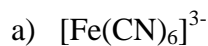


Tutorial 1

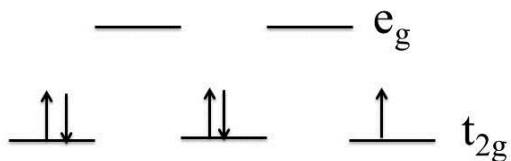
Q1: Calculate the CFSE for the following complexes.



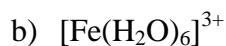
Fe: {Ar} $3d^6, 4s^2$

Fe^{3+} : {Ar} $3d^5$

For octahedral geometry the d orbitals will split as t_{2g} and e_g . Filling electrons for a strong field ligand;



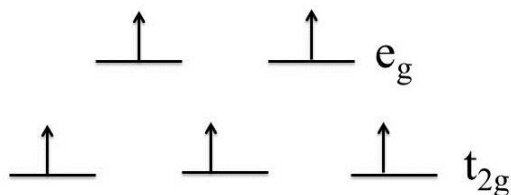
So the CFSE will be $5(-2/5) \Delta_o$



Fe: {Ar} $3d^6, 4s^2$

Fe^{3+} : {Ar} $3d^5$

For octahedral geometry the d orbitals will split as t_{2g} and e_g . Filling electrons for a weak field ligand;



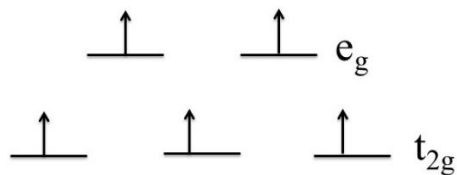
So the CFSE will be $3(-2/5) \Delta_o + 2(3/5) \Delta_o = 0$



Co: {Ar} $3d^7, 4s^2$

Co^{3+} : {Ar} $3d^6$

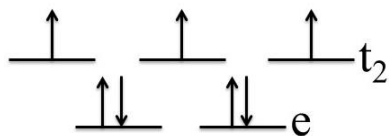
For octahedral geometry the d orbitals will split as t_{2g} and e_g . Filling electrons for a weak field ligand;



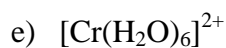
So the CFSE will be $3(-2/5) \Delta_o + 3(3/5) \Delta_o = 0$

Co: {Ar} $3d^7, 4s^2$ Co^{2+} : {Ar} $3d^7$

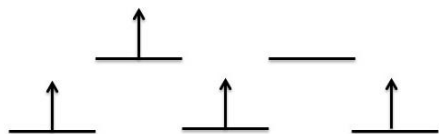
For tetrahedral geometry the d orbitals will split as e and t_2 . The tetrahedral geometry will result in a high spin complex. Though Cl^- is a weak ligand, the tetrahedral geometry is the more relevant factor. Filling electrons;



So the CFSE will be $4(-3/5) \Delta_t + 3(2/5) \Delta_t = -6/5 \Delta_t$

Cr: {Ar} $3d^5, 4s^1$ Cr^{3+} : {Ar} $3d^4$

For octahedral geometry the d orbitals will split as t_{2g} and e_g . Filling electrons for a weak field ligand;

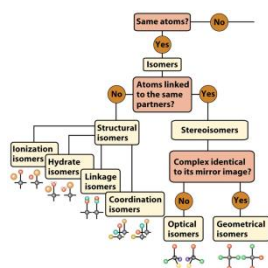


So the CFSE will be $3(-2/5) \Delta_o + 1(3/5) \Delta_o = -3/5 \Delta_o$

Q2: Which of the following are structural isomers?

- I. coordination isomers
- II. linkage isomers
- III. geometric isomers
- IV. optical isomers

- A) I, III
- B) II, IV
- C) I, III, IV
- D) II, III
- E) I, II

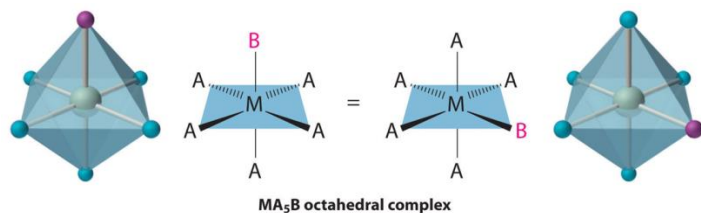


Answer: E

Q3: Which of the following complexes shows geometric isomerism?

- A) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$
- B) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
- C) $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- D) $\text{K}[\text{Co}(\text{NH}_3)_2\text{Cl}_4]$
- E) $\text{Na}_3[\text{CoCl}_6]$

Answer: D (MA_6 and MA_5B cases do not exhibit geometric isomerism)



Q4. How many of the following compounds exhibit geometric isomers?

