Chapter 5: Coordination Compounds

Exercises — Exercises

Q1 Explain the bonding in coordination compounds in terms of Werner's postulates.

SOLUTION

Werner (1898) proposed the following postulates to explain bonding in coordination compounds:

1. Metals show two types of valences — primary (ionisable) and secondary (non-ionisable).

2. Primary valence is satisfied by negative ions and corresponds to the oxidation state of the metal. These are ionisable.

3. Secondary valence is the coordination number of the metal. It is fixed and non-ionisable. It is satisfied by neutral molecules or negative ions that bond directly to the metal (Lewis base donors).

4. The groups satisfying secondary valences are arranged in definite geometric patterns around the central metal ion (coordination polyhedra such as octahedral, tetrahedral, square planar).

Example: In $[Co(NH_3)_6]Cl_3$, Co^{3+} has primary valence = 3 (satisfied by 3 Cl^-) and secondary valence = 6 (satisfied by 6 NH_3 molecules arranged octahedrally).

Werner distinguished species inside the coordination sphere (square bracket) from counter ions outside: only the counter ions ionise in solution, while the coordination sphere remains intact.

Answer: Werner postulated two valences: primary (ionisable, = oxidation state, satisfied by anions) and secondary (non-ionisable, = coordination number, satisfied by ligands arranged in a fixed geometry around the metal).

Q2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ solution in 1:1 molar ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 molar ratio does not give the test of Cu^{2+} ion. Explain why?

SOLUTION

$FeSO_4 + (NH_4)_2SO_4 \rightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$ (Mohr's salt)

This is a double salt. In aqueous solution it dissociates completely into its constituent ions:

$FeSO_4.(NH_4)_2SO_4 \rightarrow Fe^{2+} + 2\ NH_4^+ + 2\ SO_4^{2-}$

Free Fe^{2+} ions are present, so the characteristic tests for Fe^{2+} (e.g., with NaOH giving green precipitate, or with $K_3[Fe(CN)_6]$ giving blue colour) are positive.

$CuSO_4 + 4\ NH_3 \rightarrow [Cu(NH_3)_4]SO_4$ (tetraamminecopper(II) sulphate)

This is a complex salt (coordination compound). In aqueous solution, $[Cu(NH_3)_4]^{2+}$ complex ion does NOT dissociate significantly into Cu^{2+} and NH_3:

$[Cu(NH_3)_4]^{2+} \leftrightarrow Cu^{2+} + 4\ NH_3$ (Kd very small)

The concentration of free Cu^{2+} ions is negligibly small, so characteristic tests for Cu^{2+} (e.g., with NaOH giving blue precipitate) are not observed.

Difference: A double salt releases all its ions completely on dissolving; a complex (coordination compound) maintains the coordination entity intact in solution.

Answer: Mohr's salt is a double salt that releases free Fe^{2+} ions in solution; $[Cu(NH_3)_4]SO_4$ is a true coordination compound whose complex ion $[Cu(NH_3)_4]^{2+}$ does not dissociate appreciably, so no free Cu^{2+} ions are available for the characteristic tests.

Q3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.

SOLUTION

1. Coordination entity:

A central metal atom/ion bonded to a definite number of ions or molecules.

Examples: $[Fe(CN)_6]^{4-}$ (iron(II) coordinated to 6 CN^- ligands); $[Co(NH_3)_6]^{3+}$ (cobalt(III) coordinated to 6 NH_3 molecules).

2. Ligand:

An ion or molecule that donates a lone pair of electrons to the central metal atom/ion (Lewis base).

Examples: Cl^- (unidentate anion ligand); en = $H_2NCH_2CH_2NH_2$,

ethane-1,2-diamine (didentate neutral ligand).

3. Coordination number (CN):
The number of ligand donor atoms directly bonded to the central metal by sigma bonds.
Examples: In $[PtCl_6]^{2-}$, CN of Pt = 6; in $[Ni(NH_3)_4]^{2+}$, CN of Ni = 4.

4. Coordination polyhedron:
The spatial geometry defined by the ligand donor atoms around the central metal ion.
Examples: $[Co(NH_3)_6]^{3+}$ -> octahedral; $[Ni(CO)_4]$ -> tetrahedral.

5. Homoleptic complexes:
Complexes in which the metal is bound to only one kind of donor group (ligand).
Examples: $[Co(NH_3)_6]^{3+}$ (only NH_3); $[Fe(CN)_6]^{4-}$ (only CN^-).

6. Heteroleptic complexes:
Complexes in which the metal is bound to more than one kind of donor group.
Examples: $[CoCl(NH_3)_5]^{2+}$ (both Cl^- and NH_3); $[PtCl_2(NH_3)_2]$ (both Cl^- and NH_3).

Answer: Coordination entity: $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$. Ligand: Cl^-, en. Coordination number: Pt=6 in $[PtCl_6]^{2-}$, Ni=4 in $[Ni(NH_3)_4]^{2+}$. Polyhedron: octahedral ($[Co(NH_3)_6]^{3+}$), tetrahedral ($[Ni(CO)_4]$). Homoleptic: $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$. Heteroleptic: $[CoCl(NH_3)_5]^{2+}$, $[PtCl_2(NH_3)_2]$.

Q4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.

SOLUTION

1. Unidentate ligand:
A ligand that binds to the metal through only ONE donor atom.
Examples: Cl^- (donates through Cl); NH_3 (donates through N).

2. Didentate ligand:
A ligand that binds to the metal through TWO donor atoms simultaneously, forming a chelate ring.
Examples: en ($H_2NCH_2CH_2NH_2$, donates through 2 N atoms); $C_2O_4^{2-}$ (oxalate, donates through 2 O atoms).

3. Ambidentate ligand:
A ligand that has TWO different potential donor atoms but uses only ONE of them

at a time in a given complex.

Examples: NO_2^- can bind through N (giving nitro, -NO_2) or through O (giving nitrito, -ONO); SCN^- can bind through S (giving thiocyanato, M-SCN) or through N (giving isothiocyanato, M-NCS).

Answer: Unidentate (1 donor atom): Cl^-, NH_3. Didentate (2 donor atoms): en, $C_2O_4^{2-}$. Ambidentate (2 possible donor atoms, only 1 used at a time): NO_2^- (N or O), SCN^- (S or N).

Q5 Specify the oxidation numbers of the metals in the following coordination entities:

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$

(ii) $[CoBr_2(en)_2]^+$

(iii) $[PtCl_4]^{2-}$

(iv) $K_3[Fe(CN)_6]$

(v) $[Cr(NH_3)_3Cl_3]$

SOLUTION

(i) $[Co(H_2O)(CN)(en)_2]^{2+}$:

Charge of complex = +2; H_2O = 0, CN^- = -1, en = 0 (each)

Let oxidation state of Co = x

x + 0 + (-1) + 2(0) = +2

x = +3

Oxidation state of Co = +3

(ii) $[CoBr_2(en)_2]^+$:

Charge = +1; Br^- = -1 each, en = 0 each

x + 2(-1) + 2(0) = +1

x = +3

Oxidation state of Co = +3

(iii) $[PtCl_4]^{2-}$:

Charge = -2; Cl^- = -1 each

x + 4(-1) = -2

x = +2

Oxidation state of Pt = +2

(iv) $K_3[Fe(CN)_6]$:

Overall neutral; K^+ = +1 each, CN^- = -1 each

3(+1) + x + 6(-1) = 0
3 + x - 6 = 0
x = +3
Oxidation state of Fe = +3

(v) $[Cr(NH_3)_3Cl_3]$:
Neutral complex; NH_3 = 0, Cl^- = -1 each
x + 3(0) + 3(-1) = 0
x = +3
Oxidation state of Cr = +3

Answer: (i) Co = +3; (ii) Co = +3; (iii) Pt = +2; (iv) Fe = +3; (v) Cr = +3.

