{2+}$
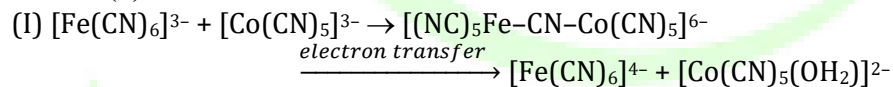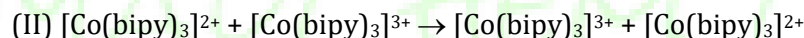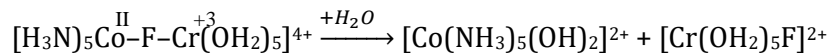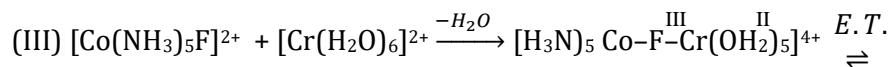
(Inner sphere mechanism)

Marcus equation is applicable only for cross-outer sphere reactions.

(B) is a self exchange reaction, its rate of electron transfer can be calculated experimentally. No need to apply marcus equation. (Reference basic inorganic chemistry by F. Albert cotton, G. Wilkinson and Paul L. Galls) third eddition.

In this equation only (d) statement is correct.

133.

Ans. (c)

Sol. $[Co(NCS)(NH_3)_5]^{2+} + [Fe(H_2O)_6]^{2+} \xrightarrow{-H_2O} [(NH)_5\ Co-SCN-Fe(H_2O)_5]^{4+} \xrightarrow[transfer]{electron} [(HN)_5Co-SCN-$
$Fe(H_2O)_5]^{4+} \xrightarrow{H_2O} [Fe(SCN)(H_2O)_5]^{2+} + [Co(NH_3)_5(H_2O)]^{2+}$
$\qquad\qquad\qquad\qquad$ (Intermediate)

$[Co(NH_3)_5(H_2O)]^{2+} \xrightarrow{+5H_3O^+} [Co(H_2O)_6]^{2+} + 5NH_4^+$

$[Fe(SCN)(H_2O)_5]^{2+}\ H_2O \rightarrow [Fe(H_2O)_6]^{3+} + SCN^-$

$\qquad$ (Intermediate)
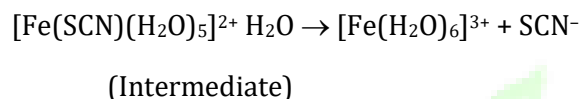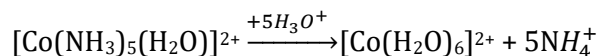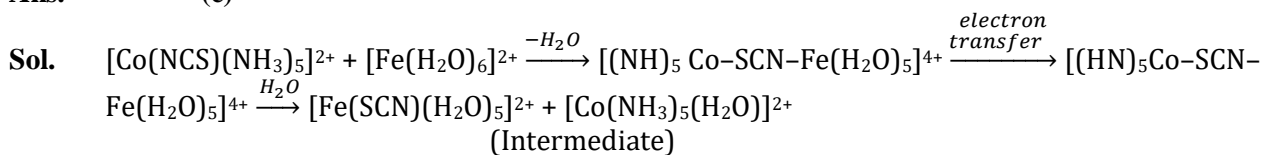
134.

Ans. (a)

Sol. For strong Jahn-Teller distortion e_g orbitals must be assymetrical filled.
(a) $t_{2g}^6\ e_g^1, t_{2g}^3\ e_g^1, t_{2g}^6\ e_g^3$
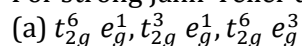
135.

Ans. (a)

Sol. The correct order of intensity of d-d transitions in the complexes follows order
cis $[M(H_2O)_4Cl_2]$ > trans $[M(H_2O)_4Cl_2]$ > $[M(H_2O)_6]^{2+}$

136.

Ans. (c)

Sol.

(a)

98%

(b)

15%

85%
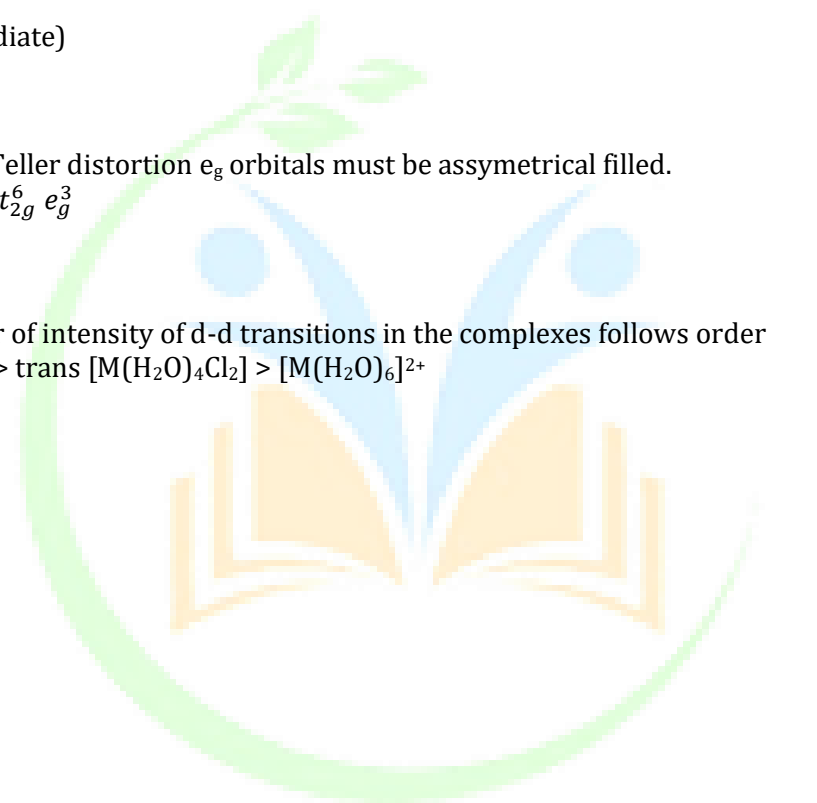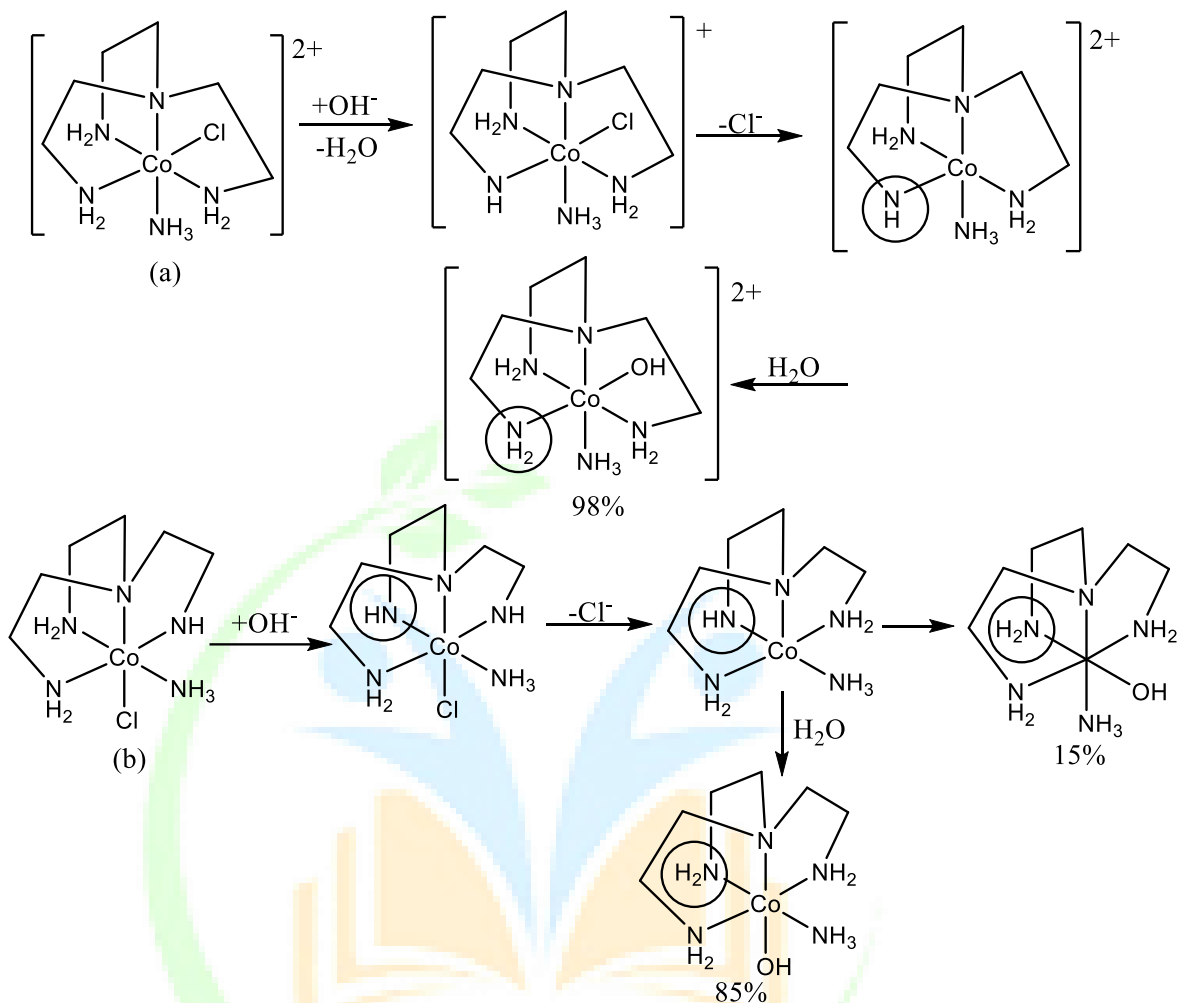
A react faster than B and B result in a mixture of product.