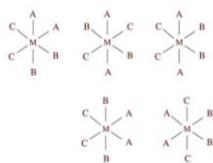
- I. $\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_2$ (square planar)
- II. $[\text{Co}(\text{H}_2\text{O})_6]\text{Br}_3$
- III. $[\text{Ni}(\text{H}_2\text{O})_4(\text{NO}_2)_2]$
- IV. $\text{K}_2[\text{CoCl}_4]$

- A) 0
- B) 1
- C) 2
- D) 3
- E) 4

Answer: C (complexes I and III)

Q5. Give the number of geometric isomers for the octahedral compound $[\text{MA}_2\text{B}_2\text{C}_2]$, where A, B, and C represent ligands.

- A) 1
- B) 2
- C) 3
- D) 5
- E) none of these



Answer: D

Q6. For the process $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{Cl}^- \rightarrow [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{NH}_3$, what would be the ratio of *cis* to *trans* isomers in the product?

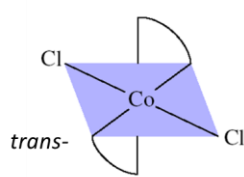
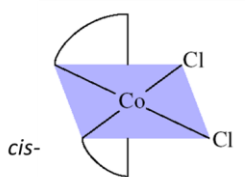
- A) 1:1
- B) 1:2
- C) 1:4
- D) 4:1
- E) 2:1

Answer: D

Q7. Which of the following statements about the complex ion $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ is true?
(en = ethylenediamine, $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$)

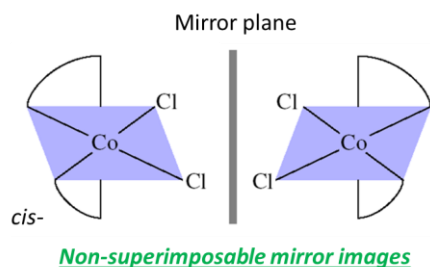
- A) The complex ion contains Co(I).
- B) The complex ion exhibits *cis* and *trans* geometric isomers, but no optical isomers.
- C) The complex ion exhibits two geometric isomers (*cis* and *trans*) and two optical isomers.
- D) The geometric isomers of the complex ion have identical chemical properties.

Answer: C



Geometric isomers:

The *cis*- form is an enantiomeric pair:



Q8. Calculate the oxidation state of the metal and the number of *d* electrons in the following coordination complexes:

- a) $[\text{CoCl}_4]^{2-}$; b) $[\text{Fe}(\text{bpy})_3]^{3+}$; c) $[\text{Cu}(\text{ox})_2]^{2-}$; d) $[\text{Cr}(\text{CO})_6]$

Answer:

a) Each Cl ligand has a charge of -1, so $4 \times -1 = -4$. Overall charge on the complex is -2, so the oxidation state of Co = +2. Ground state configuration for Co = $[\text{Ar}] 3d^7 4s^2$. On loss of $2e^-$, Co^{2+} has configuration $[\text{Ar}] 3d^7$, so seven d electrons.

b) bpy (2,2'-Bipyridyl) is uncharged = neutral. Oxidation state of Fe = +3. Ground state configuration for Fe = [Ar] $3d^6 4s^2$. On loss of $3e^-$, Fe^{3+} has configuration [Ar] $3d^5$, so five d electrons.

c) ox (oxalate, $C_2O_4^{2-}$) has charge -2 per oxalate, so total = $2 \times -2 = -4$. Overall charge on complex = -2, so the oxidation state of Cu = +2. Ground state configuration for Cu = [Ar] $3d^{10} 4s^1$. On loss of $2e^-$, Cu^{2+} has configuration [Ar] $3d^9$, so nine d electrons.

d) CO is uncharged = neutral. Oxidation state of Cr = 0. In this case, all electrons are in 3d orbitals which are now of lower energy (because filled) than 4s orbitals. Ground state configuration for Cr = [Ar] $3d^5 4s^1$. Configuration for Cr^0 = [Ar] $3d^6$, so six d electrons.

Q9. Which of the following complexes will have larger crystal field splitting (Δ) in the given series? Give brief explanation for your choice.

- (i) $[Co(en)_3]^{3+}$, $[Ir(en)_3]^{3+}$, $[Rh(en)_3]^{3+}$
- (ii) $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{2+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(CN)_6]^{3-}$
- (iii) $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$
- (iv) $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$, $[FeCl_4]^{2-}$

Answers:

(i) $[Co(en)_3]^{3+}$, $[Ir(en)_3]^{3+}$, $[Rh(en)_3]^{3+}$: Ir^{3+} having larger size 5d-orbitals and thus stronger interaction along with being larger metal ion, ligands experience less steric crowding and hence Δ is greater.

(ii) $[Cr(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{2+}$, $[Cr(NH_3)_6]^{3+}$, $[Cr(CN)_6]^{3-}$: CN^- is strong-field ligand (π -acceptor) compared to NH_3 or H_2O (σ -donors).

(iii) $[CoF_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$: Order of ligand strength: $F^- < H_2O < NH_3$ (F^- is a π -donor ligand whereas H_2O and NH_3 are σ -donors)

(iv) $[Fe(H_2O)_6]^{2+}$, $[Fe(CN)_6]^{4-}$, $[FeCl_4]^{2-}$: CN^- is strong-field ligand (π -acceptor) compared to NH_3 (σ -donor) or Cl^- (π -donor).