Q6 Using IUPAC norms write the formulas for the following:
(i) Tetrahydroxidozincate(II)
(ii) Potassium tetrachloridopalladate(II)
(iii) Diamminedichloridoplatinum(II)
(iv) Potassium tetracyanidonickelate(II)
(v) Pentaamminenitrito-O-cobalt(III)
(vi) Hexaamminecobalt(III) sulphate
(vii) Potassium tri(oxalato)chromate(III)
(viii) Hexaammineplatinum(IV)
(ix) Tetrabromidocuprate(II)
(x) Pentaamminenitrito-N-cobalt(III)

SOLUTION

Rules applied: metal listed first inside brackets, ligands in alphabetical order, charge as superscript, counter ions outside brackets.

(i) Tetrahydroxidozincate(II):
Zn(II), 4 OH^- ligands, anionic complex -> counter cation needed (not specified, so as acid form)
Formula: $[Zn(OH)_4]^{2-}$ (if potassium salt: $K_2[Zn(OH)_4]$)

(ii) Potassium tetrachloridopalladate(II):
K^+ counter ion, Pd(II), 4 Cl^- ligands
Formula: $K_2[PdCl_4]$

(iii) Diamminedichloridoplatinum(II):
Neutral complex, Pt(II), 2 NH_3, 2 Cl^-

Formula: $[PtCl_2(NH_3)_2]$

(iv) Potassium tetracyanidonickelate(II):
K^+ counter ion, Ni(II), 4 CN^-
Formula: $K_2[Ni(CN)_4]$

(v) Pentaamminenitrito-O-cobalt(III):
Co(III), 5 NH_3, 1 ONO^- (nitrito-O, bonded through oxygen)
Formula: $[Co(NH_3)_5(ONO)]^{2+}$ -> as salt: $[Co(NH_3)_5(ONO)]Cl_2$ (or as stated, the complex cation)
Ion formula: $[Co(NH_3)_5(ONO)]^{2+}$

(vi) Hexaamminecobalt(III) sulphate:
Co(III), 6 NH_3, SO_4^{2-} counter ion
Formula: $[Co(NH_3)_6]_2(SO_4)_3$

(vii) Potassium tri(oxalato)chromate(III):
K^+ counter ion, Cr(III), 3 $C_2O_4^{2-}$ ligands
Formula: $K_3[Cr(C_2O_4)_3]$

(viii) Hexaammineplatinum(IV):
Pt(IV), 6 NH_3, cationic complex (counter anion not specified)
Formula: $[Pt(NH_3)_6]^{4+}$ -> as chloride salt: $[Pt(NH_3)_6]Cl_4$

(ix) Tetrabromidocuprate(II):
Cu(II), 4 Br^-, anionic complex
Formula: $[CuBr_4]^{2-}$

(x) Pentaamminenitrito-N-cobalt(III):
Co(III), 5 NH_3, 1 NO_2^- (nitrito-N, bonded through nitrogen)
Formula: $[Co(NH_3)_5(NO_2)]^{2+}$

Answer: (i) $[Zn(OH)_4]^{2-}$ (ii) $K_2[PdCl_4]$ (iii) $[PtCl_2(NH_3)_2]$ (iv) $K_2[Ni(CN)_4]$ (v) $[Co(NH_3)_5(ONO)]^{2+}$ (vi) $[Co(NH_3)_6]_2(SO_4)_3$ (vii) $K_3[Cr(C_2O_4)_3]$ (viii) $[Pt(NH_3)_6]^{4+}$ (ix) $[CuBr_4]^{2-}$ (x) $[Co(NH_3)_5(NO_2)]^{2+}$

Q7 Using IUPAC norms write the systematic names of the following:

(i) $[Co(NH_3)_6]Cl_3$
(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$
(iii) $[Ti(H_2O)_6]^{3+}$
(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$
(v) $[Mn(H_2O)_6]^{2+}$
(vi) $[NiCl_4]^{2-}$
(vii) $[Ni(NH_3)_6]Cl_2$
(viii) $[Co(en)_3]^{3+}$
(ix) $[Ni(CO)_4]$

SOLUTION

Naming rules: name ligands alphabetically before the metal; anionic ligands end in -o (updated to -ido); neutral: aqua (H_2O), ammine (NH_3), carbonyl (CO); metal oxidation state in Roman numerals; for anion complexes, metal suffix = -ate.

(i) $[Co(NH_3)_6]Cl_3$:
Co(III), 6 ammine ligands, cationic complex, Cl^- counter ions
Name: hexaamminecobalt(III) chloride

(ii) $[Pt(NH_3)_2Cl(NH_2CH_3)]Cl$:
Pt(II), 2 NH_3 (ammine), 1 Cl^- (chlorido), 1 NH_2CH_3 (methanamine)
Ligands alphabetically: ammine, chlorido, methanamine
Name: diamminechlorido(methanamine)platinum(II) chloride

(iii) $[Ti(H_2O)_6]^{3+}$:
Ti(III), 6 aqua ligands, cationic
Name: hexaaquatitanium(III) ion

(iv) $[Co(NH_3)_4Cl(NO_2)]Cl$:
Co(III), 4 NH_3 (ammine), 1 Cl^- (chlorido), 1 NO_2^- (nitrito-N), Cl^- counter ion
Ligands alphabetically: ammine, chlorido, nitrito-N
Name: tetraamminechloridonitrito-N-cobalt(III) chloride

(v) $[Mn(H_2O)_6]^{2+}$:
Mn(II), 6 aqua ligands, cationic
Name: hexaaquamanganese(II) ion

(vi) $[NiCl_4]^{2-}$:
Ni(II), 4 Cl^- (chlorido), anionic complex -> metal suffix -ate, so nickelate
Name: tetrachloridonickelate(II) ion

(vii) $[Ni(NH_3)_6]Cl_2$:
Ni(II), 6 ammine, cationic complex, Cl^- counter ions
Name: hexaamminenickel(II) chloride

(viii) $[Co(en)_3]^{3+}$:
Co(III), 3 en (ethane-1,2-diamine) ligands, use tris- prefix for bidentate
Name: tris(ethane-1,2-diamine)cobalt(III) ion

(ix) $[Ni(CO)_4]$:
Ni(0), 4 carbonyl ligands, neutral complex
Name: tetracarbonylnickel(0)

Answer: (i) hexaamminecobalt(III) chloride (ii) diamminechlorido(methanamine)platinum(II) chloride (iii) hexaaquatitanium(III) ion (iv) tetraamminechloridonitrito-N-cobalt(III) chloride (v) hexaaquamanganese(II) ion (vi) tetrachloridonickelate(II) ion (vii) hexaamminenickel(II) chloride (viii) tris(ethane-1,2-diamine)cobalt(III) ion (ix) tetracarbonylnickel(0)

Q8 List various types of isomerism possible for coordination compounds, giving an example of each.