137.

Ans. **(b)**

Sol. As the oxidation state increases and size of central decreases ligand exchange rate decreases.

138.

Ans. **(a)**

Sol. Hg^{+2} (aq) + X^- (aq) → $[HgX]^+$ (aq)

The stability constants for $[HgX]^+$ (aq) for X = F, Cl, Br Follow the order : F < Cl < Br. Because Hg^{+2} is soft acid and Br^- is soft base.

139.

Ans. **(b)**

Sol. An aqueous solution of Fe(III) ion (A) gives a blood-red colour on reaction with KSCN the blood red colour is due to formation of $[Fe(SCN)(H_2O)_5]^{+2}$ (B). The colour may also used for the identification of iron (III). This colour is destroyed by the addition of F– ion due to the formation of $[FeF_6]^{-3}$ (C).

$[Fe(H_2O)_6]^{+3}$ + SCN^- $\longrightarrow$ $[Fe(SCN)(H_2O)_5]^{+2}$ $\xrightarrow{\text{NaF}}$ $[FeF_6]^{-3}$

(A)   (B)   (C)
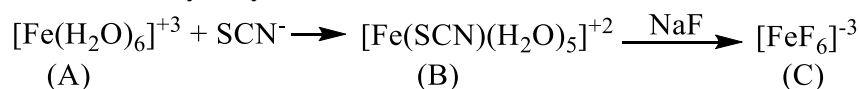
                              Blood red colour   colourles, d-d transition, laporte

                              Due to LMCT   forbidden, spin forbidden

140.

Ans. **(a)**

Sol. Electron transfer reactions by self-exchange electron transfer is fast when HOMO is π^* and LUMO is also π^* i.e. electron transfer is from π^* of reductant to the π^* of oxidant.

$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} +$

(a) $(\pi^*)^6(\sigma^*)^0 \qquad (\pi^*)^5(\sigma^*)^0 \quad \rightleftarrows [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$ Reaction is fast

$HOMO = (\pi^*)^6 \quad LUMO = (\pi^*)^5$

$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$

(b) $(\pi^*)^5(\sigma^*)^2 \qquad (\pi^*)^5(\sigma^*)^0 \quad \rightleftarrows [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$ Reaction is slow

$HOMO = (\pi^*)^5 \quad LUMO = (\sigma^*)^0$

$[Cr(H_2O)_6]^{2+} + [Cr(H_2O)_6]^{3+}$

(c) $(\pi^*)^3(\sigma^*)^1 \qquad (\pi^*)^3(\sigma^*)^0 \quad \rightleftarrows [Cr(H_2O)_6]^{3+} + [Cr(H_2O)_6]^{2+}$ Reaction is slow

$HOMO = (\sigma^*)^1 \quad LUMO = (\sigma^*)^0$

$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} +$

(d) $(\pi^*)^4(\sigma^*)^2 \qquad (\pi^*)^3(\sigma^*)^2 \quad \rightleftarrows [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ Reaction is fast

$HOMO = (\pi^*)^4 \quad LUMO = (\pi^*)^3$

Both reactions (a) and (d) are fast but reaction (a) is much faster than (d) because there is small change in M–L bond length in reaction (a) i.e. less activation energy is equired

141.
Ans. **(a)**
Sol. Selection rule for atomic transition:

$$\Delta S = 0; \Delta L = 0, \pm 1; \Delta J = 0, \pm 1 (J = 0 \rightarrow J = 0 \text{ is not allowed})$$

(a) $^3F_4 \rightarrow {}^3D_3$ So, $\Delta S = 0; \Delta L = -1; \Delta J = -1$ (allowed transition)
   S=1   S=1
   L=3   L=2
   J=4   J=3

(b) $^3F_4 \rightarrow {}^1D_3$ So, $\Delta S = -1; \Delta L = -1; \Delta J = -1$ (not allowed transition)
   S=1   S=0
   L=3   L=2
   J=4   J=3

(c) $^3F_4 \rightarrow {}^3P_4$ So, $\Delta S = 0; \Delta L = -2; \Delta J = 0$ (not allowed transition)
   S=1   S=1
   L=3   L=1
   J=4   J=4

(d) $^3F_4 \rightarrow {}^3D_2$ So, $\Delta S = 0; \Delta L = -1; \Delta J = -2$ (not allowed transition)
   S=1   S=1
   L=3   L=2
   J=4   J=2

142.
Ans. **(c)**
Sol. • $[Mn(H_2O)_6]^{2+} \Rightarrow t_{2g}^3 e_g^2$: High spin complex

In this complex, there is neither orbital contribution nor temperature independent paramagnetism (No L–S coupling) and $\alpha = 0$, Thus, $\mu_{obs} = \mu_{spin}$.

• $[Co(H_2O)_6]^{3+}$ is a low spin complex.

$Co^{3+} \rightarrow d^6$ i.e., $t_{2g}^6 e_g^0$
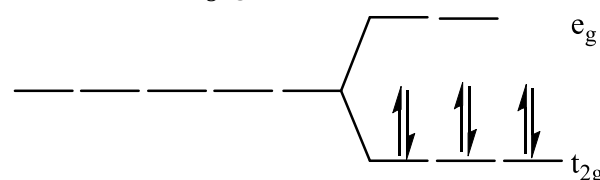
No unpaired electron.

Therefore, it is diamagnetic in nature.

143.

Ans. (c)

Sol. • $Ti^{3+} \Rightarrow d^3$ complex : $t_{2g}^1 \, e_g^0$

Ti^{+3} complex exhibit one broad band due to

(i) Vibronic coupling

(ii) Jahn-Teller distortion

(iii) Spin-orbit coupling

• $Co^{2+} \Rightarrow d^7$ complex

Exhibit three broad bands due to following transitions:

$^4T_{1g} \to {}^4T_{2g}$; $^4T_{1g} \to {}^4A_{2g}$; $^4T_{1g} \to {}^4T_{1g}$ (P)

$Cr^{3+} \Rightarrow d^3$ complex

Exhibit three broad bands due to following transitions :

$^4A_{2g} \to 4T_{2g}$; $^4A_{2g} \to {}^4T_{1g}(F)$; $^4A_{2g} \to {}^4T_{1g}(P)$

• Mn^{2+} complex $\Rightarrow d^5$ complex exhibit a series of very weak (spin forbidden, Laporte forbidden and sharp bands).

• $Ni^{2+} \Rightarrow d^8$ exhibit three broad bands due to following transitions :

$^3A_{2g} \to {}^3T_{2g}$

$^3A_{2g} \to {}^3T_{1g}(F)$; $^3A_{2g} \to {}^3T_{1g}(P)$

144.

Ans. (b)

Sol. $Trans-[CoLCl(en)_2]^+ \xrightarrow{Hydrolysis} A$

$L = NO_2^-, NCS^-, OH^-, Cl^-$

The tendency to form cis-isomer of the product (A) follows the order :

$L = NO_2^- < Cl^- < NCS^- < OH^-$

145.

Ans. (b)

Sol. An aqueous solution of Fe(III) ion (A) gives a blood-red colour on reaction with KSCN the blood red colour is due to formation of $[Fe(SCN)(H_2O)_5]^{2+}$(B). The colur may also used for the identification of Iron (III). This colour is destroyed by the addition of F$^-$ ion due to the formation of $[FeF_6]^{3-}$ (C).

$[Fe(H_2O)_6]^{3+} \ SCN^- \to [Fe(H_2O)_5(SCN)]^{2+} \xrightarrow{NaF} [FeF_6]^{3-}$

(A) Blood red color due to LMCT Colorless Compound d–d transition Laporte for bidden (B)Spin forbidde (C)

146.

Ans. (b)

Sol.

Two ligands are present on z-axis therefore, d_{z^2} – orbital is involved in σ–bonding. Also three ligands are presentin xy plane, therefore, d_{xy} and $d_{x^2-y^2}$ orbitals are involved in σ–bonding. Thus the d_{yz} and d_{xz} orbitals remain non bonding.

147.

Ans. (c)

Sol. In $[IrBr_6]^{-2}$ oxidation state of Ir is +4 and Ir^{+4} is low spin. octahedral complex with the electronic configuration:
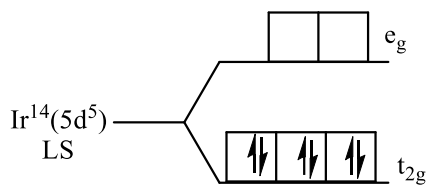
There are two charge transfer bands and their origin are ligand $\rightarrow$ metal ($\sigma \rightarrow t_{2g}$ and $\sigma \rightarrow e_g$) as shown in the figure.