SOLUTION

Coordination compounds show two principal types of isomerism:

A. STEREOISOMERISM (same bonds, different spatial arrangement):

1. Geometrical isomerism:
Arises when ligands can occupy different spatial positions (cis vs trans).
Example: cis-$[PtCl_2(NH_3)_2]$ (Cl on same side) and trans-$[PtCl_2(NH_3)_2]$ (Cl on opposite sides).
Also fac and mer isomers: fac-$[Co(NH_3)_3(NO_2)_3]$ and mer-$[Co(NH_3)_3(NO_2)_3]$.

2. Optical isomerism:
Non-superimposable mirror images (enantiomers); rotate plane-polarised light.
Example: D-$[Co(en)_3]^{3+}$ and L-$[Co(en)_3]^{3+}$ (tris-chelate octahedral complex).

B. STRUCTURAL ISOMERISM (different bonds):

3. Linkage isomerism:
Arises when an ambidentate ligand binds through different donor atoms.
Example: $[Co(NH_3)_5(NO_2)]Cl_2$ (yellow, N-bonded, nitro) and $[Co(NH_3)_5(ONO)]Cl_2$ (red, O-bonded, nitrito).

4. Coordination isomerism:
Ligands interchange between cationic and anionic coordination entities in the same compound.
Example: $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$.

5. Ionisation isomerism:
Counter ion and a ligand inside the coordination sphere exchange positions.
Example: $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5(SO_4)]Br$.

6. Solvate (hydrate) isomerism:
Water (or solvent) is present either as a ligand or as free solvent in the crystal lattice.
Example: $[Cr(H_2O)_6]Cl_3$ (violet) and $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (grey-green).

Answer: Six types: (1) Geometrical — cis/trans-$[PtCl_2(NH_3)_2]$; (2) Optical — D/L-$[Co(en)_3]^{3+}$; (3) Linkage — $[Co(NH_3)_5(NO_2)]Cl_2$ vs $[Co(NH_3)_5(ONO)]Cl_2$; (4) Coordination — $[Co(NH_3)_6][Cr(CN)_6]$ vs $[Cr(NH_3)_6][Co(CN)_6]$; (5) Ionisation — $[Co(NH_3)_5Br]SO_4$ vs $[Co(NH_3)_5(SO_4)]Br$; (6) Solvate — $[Cr(H_2O)_6]Cl_3$ vs $[Cr(H_2O)_5Cl]Cl_2.H_2O$.

Q9 How many geometrical isomers are possible in the following coordination entities?
(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[Co(NH_3)_3Cl_3]$

SOLUTION

(i) $[Cr(C_2O_4)_3]^{3-}$:
This is a homoleptic octahedral complex with three identical didentate oxalate ($C_2O_4^{2-}$) ligands.
Since all three ligands are the same, there is no geometric isomerism.
Number of geometrical isomers = 0
Note: This complex does exhibit optical isomerism (D and L enantiomers) but no geometric isomers.

(ii) $[Co(NH_3)_3Cl_3]$:
This is an octahedral complex of type $[Ma_3b_3]$ with 3 NH_3 and 3 Cl^- ligands.
Two geometric isomers are possible:
fac (facial) isomer: three NH_3 molecules occupy the corners of one triangular face of the octahedron; three Cl^- are on the opposite face.

mer (meridional) isomer: three NH_3 occupy a meridian — two NH_3 trans to each other and one NH_3 trans to one Cl^-; similarly for Cl^-.
Number of geometrical isomers = 2 (fac and mer)

Answer: (i) $[Cr(C_2O_4)_3]^{3-}$: 0 geometrical isomers (homoleptic tris-bidentate; only optical isomers exist). (ii) $[Co(NH_3)_3Cl_3]$: 2 geometrical isomers (fac and mer).

Q10 Draw the structures of optical isomers of:
(i) $[Cr(C_2O_4)_3]^{3-}$
(ii) $[PtCl_2(en)_2]^{2+}$
(iii) $[Cr(NH_3)_2Cl_2(en)]^+$

SOLUTION

(i) $[Cr(C_2O_4)_3]^{3-}$:
Tris-bidentate octahedral complex with three $C_2O_4^{2-}$ chelate rings.
The propeller-like arrangement makes this complex chiral.
Two optical isomers (enantiomers) exist: the D (delta) form and the L (lambda) form.
These are non-superimposable mirror images; neither has a plane or centre of symmetry.
[Structure description: D form — all three oxalate rings wind clockwise when viewed along the C_3 axis; L form — counterclockwise winding]

(ii) $[PtCl_2(en)_2]^{2+}$:
Octahedral complex with 2 bidentate en and 2 Cl^- ligands.
Two geometric isomers exist: cis (two Cl^- adjacent) and trans (two Cl^- opposite).
Only the CIS isomer is chiral — it has no plane of symmetry; two enantiomers (D and L) exist.
The TRANS isomer has a plane of symmetry and is optically inactive (not chiral).
Optical isomers: D-cis-$[PtCl_2(en)_2]^{2+}$ and L-cis-$[PtCl_2(en)_2]^{2+}$.

(iii) $[Cr(NH_3)_2Cl_2(en)]^+$:
Octahedral complex; en spans 2 cis positions. 2 NH_3 and 2 Cl^- fill the remaining 4 positions.
Several geometric isomers are possible. The isomer where NH_3 and Cl^- occupy the two positions trans to the en donor atoms, with the other NH_3 and Cl^- mutually cis, is chiral.
The complex lacks any symmetry element => two optical isomers (D and L) exist

for each chiral geometric form.

Answer: (i) D and L enantiomers of tris-chelate $[Cr(C_2O_4)_3]^{3-}$ (propeller arrangement). (ii) Only cis-$[PtCl_2(en)_2]^{2+}$ is optically active; gives D and L forms. Trans isomer is achiral. (iii) The geometric isomer(s) of $[Cr(NH_3)_2Cl_2(en)]^+$ lacking a plane of symmetry exist as D and L optical isomers.

Q11 Draw all the isomers (geometrical and optical) of:
(i) $[CoCl_2(en)_2]^+$
(ii) $[Co(NH_3)Cl(en)_2]^{2+}$
(iii) $[Co(NH_3)_2Cl_2(en)]^+$

SOLUTION

(i) $[CoCl_2(en)_2]^+$:
Octahedral, 2 bidentate en and 2 Cl^- ligands.
Geometric isomers:
a) trans-$[CoCl_2(en)_2]^+$: the two Cl^- are trans to each other, 2 en occupy equatorial positions.
This isomer has a C_2 rotation axis and a plane of symmetry -> ACHIRAL, no optical isomers.
b) cis-$[CoCl_2(en)_2]^+$: the two Cl^- are on adjacent (cis) positions.
This isomer has no plane of symmetry -> CHIRAL, exists as D and L optical isomers.
Total isomers: 3 (trans + cis-D + cis-L).

(ii) $[Co(NH_3)Cl(en)_2]^{2+}$:
Octahedral, 2 bidentate en, 1 NH_3, 1 Cl^-.
Geometric isomers based on relative position of NH_3 and Cl^-:
a) trans-$[Co(NH_3)Cl(en)_2]^{2+}$: NH_3 and Cl^- are trans to each other.
This isomer is ACHIRAL (has a C_2 axis); no optical isomers.
b) cis-$[Co(NH_3)Cl(en)_2]^{2+}$: NH_3 and Cl^- are cis to each other.
This isomer is CHIRAL; exists as D and L optical isomers.
Total isomers: 3 (trans + cis-D + cis-L).

(iii) $[Co(NH_3)_2Cl_2(en)]^+$:
Octahedral, en (didentate) spans 2 cis positions; remaining 4 positions for 2 NH_3 and 2 Cl^-.
The 4 remaining positions form two pairs of mutually trans positions.
Geometric isomers:

A) 2 NH_3 trans to each other (and to 2 Cl^- trans to each other): Cl^- both trans to en N-atoms.
B) 2 Cl^- trans to each other (and to 2 NH_3 trans to each other): NH_3 both trans to en N-atoms.
C) 1 NH_3 trans to one en N, 1 Cl^- trans to other en N (NH_3 and Cl^- cis to each other in remaining positions).

Isomers A and B both lack a plane of symmetry -> each gives D and L optical isomers.

Isomer C also lacks a plane of symmetry -> gives D and L optical isomers.

Total: 3 geometric isomers, each chiral, giving D and L forms = 6 total isomers (3 enantiomeric pairs).

Answer: (i) 3 isomers: trans (achiral) + cis-D + cis-L. (ii) 3 isomers: trans (achiral) + cis-D + cis-L. (iii) 3 geometric isomers (A, B, C), each chiral, giving 6 total (3 pairs of enantiomers).

Q12 Write all the geometrical isomers of [Pt(NH_3)(Br)(Cl)(py)] and how many of these will exhibit optical isomers?

SOLUTION

[Pt(NH_3)(Br)(Cl)(py)]: square planar complex with 4 different unidentate ligands (NH_3, Br^-, Cl^-, py = pyridine). Type MABCD.

For a square planar MABCD complex, 3 geometrical isomers exist based on which pair of ligands are trans to each other:

Isomer 1: NH_3 trans to Br; Cl trans to py
Isomer 2: NH_3 trans to Cl; Br trans to py
Isomer 3: NH_3 trans to py; Br trans to Cl

Total geometrical isomers = 3.

Optical activity in square planar complexes:
Square planar complexes of type MABCD have the molecular plane as a plane of symmetry (sigma-h). This plane makes each of the 3 isomers superimposable on its mirror image.
Therefore, NONE of the 3 geometrical isomers exhibits optical isomerism.

Number exhibiting optical isomers = 0.

Answer: 3 geometrical isomers: (1) NH_3 trans to Br, Cl trans to py; (2) NH_3 trans to Cl, Br trans to py; (3) NH_3 trans to py, Br trans to Cl. None exhibit optical isomerism (the molecular plane acts as a plane of symmetry for all three).

Q13 Aqueous copper sulphate solution (blue in colour) gives:
(i) a green precipitate with aqueous potassium fluoride and
(ii) a bright green solution with aqueous potassium chloride.
Explain these experimental results.

SOLUTION

Aqueous $CuSO_4$ contains the blue complex $[Cu(H_2O)_4]^{2+}$ (tetraaquacopper(II) ion).

(i) Addition of KF:
F^- is a small, hard anion that cannot enter the coordination sphere of Cu^{2+} easily for ligand substitution. Instead, F^- reacts with Cu^{2+} to form an insoluble precipitate of CuF_2.
$CuSO_4$ (aq) + 2 KF (aq) -> CuF_2 (s) [green precipitate] + K_2SO_4 (aq)
The green colour of the precipitate is characteristic of CuF_2.
Alternatively: F^- may replace water ligands giving $[CuF_4]^{2-}$ or Cu^{2+} simply precipitates as CuF_2 because CuF_2 is insoluble.

(ii) Addition of KCl:
Cl^- is a larger, softer ligand that can substitute for H_2O in the coordination sphere of Cu^{2+}.
$[Cu(H_2O)_4]^{2+}$ + 4 Cl^- -> $[CuCl_4]^{2-}$ + 4 H_2O
The tetrachloridocuprate(II) complex $[CuCl_4]^{2-}$ is yellow, and mixing with the blue $[Cu(H_2O)_4]^{2+}$ gives a bright green solution.
The green colour arises from the combination of blue (unreacted $[Cu(H_2O)_4]^{2+}$) and yellow ($[CuCl_4]^{2-}$).
With excess Cl^-, the equilibrium shifts to form more $[CuCl_4]^{2-}$, intensifying the green colour.

Answer: (i) With KF: CuF_2 (insoluble, green) precipitates because F^- does not easily substitute H_2O and Cu^{2+} forms an insoluble fluoride. (ii) With KCl: Cl^- substitutes H_2O to form yellow $[CuCl_4]^{2-}$; mixture of blue $[Cu(H_2O)_4]^{2+}$ and yellow $[CuCl_4]^{2-}$ appears bright green.

Q14 What is the coordination entity formed when excess of aqueous KCN is added to an aqueous solution of copper sulphate? Why is it that no precipitate of copper sulphide is obtained when $H_2S(g)$ is passed through this solution?

SOLUTION

When excess KCN is added to $CuSO_4$ solution:
Cu^{2+} is first reduced to Cu^+ by CN^- (with liberation of $(CN)_2$, cyanogen):
$2\ Cu^{2+} + 4\ CN^- \rightarrow 2\ CuCN + (CN)_2$
Then excess CN^- complexes the Cu^+ to form a very stable tetracyanidocuprate(I) complex:
$CuCN + 3\ CN^- \rightarrow [Cu(CN)_4]^{3-}$
The coordination entity formed is $[Cu(CN)_4]^{3-}$ (tetracyanidocuprate(I)).

Why no CuS precipitate with H_2S?
The $[Cu(CN)_4]^{3-}$ complex has a very high stability constant (formation constant very large, Kf >> 1).
Equilibrium: $[Cu(CN)_4]^{3-} \leftrightarrow Cu^+ + 4\ CN^-$ (Kdissociation very small)
The concentration of free Cu^+ ions in solution is negligibly small.
The ionic product $[Cu^+][S^{2-}]$ does not exceed the solubility product (Ksp) of CuS.
Therefore, no precipitate of copper sulphide (CuS) is obtained.

In other words: the complex $[Cu(CN)_4]^{3-}$ sequesters Cu^+ so effectively that free Cu^+ concentration is below the threshold needed to precipitate CuS.

Answer: The coordination entity formed is $[Cu(CN)_4]^{3-}$ (tetracyanidocuprate(I)). No CuS precipitate forms because $[Cu(CN)_4]^{3-}$ has an extremely high stability constant, leaving $[Cu^+]$ far too low for the solubility product of CuS to be exceeded.