$[IrBr_6]^{2-}$
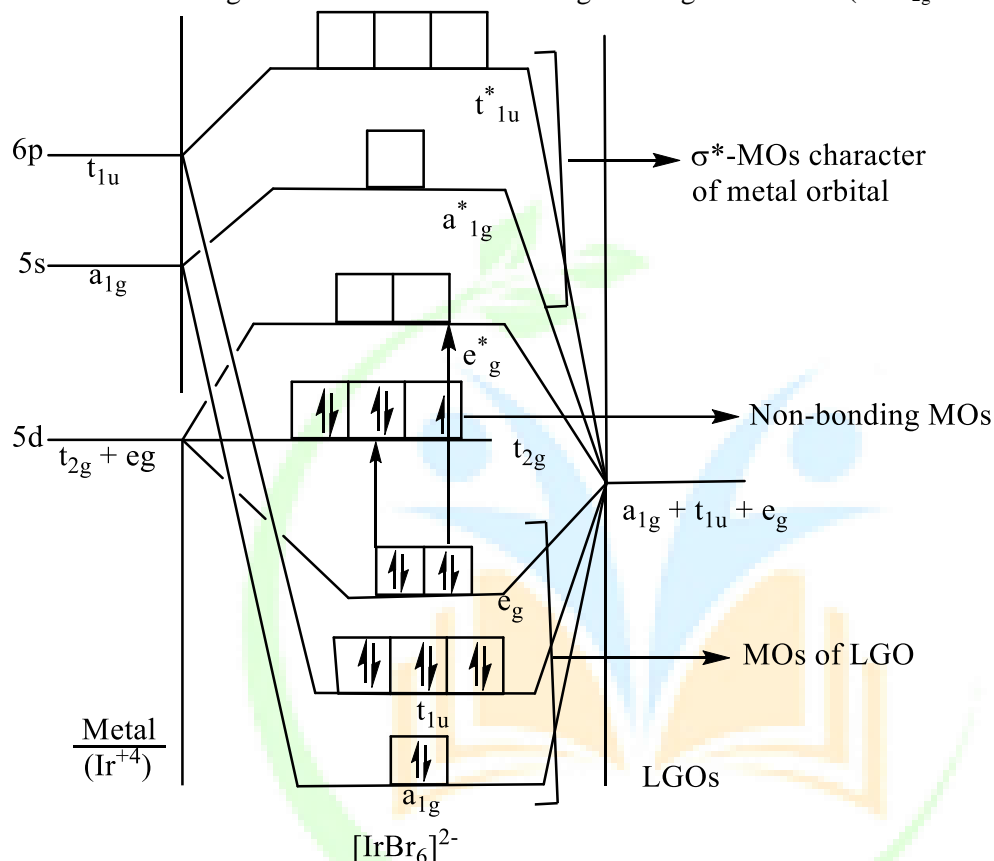
Other transitions are of high energy and do not observed.

148.

Ans. **(b)**

Sol. molar Extinction cofficent $\times$ molar absorbtivity $\times$ Intensity of absorphon.

Clorophycl $>$ Nicl$_4$ $>$ $[Cr(H_2O)_6]^{+2}$ Mn^{+2} $\rightarrow$ $\Delta S \neq O$

Spinalloved $\qquad\qquad$ $\Delta S = O$ $\qquad\qquad$ $\Delta l \neq \pm 1$

non-centrosymmetric (gevade)

149.

Ans. **(a)**

Sol. $\Rightarrow C_6O$ – bulkministerfullence

axailable for donation

$M \longrightarrow \|$

$\eta 2$
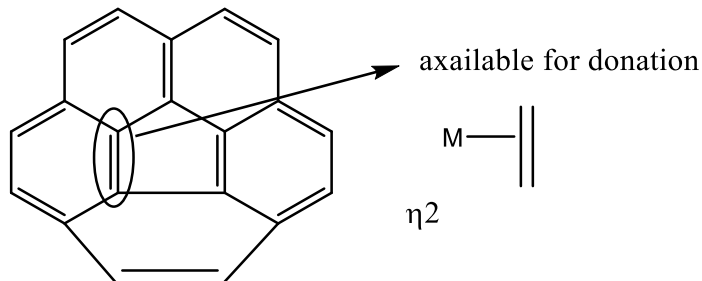
Hepaticity is no. of carbon attached to metal.

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150.
Ans. (b)
Sol. $P + e^- \rightarrow n + \gamma e$
(From k shell or L–Shell)
P = proton, e^- = electron, n = neutron, γe–neutron

151.
Ans. (b)
Sol.
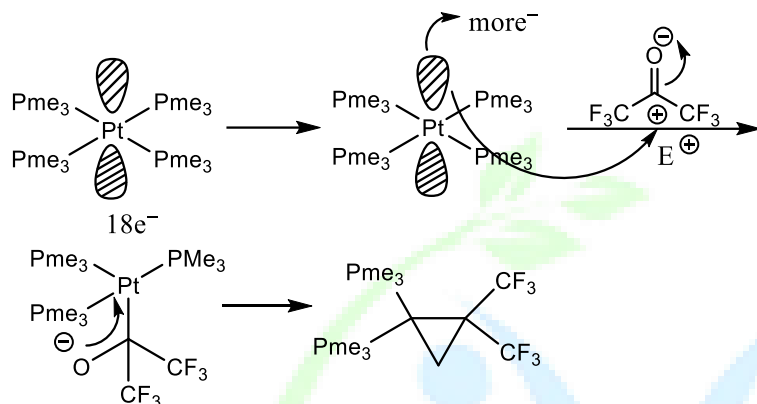
152.
Ans. (b)
Sol. B and D
(A) $[Fe(ox)_3]^{-3} \rightarrow$ High spin
$x - 6 = -3$
$x = +3 \quad n = 5$
(B) $[Fe(CN)_6]^{-3} \rightarrow Fe(l.S)$ \qquad (n=1)
(C) $Ni^{+2}(H.S)Td$
(d^8)

n = 2
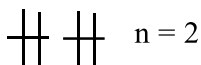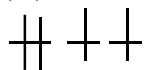
(d) $[Cu(NH_3)_4]^{+2}$
$Cu^{+2}(sp2d) \rightarrow L.S$

d^9 n = 1

153.
Ans. (b)
Sol. $FeCr_2O_4$
$Fe^{+2}(d^6) \quad\quad \rightarrow Cr^{+3} CFSE > Fe^{+2} CFSE$
$Cr^{+3}(d^3) \quad\quad\quad\quad$ Normal
$\quad\quad\quad\quad\quad\quad\quad\quad \downarrow$
$\quad\quad\quad\quad A^{+2} \rightarrow Td$
$\quad\quad\quad\quad B^{+3} - Oh$ void

154.
Ans. (c)
Sol. $[Fe^{+2}(Phen)_2(Ncs-N)_2] = 300$ k

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H.S

$d^6 \longrightarrow$ ⊥ ⊥

⊥⊥ ⊥ ⊥ $n = 4 \ = 4.89m$

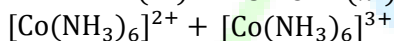$[Fe(phen)_3]^{+2}$ (d⁶) (l.S) ⊥⊥ ⊥⊥ ⊥⊥

$n = o$
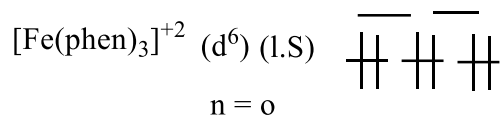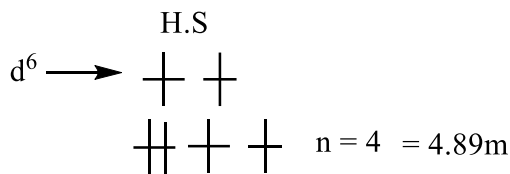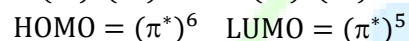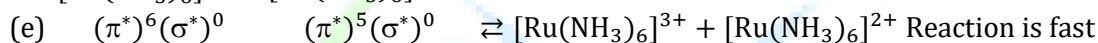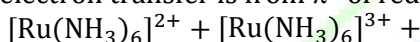
155.
Ans.   **(b)**
Sol.   No acidic proton is available so, not depend on hydroxide ion.
156.
Ans.   **(a)**
Sol.   Electron transfer reactions by self-exchange electron transfer is fast when HOMO is π^* and LUMO is also π^*
i.e. electron transfer is from π^* of reductant to the π^* of oxidant.

$[Ru(NH_3)_6]^{2+} + [Ru(NH_3)_6]^{3+} +$

(e) $(\pi^*)^6(\sigma^*)^0$ $(\pi^*)^5(\sigma^*)^0$ $\rightleftarrows [Ru(NH_3)_6]^{3+} + [Ru(NH_3)_6]^{2+}$ Reaction is fast
      HOMO $= (\pi^*)^6$ LUMO $= (\pi^*)^5$

$[Co(NH_3)_6]^{2+} + [Co(NH_3)_6]^{3+}$

(f) $(\pi^*)^5(\sigma^*)^2$ $(\pi^*)^5(\sigma^*)^0$ $\rightleftarrows [Co(NH_3)_6]^{3+} + [Co(NH_3)_6]^{2+}$ Reaction is slow
      HOMO $= (\pi^*)^5$ LUMO $= (\sigma^*)^0$

$[Cr(H_2O)_6]^{2+} + [Cr(H_2O)_6]^{3+}$

(g) $(\pi^*)^3(\sigma^*)^1$ $(\pi^*)^3(\sigma^*)^0$ $\rightleftarrows [Cr(H_2O)_6]^{3+} + [Cr(H_2O)_6]^{2+}$ Reaction is slow
      HOMO $= (\sigma^*)^1$ LUMO $= (\sigma^*)^0$

$[Fe(H_2O)_6]^{2+} + [Fe(H_2O)_6]^{3+} +$

(h) $(\pi^*)^4(\sigma^*)^2$ $(\pi^*)^3(\sigma^*)^2$ $\rightleftarrows [Fe(H_2O)_6]^{3+} + [Fe(H_2O)_6]^{2+}$ Reaction is fast
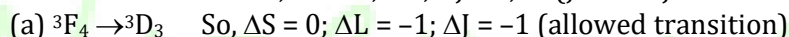   HOMO $= (\pi^*)^4$ LUMO $= (\pi^*)^3$
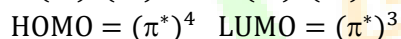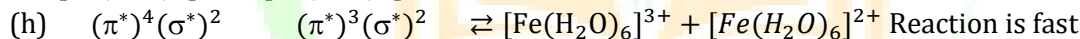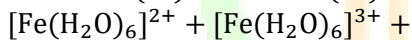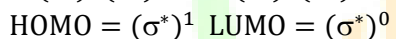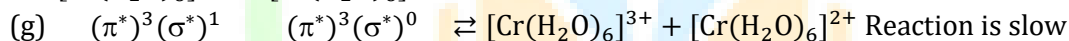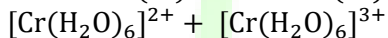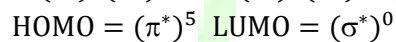
Both reactions (a) and (d) are fast but reaction (a) is much faster than (d) because there is small change
in M–L bond length in reaction (a) i.e. less activation energy is equired
157.
Ans.   **(a)**
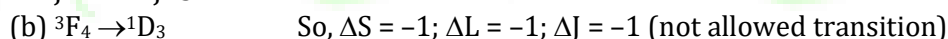**Sol.**   Selection rule for atomic transition:
                    $\Delta S = 0; \Delta L = 0, \pm 1; \Delta J = 0, \pm 1 (J = 0 \rightarrow J = 0$ is not allowed)
(a) $^3F_4 \rightarrow {}^3D_3$ So, $\Delta S = 0; \Delta L = -1; \Delta J = -1$ (allowed transition)
    S=1   S=1
    L=3   L=2
    J=4   J=3
(b) $^3F_4 \rightarrow {}^1D_3$ So, $\Delta S = -1; \Delta L = -1; \Delta J = -1$ (not allowed transition)
    S=1   S=0
    L=3   L=2
    J=4   J=3
(c) $^3F_4 \rightarrow {}^3P_4$ So, $\Delta S = 0; \Delta L = -2; \Delta J = 0$ (not allowed transition)
     S=1   S=1
    L=3   L=1
    J=4   J=4
(d) $^3F_4 \rightarrow {}^3D_2$ So, $\Delta S = 0; \Delta L = -1; \Delta J = -2$ (not allowed transition)
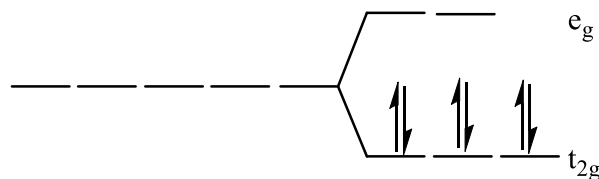   S=1   S=1
    L=3   L=2
    J=4   J=2
158.
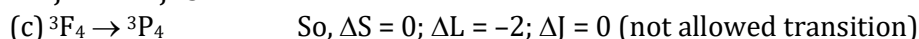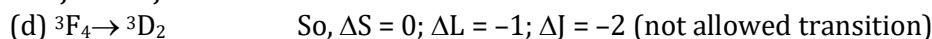
Ans. **(c)**

Sol. • $[Mn(H_2O)_6]^{2+} \Rightarrow t_{2g}^3 \, e_g^2$: High spin complex

In this complex, there is neither orbital contribution nor temperature independent paramagnetism (No L–S coupling) and $\alpha = 0$, Thus, μ_{obs}, $= \mu_{spin}$.

• $[Co(H_2O)_6]^{3+}$ is a low spin complex.

$Co^{3+} \rightarrow d^6$ i.e., $t_{2g}^6 e_g^0$

No unpaired electron.

Therefore, it is diamagnetic in nature.

159.

Ans. **(c)**

Sol. • $Ti^{3+} \Rightarrow d^3$ complex : $t_{2g}^1 \, e_g^0$

Ti^{+3} complex exhibit one broad band due to

(i) Vibronic coupling

(ii) Jahn-Teller distortion

(iii) Spin-orbit coupling

• $Co^{2+} \Rightarrow d^7$ complex

Exhibit three broad bands due to following transitions:

$^4T_{1g} \rightarrow {}^4T_{2g}$; $^4T_{1g} \rightarrow {}^4A_{2g}$; $^4T_{1g} \rightarrow {}^4T_{1g}$ (P)

$Cr^{3+} \Rightarrow d^3$ complex

Exhibit three broad bands due to following transitions :

$^4A2g \rightarrow 4T_{2g}$; $^4A_{2g} \rightarrow {}^4T_{1g}(F)$; $^4A_{2g} \rightarrow {}^4T_{1g}(P)$

• Mn^{2+} complex $\Rightarrow d^5$ complex exhibit a series of very weak (spin forbidden, Laporte forbidden and sharp bands).

• $Ni^{2+} \Rightarrow d^8$ exhibit three broad bands due to following transitions :

$^3A_{2g} \rightarrow {}^3T_{2g}$

$^3A_{2g} \rightarrow {}^3T_{1g}(F)$; $^3A_{2g} \rightarrow {}^3T_{1g}(P)$

160.

Ans. **(b)**

Sol. $Trans-[CoLCl(en)_2]^+ \xrightarrow{Hydrolysis} A$

$L = NO_2^-, NCS^-, OH^-, Cl^-$

The tendency to form cis-isomer of the product (A) follows the order :

$L = NO_2^- < Cl^- < NCS^- < OH^-$

161.

Ans. **(b)**

Sol. An aqueous solution of Fe(III) ion (A) gives a blood-red colour on reaction with KSCN the blood red colour is due to formation of $[Fe(SCN)(H_2O)_5]^{2+}$(B). The colur may also used for the identification of Iron (III). This colour is destroyed by the addition of F- ion due to the formation of $[FeF_6]^{3-}$ (C).
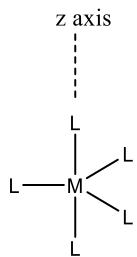
$[Fe(H_2O)_6]^{3+}\ SCN^- \rightarrow [Fe(H_2O)_5(SCN)]^{2+} \xrightarrow{NaF} [FeF_6]^{3-}$

(A)   Blood red color due to LMCT   Colorless Compound d–d transition Laporte for bidden
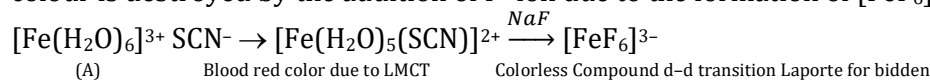
(B)   Spin forbidden

(C)

162.

Ans. **(b)**

Sol.

z axis

Two ligands are present on z-axis therefore, d_{z^2} – orbital is involved in σ–bonding. Also three ligands are presentin xy plane, therefore, d_{xy} and $d_{x^2-y^2}$ orbitals are involved in σ–bonding. Thus the d_{yz} and d_{xz} orbitals remain non bonding.

163.
Ans.   **(b)**
Sol.   In the complexes, $[Fe(bpy)_3]^{+2}$, $[Ru(bpy)_3]^{+2}$ and $[Fe(phen)_3]^{+2}$, ligands bpy and phen have empty π* orbitals, thus, band in electronic spectra is due to metal to ligand charge transfer (MLCT). Whereas, the other complexes i.e. $[FeCl_4]^{2-}$ (220 nm), $[FeBr_4]^{2-}$ (244 nm), $[ReO_4]^-$ (227nm) and $[TcO_4]^-$ (286 nm) show LMCT bands.