Q15 Discuss the nature of bonding in the following coordination entities on the basis of valence bond theory:
(i) $[Fe(CN)_6]^{4-}$
(ii) $[FeF_6]^{3-}$
(iii) $[Co(C_2O_4)_3]^{3-}$
(iv) $[CoF_6]^{3-}$

SOLUTION

(i) $[Fe(CN)_6]^{4-}$:
Central ion: Fe^{2+} (electronic configuration: $[Ar]_3d^6$).
CN^- is a strong field ligand (high field strength in spectrochemical series).

Under the strong field of CN^-, the $3d^6$ electrons pair up completely in three 3d orbitals (leaving two 3d orbitals empty): 3d: (^)(^)(^) 0 0.
Hybridisation: d^2sp^3 (using 2 inner 3d, 1 4s, 3 4p orbitals) — inner orbital complex.
Geometry: octahedral.
6 CN^- each donate 1 lone pair into these 6 hybrid orbitals.
Unpaired electrons = 0 -> DIAMAGNETIC.

(ii) $[FeF_6]^{3-}$:
Central ion: Fe^{3+} (electronic configuration: $[Ar]_3d^5$).
F^- is a weak field ligand (bottom of spectrochemical series).
Under the weak field, $3d^5$ electrons do NOT pair up: 3d: (^)(^)(^)(^)(^).
For octahedral hybridisation, the 3d orbitals are already half-filled; sp^3d^2 uses 4s, 4p, and outer 4d orbitals — outer orbital complex.
Hybridisation: sp^3d^2.
Geometry: octahedral.
Unpaired electrons = 5 -> STRONGLY PARAMAGNETIC.
Magnetic moment mu = sqrt(5(5+2)) = sqrt(35) = 5.92 BM.

(iii) $[Co(C_2O_4)_3]^{3-}$:
Central ion: Co^{3+} (electronic configuration: $[Ar]_3d^6$).
$C_2O_4^{2-}$ is a moderate-to-strong field didentate ligand.
Under this field, $3d^6$ electrons pair up, freeing two 3d orbitals.
Hybridisation: d^2sp^3 (inner orbital complex).
Geometry: octahedral.
Unpaired electrons = 0 -> DIAMAGNETIC.

(iv) $[CoF_6]^{3-}$:
Central ion: Co^{3+} (electronic configuration: $[Ar]_3d^6$).
F^- is a weak field ligand.
Under the weak field, the $3d^6$ electrons remain partly unpaired (high spin).
Hybridisation: sp^3d^2 (outer orbital complex using 4d).
Geometry: octahedral.
d^6 high spin: t_2g^4 eg^2 -> 4 unpaired electrons.
Unpaired electrons = 4 -> PARAMAGNETIC.
Magnetic moment mu = sqrt(4(4+2)) = sqrt(24) = 4.90 BM.

Answer: (i) $[Fe(CN)_6]^{4-}$: d_2sp_3 hybridisation, inner orbital, octahedral, diamagnetic (0 unpaired). (ii) $[FeF_6]^{3-}$: sp^3d^2 hybridisation, outer orbital, octahedral, paramagnetic (5 unpaired, mu=5.92 BM). (iii) $[Co(C_2O_4)_3]^{3-}$: d_2sp_3 hybridisation, inner orbital, octahedral, diamagnetic (0 unpaired). (iv) $[CoF_6]^{3-}$: sp^3d^2 hybridisation, outer orbital, octahedral, paramagnetic (4 unpaired, mu=4.90 BM).

Q16 Draw figure to show the splitting of d orbitals in an octahedral crystal field.

SOLUTION

In an octahedral crystal field, the five degenerate d orbitals split into two sets:

Higher energy set — e_g (2 orbitals): d_{x²-y²} and d_{z²}
These orbitals point directly along the x, y, z axes toward the ligands.
They experience maximum repulsion from the approaching ligands.
Energy raised by +(3/5)Do = +0.6 Do above the barycentre.

Lower energy set — t_{2g} (3 orbitals): d_{xy}, d_{yz}, d_{xz}
These orbitals point between the axes (between ligands).
They experience less repulsion.
Energy lowered by -(2/5)Do = -0.4 Do below the barycentre.

Energy diagram (schematic):

e_g ___|___ ___|___ (d_{x²-y²} and d_{z²})
+0.6 Do above barycentre
Barycentre --------- (average energy of 5d in spherical field)
-0.4 Do below barycentre
t_{2g} __|__ __|__ __|__ (d_{xy}, d_{yz}, d_{xz})

Do = crystal field splitting energy for octahedral field.
The total energy is conserved: 2(+0.6 Do) + 3(-0.4 Do) = 0.

Answer: In an octahedral field, 5 d-orbitals split into lower t_2g (d_xy, d_yz, d_xz; energy -0.4 Do) and upper eg ($d_{x_2-y_2}$, d_{z_2}; energy +0.6 Do). The separation Do is the octahedral crystal field splitting energy.

Q17 What is spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.

SOLUTION

Spectrochemical series:

An experimentally determined sequence of ligands arranged in order of increasing crystal field splitting energy (Do) that they produce around the same metal ion.

Series (increasing field strength):

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < EDTA^{4-} < NH_3 <$ en $< CN^- < CO$

Weak field ligand:

A ligand that produces a SMALL crystal field splitting (small Do).

When Do < P (pairing energy), electrons prefer to occupy the higher e_g orbitals singly rather than pair up in t_{2g}.

This gives HIGH SPIN complexes with the maximum number of unpaired electrons.

Examples: I^-, Br^-, Cl^-, F^-, OH^-, H_2O.

Example complex: $[FeF_6]^{3-}$ (5 unpaired electrons, high spin).

Strong field ligand:

A ligand that produces a LARGE crystal field splitting (large Do).

When Do > P, it is energetically more favourable for electrons to pair in the t_{2g} orbitals.

This gives LOW SPIN complexes with fewer unpaired electrons.

Examples: CN^-, CO, NO^+, en, NH_3.

Example complex: $[Fe(CN)_6]^{4-}$ (0 unpaired electrons, low spin).

Answer: Spectrochemical series is the order of ligands by increasing crystal field splitting ability: $I^- < Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 <$ en $< CN^- < CO$. Weak field ligands (e.g., F^-, H_2O) give small Do -> high spin complexes. Strong field ligands (e.g., CN^-, CO) give large Do -> low spin complexes.

Q18 What is crystal field splitting energy? How does the magnitude of Do decide the actual configuration of d orbitals in a coordination entity?

SOLUTION

Crystal field splitting energy (Do):
The energy difference between the e_g set (higher energy) and the t_{2g} set (lower energy) of d orbitals in an octahedral complex due to the electrostatic field of the ligands.
Do = E(e_g) - E(t_{2g}); the e_g orbitals are +0.6 Do and t_{2g} are -0.4 Do relative to the barycentre.

How the magnitude of Do determines d-orbital configuration:

For d^1, d^2, d^3 ions: electrons occupy t_{2g} singly (no choice).

For d^4 to d^7 ions, two configurations are possible depending on Do vs P (pairing energy):

Case 1 — Weak field (Do < P):
It costs less energy to place an electron in the e_g level (avoiding pairing energy P) than to pair it in t_{2g}.
Electrons fill all available orbitals singly before pairing -> HIGH SPIN configuration (maximum unpaired electrons).
Example for d^4: $t_{2g}^3 e_g^1$ (high spin).