164.
Ans.   **(b)**
Sol. d^5– electronic configuration:

+2	+1	0	-1	-2
↑	↑	↑		

L = 2 + 1 + 0 = 3 i.e. 'F'
S = 3 × 1/2 = 3/2
2S + 1 = 2 × 3/2 + 1 = 4
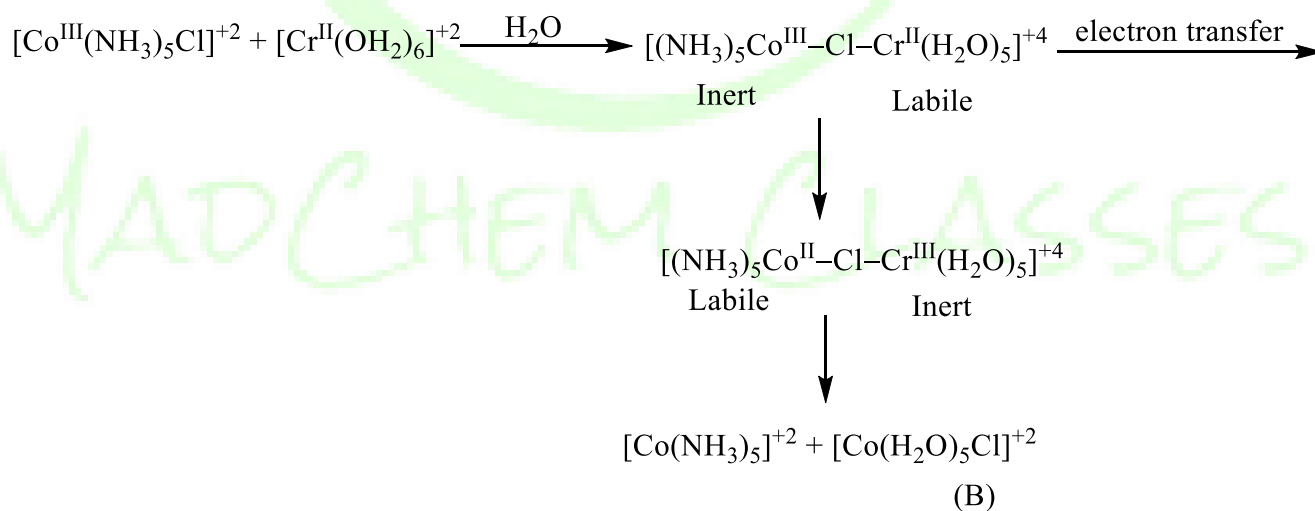J = Less than half filled = L–S = 3-3/2 = 3/2
Thus, ground state term is = $^{2S+1}L_J = {}^4F_{3/2}$

165.
Ans.   **(c)**
Sol.

$[Co^{III}(NH_3)_5Cl]^{+2} + [Cr^{II}(OH_2)_6]^{+2} \xrightarrow{H_2O} [(NH_3)_5Co^{III}-Cl-Cr^{II}(H_2O)_5]^{+4} \xrightarrow{\text{electron transfer}}$

Inert   Labile

$\downarrow$

$[(NH_3)_5Co^{II}-Cl-Cr^{III}(H_2O)_5]^{+4}$
Labile   Inert

$\downarrow$

$[Co(NH_3)_5]^{+2} + [Co(H_2O)_5Cl]^{+2}$
(B)

$[Co(NH_3)_5]^{+2} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{+2} \xrightarrow{+5H_3O^+} [Co(H_2O)_6]^{+2} + 5NH_4^+$
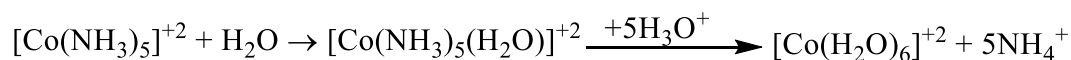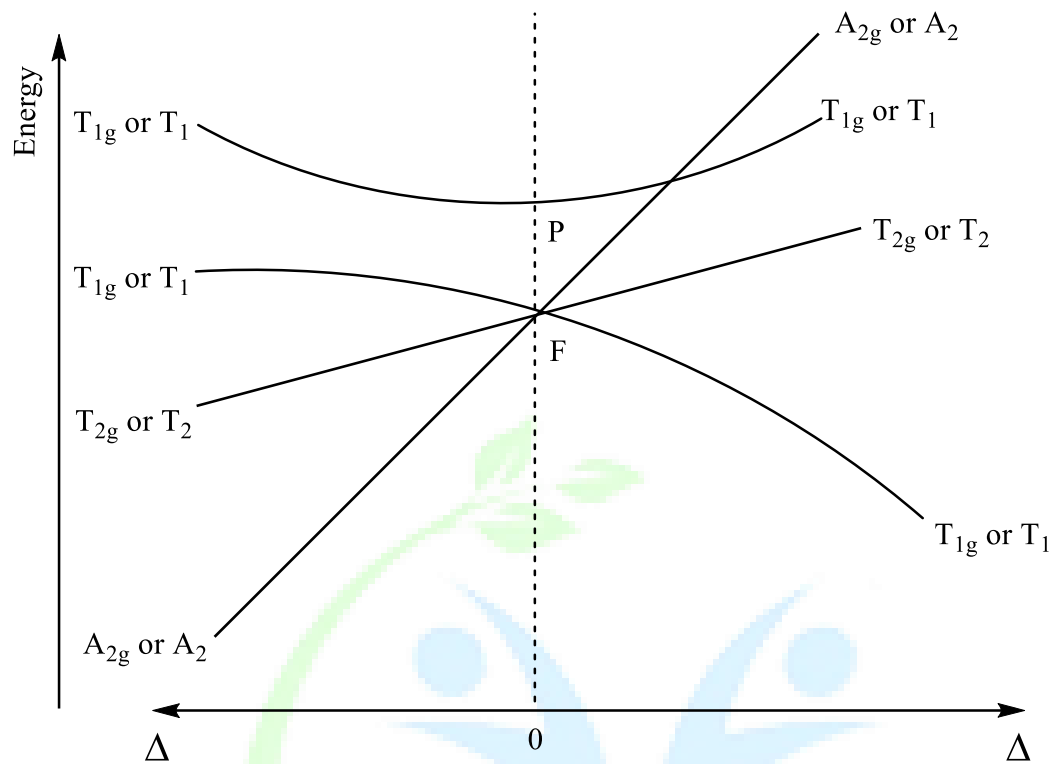
166.
Ans.   **(d)**
Sol.   In $[Cr(en)_3]^{+3}$, which is an octahedral complex, three spin allowed electronic transitions are observed.
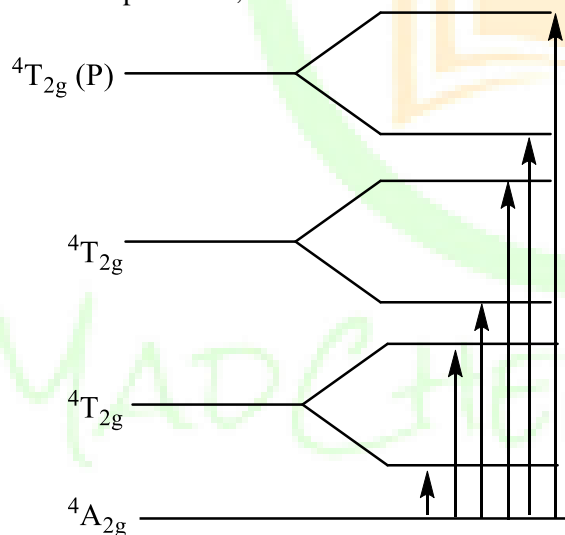
d^2, d^7 tetrahedral d^2, d^7 octahedral

d^3, d^8 octahedral d^3, d^8 tetrahedral
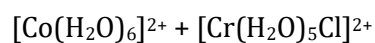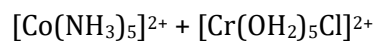
Trans-$[Cr(en)_2F_2]+$ is a tetragonal complex. Therefore, there is splitting of $^4T_{2g}$, $^4T_{1g}$, and $^4T_{1g}(P)$ states. $^4A_{2g}$ term does not split. Thus, 6 electronic transitions are observed.

167.

Ans.   **(c)**

Sol. $[Co(NH_3)_5Cl]^{2+} + [Cr(OH)_2)_6]^{2+} \rightarrow 5H_3O^+ \rightarrow A + B$

inner sphene electron transfer.

$[Co(NH_3)_5]^{2+} + [Cr(OH_2)_5Cl]^{2+}$

$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5Cl]^{2+}$

168.

Ans.   **(d)**

Sol. $Cr^{3+} \rightarrow d^3$

trans $(r(en) E_2]^{2+}$

4P ——————— 4T1g(P)

4T1g(F)

3 transition

D4h symmetry spliting

4F   2g

4_{A2g}

TS

E   A or B   E

A   B
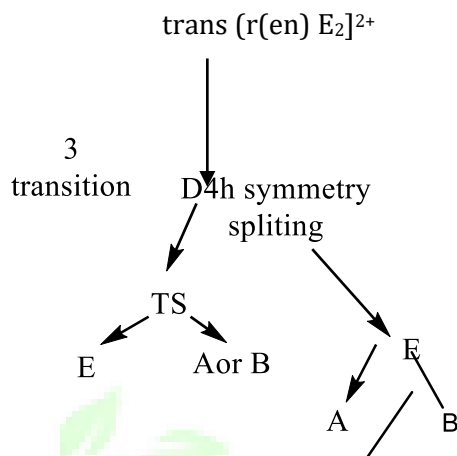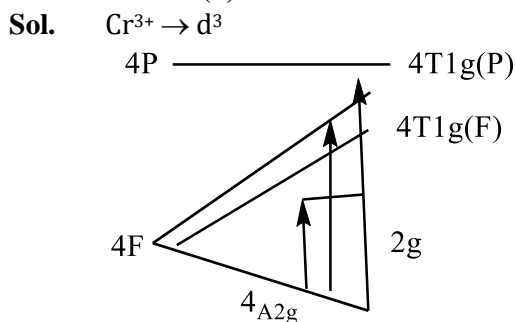
So total six transition occurs.

169.

Ans.   **(a)**

Sol. $[Fe(acac)_3] \rightarrow d^5$

So, High spin as acac weak field
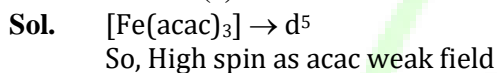
So, The value of Magnetic moment will be independent of temperature .

170.

Ans.   **(b)**

Sol.

ei

aig

Mn

e_{2g}

$e^4_{2g} \, a^1_{1g}$

If Cp was used the $e^2_{2g} a^1_{1g} \, e^2_{1g}$

171.

Ans.   **(c)**

Sol. $[*Co(L)_n]^{2+} + [Co(L)_n]^{3+} \rightarrow [*Co(L)_n]^{3+} + [Co(L)_n]^{2+}$

NH_3 = Not a good π-acceptor n = 6

O-phen

good π acceptor   n = 3

bidentate
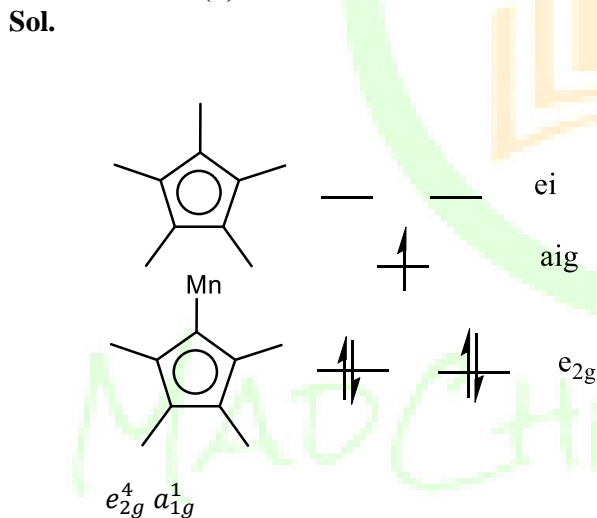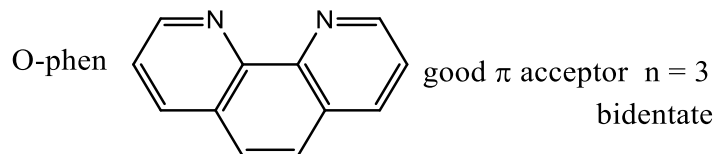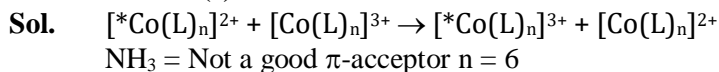
π–acceptor ligands complex andergo fast electron transfer by accepting electrons in antibonding orbitals.

So, correct Ans (c) very slow electron transfer L = NH₃, n = 6

172.
Ans.　　　**(b)**
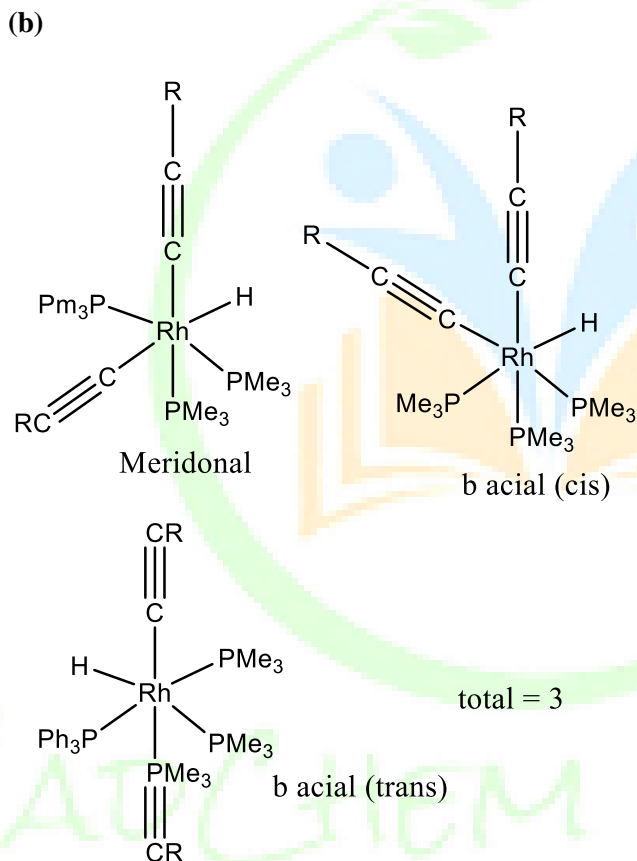**Sol.**　　LMCT condition
　　(1) Metal in high oridation state
　　(2) Ligands that are µ donors
　　　　Heve　　　　(A) $[FeCl_4]^2 \rightarrow$ LMCT $[Fe(6Py)_3]^{2+} \rightarrow$ MLCT
　　　　　　　　　(B) $[FeBr_4]^{2+}$ and $[TcO_4] \rightarrow$ Both LMCT
　　　　　　　　　(C) $[ReO_4] \rightarrow$ LMCT $(Ru(Bby)_3)^{2+} \rightarrow$ MLCT
　　　　　　　　　(D) $[Fe(Phen)_3]^{2+} \rightarrow$ MLCT $[FeCl_4]^{2-} \rightarrow$ LMCT

173.
Ans.　　　**(b)**
Sol.

Meridonal

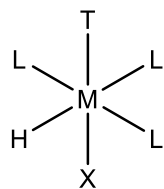b acial (cis)

total = 3

b acial (trans)

174.
Ans.　　　**(b)**
Sol.　　Dissociation substitution for octahedral complex

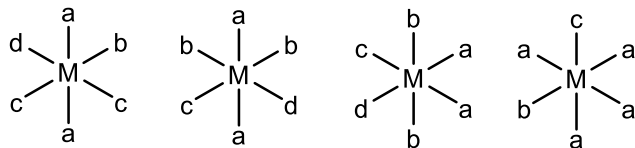(A) High steric hindrance between ligand courses repulsion and favours dissociation
(C) Penta Coordinated intermediate is observed as complex loses one ligand. a and c is correct.
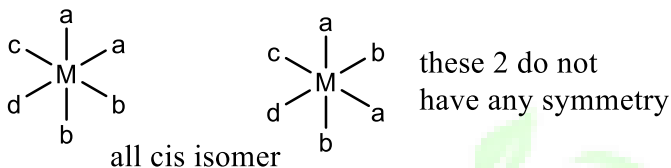
175.

Ans.   **(b)**
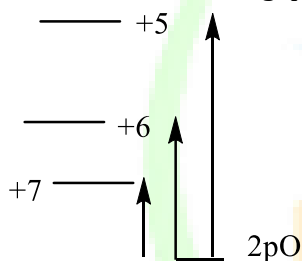**Sol.** Ma_2b_2cd

all 4 have one plane

all cis isomer   these 2 do not
have any symmetry

So the form enantiomeric pair

176.
Ans.   **(a)**
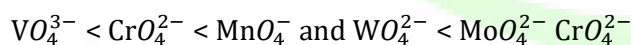**Sol.**   Oxidation state increase the gap decrease

Hence λ max increase

down the group eletronegativity increase So gap decrease and λ increase.

So, correct option (a)

$VO_4^{3-} < CrO_4^{2-} < MnO_4^-$ and $WO_4^{2-} < MoO_4^{2-}\ CrO_4^{2-}$

177.
Ans.   **(a) and (b)**
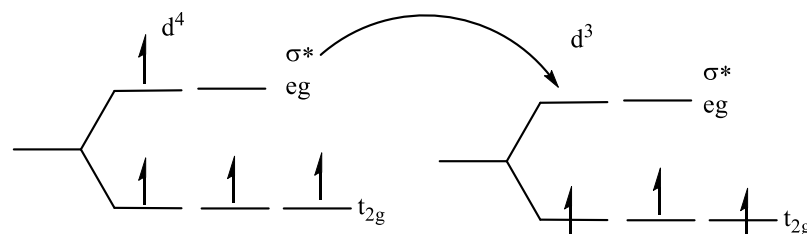**Sol.** $[Cr(H_2O)_6]^{2+/3+}$ self electron mechanism
Cr^{+2} Cr^{+3}

d^4 d^3

σ^* orbitals are involved

It involves large inner sphene neorganization energy as bond length changes $\sigma^* \to \sigma^*$ slow transfer.
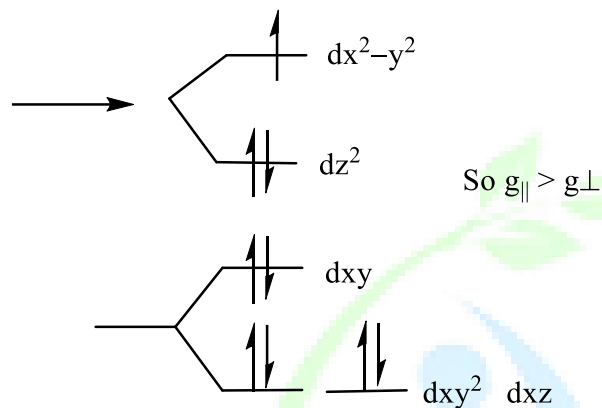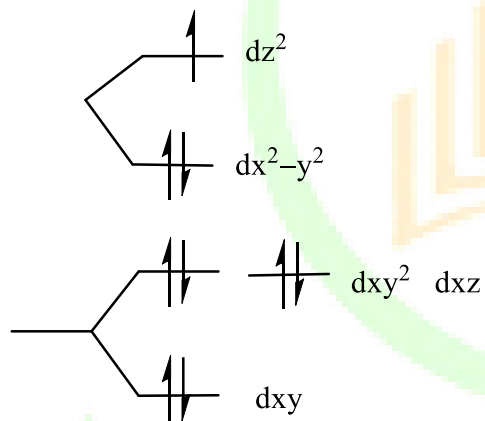
Correct option (ii) a and b