Case 2 — Strong field (Do > P):
It costs less energy to pair in t_{2g} than to promote to e_g.
Electrons pair in t_{2g} before entering e_g -> LOW SPIN configuration (fewer unpaired electrons).
Example for d^4: $t_{2g}^4 e_g^0$ (low spin).

For d^8, d^9, d^{10}: no ambiguity; the configuration is the same regardless of Do.

Summary: a large Do (strong field) favours low spin; a small Do (weak field) favours high spin.

Answer: Crystal field splitting energy (Do) is the energy gap between e_g and t_{2g} orbital sets in an octahedral complex. If Do > P (pairing energy) -> low spin (electrons pair in t_{2g}); if Do < P -> high spin (electrons spread across t_{2g} and eg to maximise unpaired count). This determines the number of unpaired electrons and hence magnetic properties.

Q19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why?

SOLUTION

$[Cr(NH_3)_6]^{3+}$:
Central ion: Cr^{3+} with electronic configuration $[Ar]_3d^3$.
NH_3 is a strong field ligand, but for a d^3 ion there is only one possible arrangement: t_{2g}³ (three unpaired electrons in t_{2g}).
Regardless of field strength, Cr^{3+} (d^3) always has 3 unpaired electrons in octahedral complexes.
Number of unpaired electrons = 3 -> PARAMAGNETIC.
Spin-only magnetic moment = sqrt(3 x 5) = 3.87 BM.

$[Ni(CN)_4]^{2-}$:
Central ion: Ni^{2+} with electronic configuration $[Ar]_3d^8$.
CN^- is a very strong field ligand -> produces a large crystal field.
In a square planar complex (dsp^2 hybridisation), the d orbitals split such that one d orbital is at very high energy.
The 8 d electrons of Ni^{2+} pair up completely in the four lower-energy d orbitals, leaving no unpaired electrons.
Hybridisation: dsp^2 (using one 3d, one 4s, two 4p orbitals).
Number of unpaired electrons = 0 -> DIAMAGNETIC.

Summary: Cr^{3+} always has 3 unpaired d electrons (d^3, can't pair further); Ni^{2+} in $[Ni(CN)_4]^{2-}$ adopts square planar geometry with CN^- forcing complete pairing of all 8 electrons.

Answer: $[Cr(NH_3)_6]^{3+}$ is paramagnetic because Cr^{3+} is d^3 with 3 unpaired electrons regardless of field strength. $[Ni(CN)_4]^{2-}$ is diamagnetic because CN^- forces square planar (dsp^2) geometry on Ni^{2+} (d^8), pairing all 8 electrons with 0 unpaired.

Q20 A solution of $[Ni(H_2O)_6]^{2+}$ is green but a solution of $[Ni(CN)_4]^{2-}$ is colourless. Explain.

SOLUTION

$[Ni(H_2O)_6]^{2+}$ (green):
Ni^{2+} is d^8. H_2O is a weak-to-moderate field ligand.
In the octahedral $[Ni(H_2O)_6]^{2+}$ complex, the d-d electronic transition occurs in the VISIBLE region of the spectrum.
Light in the red region (~600-650 nm) is absorbed, and the complementary colour

(green) is transmitted/observed.
Hence the solution appears green.

$[Ni(CN)_4]^{2-}$ (colourless):
Ni^{2+} is d^8. CN^- is an extremely strong field ligand.
In the square planar $[Ni(CN)_4]^{2-}$ complex, CN^- causes a very large splitting of the d orbitals.
The d-d electronic transition now requires much higher energy -> the absorption occurs in the ULTRAVIOLET region (not visible).
No wavelength in the visible region is absorbed -> all visible light is transmitted -> the solution appears COLOURLESS.

Key principle: The colour of a complex depends on the wavelength of visible light absorbed. Strong field CN^- shifts the d-d transition absorption to the UV, leaving the visible spectrum unaffected.

Answer: $[Ni(H_2O)_6]^{2+}$ is green because its d-d transition absorbs red light (visible region) and transmits green. $[Ni(CN)_4]^{2-}$ is colourless because the strong field of CN^- shifts the d-d transition energy into the ultraviolet region, so no visible light is absorbed.

Q21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?

SOLUTION

Both complexes contain Fe^{2+} (d^6) but they have very different colours because the crystal field splitting (Do) differs greatly.

$[Fe(CN)_6]^{4-}$:
CN^- is a strong field ligand -> large Do.
The d-d electronic transition ($t_{2g}->e_g$) requires a large amount of energy.
The absorbed wavelength corresponds to a high-energy (short-wavelength) visible photon.
The complex absorbs at the blue-green end of the spectrum and appears yellow-orange/red.

$[Fe(H_2O)_6]^{2+}$:
H_2O is a weak field ligand -> small Do.
The d-d transition requires less energy -> the absorbed photon has a lower energy (longer wavelength, in the red/orange region).
The complex absorbs in the red region and appears pale green/blue-green.

Since the two ligands produce very different values of Do, the energy of the d-d transition differs, causing different wavelengths to be absorbed, and hence the two complexes display different colours.

Answer: Both have Fe^{2+} (d^6), but CN^- (strong field, large Do) causes a high-energy d-d transition absorbing short-wavelength light, while H_2O (weak field, small Do) causes a low-energy transition absorbing long-wavelength light. Different absorbed wavelengths give different colours.

Q22 Discuss the nature of bonding in metal carbonyls.

SOLUTION

Metal carbonyls (M-CO complexes) involve a unique SYNERGIC BONDING involving both sigma and pi components:

1. Sigma (sigma) donation (ligand -> metal):
The carbonyl carbon has a lone pair of electrons.
CO donates this lone pair to a vacant orbital of the metal atom (Lewis acid-base interaction).
This forms a sigma bond: CO -> M (forward donation, ligand to metal).

2. Pi (pi) back-donation (metal -> ligand):
The CO ligand has a vacant antibonding pi* orbital (pi* of C=O).
A filled d orbital (d_pi) of the metal donates electron density back into this pi* orbital.
This forms a pi back-bond: M -> CO (back donation, metal to ligand).

Synergic effect:
The two components reinforce each other (synergic bonding).
Sigma donation from CO -> metal increases electron density on the metal, which in turn enhances back-donation from metal -> CO pi*.
This mutual reinforcement stabilises the M-C bond and strengthens bonding.

Effect on C=O bond:
Back-donation populates the pi* of CO, weakening the C=O bond (lower C=O stretching frequency in IR compared to free CO at 2143 cm^{-1}).
The M-C bond has partial double-bond character (strengthened), while C=O has partial weakened bond (but CO is still bound as a ligand).

Metal carbonyls are generally formed with transition metals in low/zero oxidation

states.

Answer: Metal carbonyls involve synergic bonding: (1) sigma bond by lone pair donation from carbonyl C to a vacant metal d/s orbital (CO->M), and (2) pi back-bond by metal filled d orbital donating into the empty antibonding pi* of CO (M->CO). The two reinforce each other, strengthening M-C and partially weakening C=O.