178.
Ans. **(c)**
Sol. Allowed transition $\Delta M_s = \pm 1$ and $\Delta M_1 = 0$
Tetragonally elongated Cu(II)

dx^2-y^2

dz^2

So $g_{\parallel} > g\perp$

dxy

dxy^2 dxz

tetrahonally compressed Cu(II)

dz^2

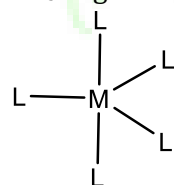dx^2-y^2

dxy^2 dxz

dxy

179.
Ans. **(d)**
Sol. ML_5 trigonal Bipyramidal

Point group D_{3h}

$dz^2 > dx^2-y^2, dxy > dxz, dyz$

180.
Ans. **(c)**
Sol. (i) Trigonal bipyramidal

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		Point	IR bonds
axial -Fe(CO)$_4$L A		C$_{3v}$	3
equitorial -Fe(CO)$_4$L B		C$_{2v}$	4

(ii)Octahedral isomer

fac - Mo(CO)$_3$L$_3$ C		C$_{2v}$	3
Mer-Mo(CO)$_3$L D		C$_{3v}$	2

181.
Ans.   **(c)**
Sol. $[Cr(\underline{NH_3})_6]^{3+}$ d^3 system
              $\underset{-1}{} \quad \underset{-2}{}$

$\underset{+2}{} \quad \underset{+1}{} \quad \underset{0}{}$

L = +2 + 1 = F(3)

S = $\frac{3}{2}$ (2S + 1) = 4

G.S. term : ^{4}F

$^4T_{1g}(F)$

$T_{2g}(F)$

$^4A_{2g}C$
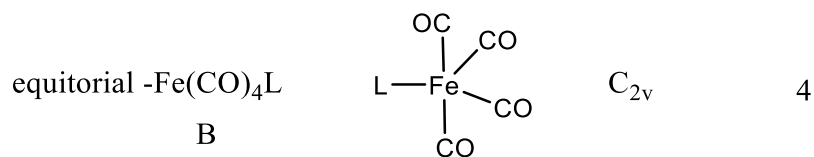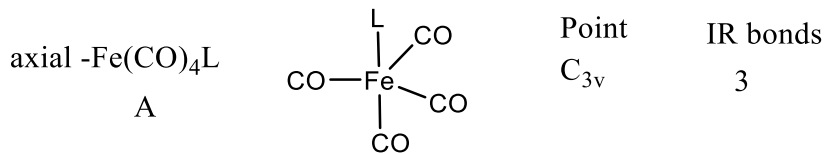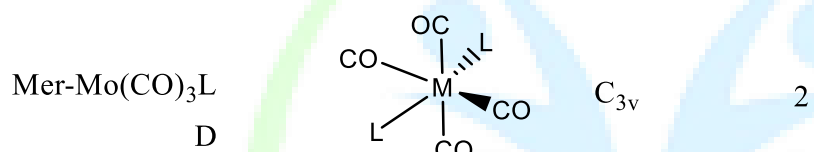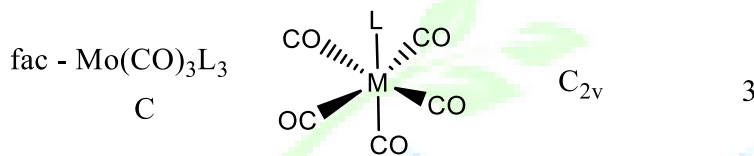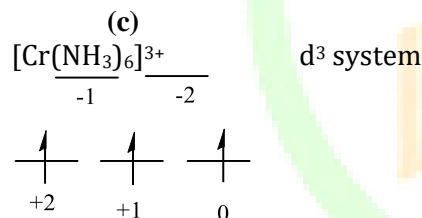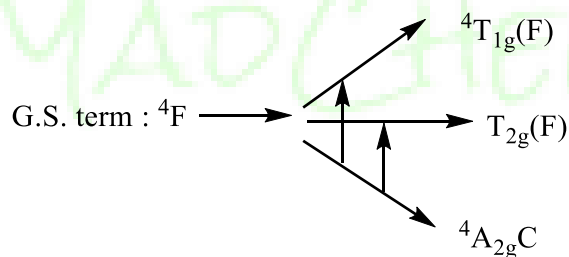
Correct option (2) ^{4}F, $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$

182.
Ans.   **(c)**
Sol.   JTD is expected in unsymmetrically filled.
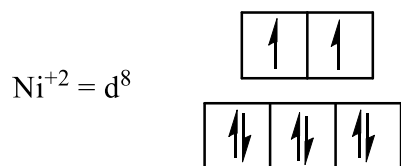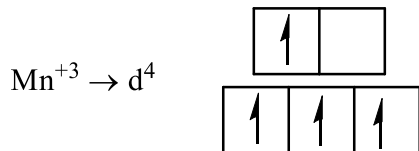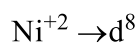
$Mn^{+3} \rightarrow d^4$

$Ni^{+2} = d^8$

$VCl_4 \rightarrow v^{+4} = d^2$

183.
Ans.   **(b)**
Sol.

$Ni^{+2} \rightarrow d^8$

give in (nm) [Wavelength]

$^3Tg(P)$

$3\,9(f)$

B C

3^P

$^3T_{2g}$

Energy$\rightarrow$ A < B < C

$^3A_{2g}$

Wavelength C > B > A
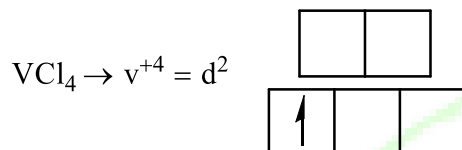
A

energy
small
means wavelnegth maximum

Hence
$T_{1g}(P) \leftarrow {}^3A_{2g}$, ${}^3T_{1g}(F) \leftarrow {}^3A_{2g}$ and ${}^3T_{2g} \leftarrow {}^3A_2$
   (A)   (B)   (C)
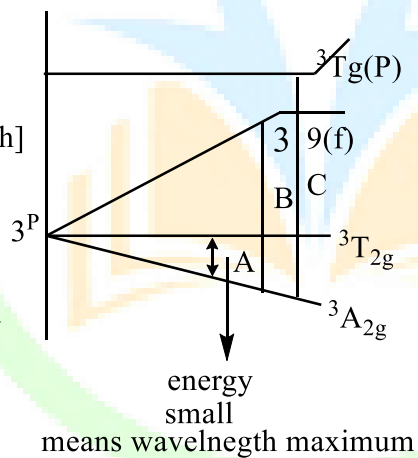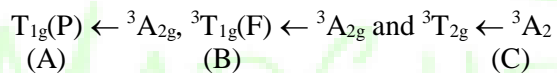
184.
Ans.   **(a)**
Sol.   (1) Nature of ligand
π-acceptor $\uparrow$es rate of e^- transfer also $\uparrow$es
(2) Principle quantum no $\uparrow$rate of e^- transfer also $\uparrow$es

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(3) $\pi - \pi* \;>\; \pi* - \sigma* \;>\; \sigma - \sigma*$

or   HOMO LUMO , HOMO LUMO , HOMO LUMO

or $t_{2g} - t_{2g}$, $t_{2g} - e_g$, $e_g - e_g$

Ru^{+2} Ru^{+3} But

d^6 d^5

Ru^{+2} Ru^{+3} π to $\pi*$ or T_{2g} to T_{2g}. CO^{+2} CO^{+3}

no change in electrons   Change in electrons in CO^{+2}/CO^{+3}
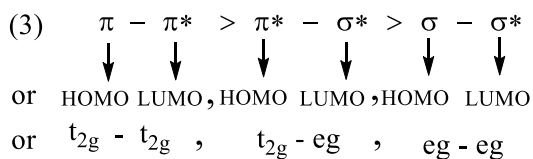
185.
Ans.   **(c)**
Sol.   Single spin allowed → Means High spin