Q23 Give the oxidation state, d orbital occupation and coordination number of the central metal ion in the following complexes:
(i) $K_3[Co(C_2O_4)_3]$
(ii) cis-$[CrCl_2(en)_2]Cl$
(iii) $(NH_4)_2[CoF_4]$
(iv) $[Mn(H_2O)_6]SO_4$

SOLUTION

(i) $K_3[Co(C_2O_4)_3]$:
Counter ions: 3 K^+ (+3 total). Complex ion: $[Co(C_2O_4)_3]^{3-}$.
3 $C_2O_4^{2-}$ contribute 3(-2) = -6; let Co = x: x + (-6) = -3 -> x = +3.
Oxidation state of Co = +3.
Co^{3+} = $[Ar]_3d^6$ -> d orbital occupation: $3d^6$.
Each $C_2O_4^{2-}$ is didentate (2 donor O atoms); 3 $C_2O_4^{2-}$ -> CN = 3 x 2 = 6.
Coordination number = 6.

(ii) cis-$[CrCl_2(en)_2]Cl$:
Outer Cl^- is counter ion. Complex cation: $[CrCl_2(en)_2]^+$.
2 Cl^- contribute -2; en = 0 each: x + (-2) + 0 = +1 -> x = +3.
Oxidation state of Cr = +3.
Cr^{3+} = $[Ar]_3d^3$ -> d orbital occupation: $3d^3$.
2 Cl (2 donor atoms) + 2 en (2 x 2 = 4 donor atoms) = 6 total.
Coordination number = 6.

(iii) $(NH_4)_2[CoF_4]$:
Counter ion: 2 NH_4^+ (+2 total). Complex ion: $[CoF_4]^{2-}$.
4 F^- contribute -4: x + (-4) = -2 -> x = +2.
Oxidation state of Co = +2.
Co^{2+} = $[Ar]_3d^7$ -> d orbital occupation: $3d^7$.
4 F^- (4 donor atoms) -> CN = 4.
Coordination number = 4.

(iv) $[Mn(H_2O)_6]SO_4$:
Counter ion: SO_4^{2-} (-2). Complex cation: $[Mn(H_2O)_6]^{2+}$.
6 H_2O = 0 each: x + 0 = +2 -> x = +2.
Oxidation state of Mn = +2.
Mn^{2+} = $[Ar]_3d^5$ -> d orbital occupation: $3d^5$.
6 H_2O (6 donor O atoms) -> CN = 6.
Coordination number = 6.

Answer: (i) Co: +3, $3d^6$, CN=6. (ii) Cr: +3, $3d^3$, CN=6. (iii) Co: +2, $3d^7$, CN=4. (iv) Mn: +2, $3d^5$, CN=6.

Q24 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number. Also give stereochemistry and magnetic moment of the complex:
(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$
(ii) $[Co(NH_3)_5Cl]Cl_2$
(iii) $[CrCl_3(py)_3]$
(iv) $Cs[FeCl_4]$
(v) $K_4[Mn(CN)_6]$

SOLUTION

(i) $K[Cr(H_2O)_2(C_2O_4)_2].3H_2O$:
Complex ion: $[Cr(H_2O)_2(C_2O_4)_2]^-$.
Cr + 2(0) + 2(-2) = -1 -> Cr = +3.
IUPAC name: potassium diaquabis(oxalato)chromate(III) trihydrate
Oxidation state: Cr(III) = +3.
Electronic configuration: Cr^{3+} = $[Ar]_3d^3$ -> $3d^3$.
Coordination number: 2 H_2O + 2 bidentate C_2O_4 = 2 + 4 = 6.
Stereochemistry: Octahedral; shows geometric isomers (cis and trans); cis form also shows optical isomerism (D and L).
Unpaired electrons: Cr^{3+} (d^3) -> 3 unpaired always (both weak and strong field).
Magnetic moment: mu = sqrt(3 x 5) = sqrt(15) = 3.87 BM.

(ii) $[Co(NH_3)_5Cl]Cl_2$:
Complex cation: $[Co(NH_3)_5Cl]^{2+}$.
Co + 5(0) + (-1) = +2 -> Co = +3.
IUPAC name: pentaamminechloridocobalt(III) chloride
Oxidation state: Co(III) = +3.

Electronic configuration: Co^{3+} = $[Ar]_3d^6$.
Coordination number: 5 NH_3 + 1 Cl = 6.
Stereochemistry: Octahedral; NH_3 is a strong field ligand -> inner orbital d^2sp^3 hybridisation; low spin.
Unpaired electrons: Co^{3+} d^6 low spin -> t_{2g}^{6} e_g^0 -> 0 unpaired.
Magnetic moment: mu = 0 BM (diamagnetic).

(iii) $[CrCl_3(py)_3]$: (py = pyridine, C_5H_5N)
Neutral complex; Cr + 3(-1) + 3(0) = 0 -> Cr = +3.
IUPAC name: trichloridotris(pyridine)chromium(III)
Oxidation state: Cr(III) = +3.
Electronic configuration: Cr^{3+} = $[Ar]_3d^3$.
Coordination number: 3 Cl + 3 py = 6.
Stereochemistry: Octahedral; geometric isomers: fac (facial) and mer (meridional).
Unpaired electrons: Cr^{3+} d^3 -> 3 unpaired.
Magnetic moment: mu = sqrt(3 x 5) = 3.87 BM.

(iv) $Cs[FeCl_4]$:
Complex ion: $[FeCl_4]^-$.
Fe + 4(-1) = -1 -> Fe = +3.
IUPAC name: caesium tetrachloridoferrate(III)
Oxidation state: Fe(III) = +3.
Electronic configuration: Fe^{3+} = $[Ar]_3d^5$.
Coordination number: 4 Cl = 4.
Stereochemistry: Tetrahedral (CN=4, Cl^- weak field, no driving force for square planar); sp^3 hybridisation.
Unpaired electrons: Fe^{3+} d^5, Cl^- weak field -> high spin, all 5 d orbitals singly occupied = 5 unpaired.
Magnetic moment: mu = sqrt(5 x 7) = sqrt(35) = 5.92 BM.

(v) $K_4[Mn(CN)_6]$:
Complex ion: $[Mn(CN)_6]^{4-}$.
Mn + 6(-1) = -4 -> Mn = +2.
IUPAC name: potassium hexacyanidomanganate(II)
Oxidation state: Mn(II) = +2.
Electronic configuration: Mn^{2+} = $[Ar]_3d^5$.
Coordination number: 6 CN = 6.

Stereochemistry: Octahedral; CN^- is a strong field ligand -> low spin d^2sp^3 inner orbital complex.
Unpaired electrons: Mn^{2+} d^5, CN^- strong field -> t_{2g}^5 e_g^0 -> 1 unpaired electron.
Magnetic moment: mu = sqrt(1 x 3) = sqrt(3) = 1.73 BM.