$$\sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.9$$

^5E_g

$2nI + 1$
spin multiplication $2 \times 4 \times 1/2 + 1 = 5$

$^5T_{2g}$

186.
Ans.   **(d)**
Sol.   (a) $[IrCl_6]^{2-} + [Cu^{+2}/H_2O)_6] \rightarrow$ Product
$Ir^{+4}(d5^)$ $Cl^{+2} (d^4)$
Inert   Labrile
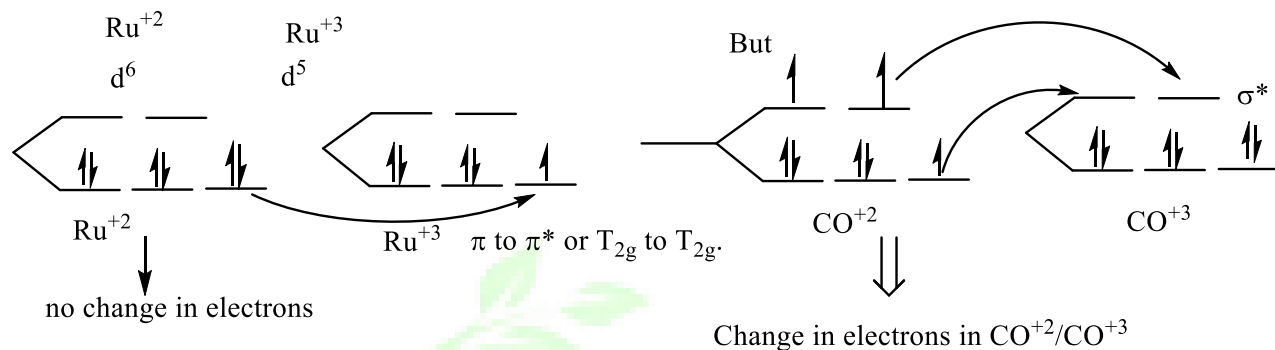Oxidant   Reductant

$$\left[Cl_5 \text{——} Ir \text{——} Cl \text{——} Cr(H_2O)_5 \right]^{4+}$$

$d^5 < \sim\sim\sim d^4$

$$\left[Cl_5 \text{——} Ir \text{——} Cl \text{——} Cr(H_2O)_5 \right]$$
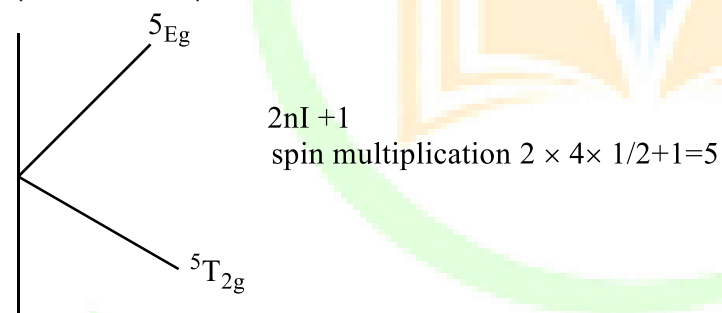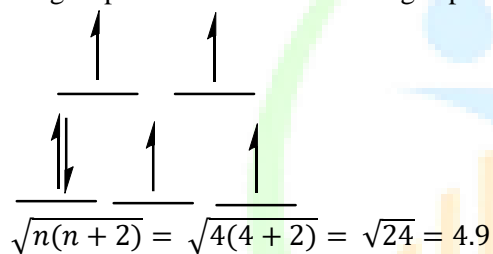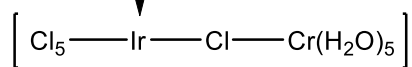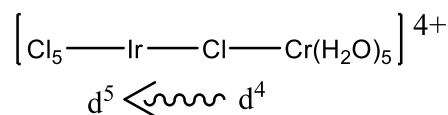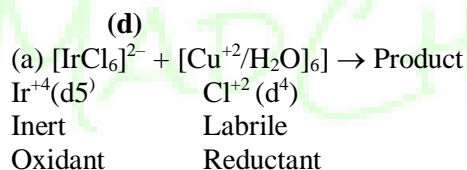
Inert ← d^6 $d^3 \rightarrow$ Inert
           CFSE = 12 Dq

CFSE
= -24Dq

In thus only electron transfer tabe place not ligand transfer tabs place because CFSE Cl vely talge or after electron transfer both become inert similarly check option

(b) Again CFSE more so only electron transfer tabe planar

(c) $[Fe(CN)_6]^{4-} + [Ir[?]]^{2-} \rightarrow$ Product

$\quad\quad\quad\quad$ Fe^{+2} $\quad\quad\quad\quad\quad$ Ir^{+4}

$\quad\quad\quad\quad$ d^6 $\quad\quad\quad\quad\quad\quad$ d^5

$\quad\quad\quad\quad$ Inert $\quad\quad\quad\quad\quad$ Inert

$\quad\quad\quad\quad\quad\quad$ both all inert only e– transfer tabe place.

(d) $[CrO_4]^{2-} + [Fe(CN)_6]^{4-} \rightarrow$ Product

$\quad\quad\quad\quad$ ↓

$\quad\quad\quad\quad$ Td

Low CFSE → act as bridging legand.

187.
Ans. $\quad\quad\quad\quad\quad\quad\quad$ **(d)**
Sol. $\quad$ $[Co(NH_3)_5d]^{+2}$ $\quad\quad\quad$ + $\quad\quad$ $[Cr(H_2O)_6]^{+2}$

$\quad\quad$ $CO^{+3}(l.s)$ $\quad\quad\quad\quad\quad\quad\quad\quad$ Cr^{+2} (H.S)

$\quad\quad\quad\quad$ Inest $\quad\quad\quad\quad\quad\quad\quad$ Labile

$\quad\quad$ (Oxidant)
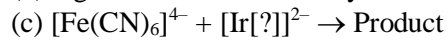
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ (Reductant)

$\quad\quad\quad\quad\quad\quad\quad\quad$ Reductant to oxidant

$\quad$ $[IrCl_6]^{-2} + [cr(OH_2)_6]^{+2}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ In this reaction ligand

is not Transfered, only e^- transport

Takes place

$\quad\quad\quad\quad$ $[CrO_4]^{-2} + [Fe(CN)_6]^{-4}$

$\quad\quad\quad\quad\quad\quad\quad\quad\quad$ $x-6=-4$

$\quad\quad\quad\quad$ oxygen is $\quad\quad$ $(x = +2)$ (l.s)

$\quad\quad\quad$ participates in

$\quad\quad\quad\quad\quad$ bridging

$\quad\quad\quad$ (Reductant)

188.
Ans. $\quad\quad\quad$ **(c)**
Sol.

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$d^3 d^8 Oh$ $d^2 d^7 Oh$

$d^2 d^7 Td$ $d^3 d^8 Td$

Max wavelength = 1070 nm

$A_{2g} \rightarrow T_{2g}$ 1070 nm   (C)

$A_{2g} \rightarrow T_{1g}$ 690 nm (B)

$A_{2g} \rightarrow T_{1g}(P)$ 400 nm (A)

189.

Ans.   **(a)**

Sol. $[Mn(H_2O)_6]^{+3}$

           $Mn^{+3}, d^4(hs)$

eg orbital is unsymmetrically filled, So, J.T.D. is present

$\overset{+2}{Ni} (d^8)$ orbirtals are symmetrically filled So, J.T.D. is absent

$\overset{+4}{V} (d^1)$ e is unsymmetrically filled, J.T.D is present

190.

Ans.   **(a)**

Sol.   Nature of ligand – π acceptor ligand ↑es Rate ↑es.

                         – principle quantum no ↑ Rate ↑es.

$$\pi - \pi^* \rangle \pi - \sigma^* \rangle \sigma - \sigma^*$$

HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
t_{2g}	t_{2g}	t_{2g}	t_{2g}	eg	eg
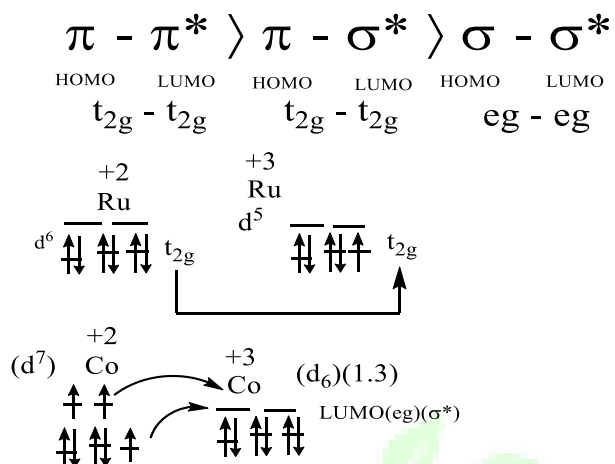
191.
Ans. (a)
Sol. $[Co(tren)(NH_3)Cl]^{+2}$
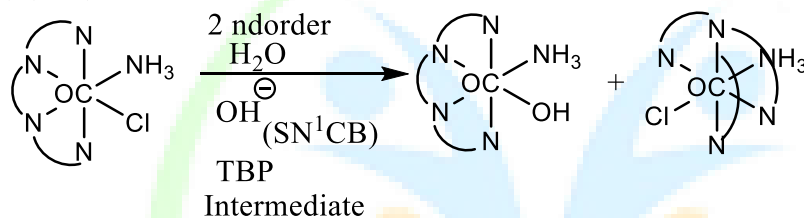
Purple Isomer give TBP Intermediate.

192.
Ans. (c)
Sol.

Oh, d^6

spin allowed

→ High spin
→ $\Delta S \neq 0$

$\mu = \sqrt{n(n+2)}$ $S = 4/2$
$\quad = \sqrt{4(6)}$ $S = 2$
$\mu = 4.9$ B.M $2s + 1$

$2 \times 2 + 1$
$= 5$

^5Eg

$^5T_{2g}$

$^5T_{2g} \longrightarrow ^5Eg$

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