Answer: (i) potassium diaquabis(oxalato)chromate(III) trihydrate; Cr+3, $3d_3$, CN=6, octahedral, geometric+optical isomers, mu=3.87 BM. (ii) pentaamminechloridocobalt(III) chloride; Co+3, $3d_6$, CN=6, octahedral, diamagnetic, mu=0 BM. (iii) trichloridotris(pyridine)chromium(III); Cr+3, $3d_3$, CN=6, octahedral, fac/mer isomers, mu=3.87 BM. (iv) caesium tetrachloridoferrate(III); Fe+3, $3d_5$, CN=4, tetrahedral, mu=5.92 BM. (v) potassium hexacyanidomanganate(II); Mn+2, $3d_5$, CN=6, octahedral, low spin, mu=1.73 BM.

Q25 Explain the violet colour of the complex $[Ti(H_2O)_6]^{3+}$ on the basis of crystal field theory.

SOLUTION

$[Ti(H_2O)_6]^{3+}$: Ti^{3+} has electronic configuration $[Ar]_3d^1$ (one d electron).
This is an octahedral complex with H_2O ligands.

In the octahedral crystal field:
- The single d electron occupies the lower energy t_{2g} level in the ground state: t_{2g}^1 e_g^0.
- The excited state has the electron in the e_g level: t_{2g}^0 e_g^1.

When white light passes through the solution, photons corresponding to blue-green light (~498 nm) are absorbed.
This energy matches exactly the crystal field splitting Do of $[Ti(H_2O)_6]^{3+}$.
The electron is excited from t_{2g} to e_g: t_{2g}^1 e_g^0 -> t_{2g}^0 e_g^1.

Since blue-green light is absorbed, the complementary colour is transmitted.
The complementary colour of blue-green is violet/red.
The complex therefore appears VIOLET in colour.

This is a d-d electronic transition — characteristic of coordination compounds and the basis of their colour as explained by CFT.

Answer: $[Ti(H_2O)_6]^{3+}$ is d^1 (Ti^{3+}). In the octahedral field, the single electron is in t_{2g} (ground state). Absorption of blue-green light (~498 nm) excites the electron to eg. The complementary colour — violet — is observed. This d-d transition is the basis of colour in CFT.

Q26 What is meant by the chelate effect? Give an example.

SOLUTION

Chelate effect:

The enhanced thermodynamic stability of complexes containing chelating (ring-forming didentate or polydentate) ligands compared to analogous complexes with unidentate ligands of the same donor atoms.

The chelate effect arises primarily from a favourable entropy contribution.

When a chelate ligand replaces two unidentate ligands, the number of independent species in solution INCREASES (more particles), giving a positive DS (increase in entropy).

Since DG = DH - TDS, a more positive DS makes DG more negative -> greater stability.

Example:

Comparing $[Ni(NH_3)_6]^{2+}$ with $[Ni(en)_3]^{2+}$:

$[Ni(NH_3)_6]^{2+}$ + 3 en -> $[Ni(en)_3]^{2+}$ + 6 NH_3

en (ethane-1,2-diamine) is a didentate chelate ligand forming 5-membered rings with Ni.

The log K (stability constant) for $[Ni(en)_3]^{2+}$ is much larger than for $[Ni(NH_3)_6]^{2+}$.

This extra stability of the chelate complex is the chelate effect.

$EDTA^{4-}$ (hexadentate) forms even more stable complexes due to the chelate effect with 6 donor atoms forming multiple rings.

Answer: The chelate effect is the greater stability of complexes with chelating (ring-forming) ligands compared to analogous unidentate-ligand complexes, arising mainly from entropy gain. Example: $[Ni(en)_3]^{2+}$ is much more stable than $[Ni(NH_3)_6]^{2+}$ because en forms 5-membered chelate rings.

Q27 Discuss briefly giving an example in each case the role of coordination compounds in:
(i) biological systems
(ii) medicinal chemistry
(iii) analytical chemistry
(iv) extraction/metallurgy of metals.

SOLUTION

(i) Biological systems:
Coordination compounds are essential in living systems.
Haemoglobin: an iron(II) porphyrin coordination complex that carries O_2 in blood. Each haem unit has Fe^{2+} coordinated to 4 N atoms of porphyrin + 1 N of histidine + 1 O_2.
Chlorophyll: a magnesium porphyrin coordination compound essential for photosynthesis.
Vitamin B_{12} (cyanocobalamin): a coordination compound of cobalt essential for nerve function and prevention of pernicious anaemia.
Carbonic anhydrase and carboxypeptidase A: zinc-containing enzyme coordination compounds.

(ii) Medicinal chemistry:
cis-Platin (cis-$[PtCl_2(NH_3)_2]$): a coordination compound used as an anticancer drug; it crosslinks DNA strands and inhibits tumour cell replication.
D-penicillamine: a chelating ligand used to treat excess copper accumulation (Wilson's disease).
Desferrioxamine B: a coordination compound used to remove excess iron from the body (iron poisoning).
EDTA salts: used in treatment of lead poisoning by forming stable complexes with Pb^{2+}.

(iii) Analytical chemistry:
Coordination compounds are used in both qualitative and quantitative analysis.
EDTA: used in complexometric titrations to determine hardness of water (Ca^{2+}, Mg^{2+} concentrations).
DMG (dimethylglyoxime): forms a red chelate precipitate with Ni^{2+} ions — used to detect and estimate nickel.
Cu^{2+} is detected by the deep blue colour of $[Cu(NH_3)_4]^{2+}$ complex with excess NH_3.

(iv) Extraction/metallurgy of metals:

Hydrometallurgy uses coordination chemistry to extract metals.
Silver and gold extraction: metals dissolve in dilute NaCN solution in the presence of air/O_2 to form stable cyanide complexes:
$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \rightarrow 4\ [Au(CN)_2]^- + 4\ OH^-$
Gold is then recovered by adding zinc: $2\ [Au(CN)_2]^- + Zn \rightarrow [Zn(CN)_4]^{2-} + 2\ Au$.
Nickel refining (Mond process): impure Ni is converted to $[Ni(CO)_4]$ (tetracarbonylnickel) which is volatile; on heating it decomposes to give pure nickel.

Answer: (i) Haemoglobin (Fe-porphyrin, O_2 carrier), Chlorophyll (Mg-porphyrin, photosynthesis), Vitamin B_{12} (Co complex). (ii) cis-platin (anticancer), EDTA (lead poisoning treatment). (iii) EDTA (water hardness titration), DMG (Ni^{2+} detection). (iv) $[Au(CN)_2]^-$ for gold extraction; $[Ni(CO)_4]$ in Mond process for Ni refining.

Q28 How many ions are produced from the complex $Co(NH_3)_6Cl_2$ in solution?
(i) 6 (ii) 4 (iii) 3 (iv) 2

SOLUTION

The complex $Co(NH_3)_6Cl_2$ is written as $[Co(NH_3)_6]Cl_2$.
The coordination entity is $[Co(NH_3)_6]^{2+}$ (Co with 6 NH_3 ligands; Co is in +2 oxidation state).
The counter ions are 2 Cl^-.

In aqueous solution, it ionises as:
$[Co(NH_3)_6]Cl_2 \rightarrow [Co(NH_3)_6]^{2+} + 2\ Cl^-$

Ions produced: 1 complex cation $[Co(NH_3)_6]^{2+}$ + 2 Cl^- ions = 3 ions total.

Answer: (iii) 3

Answer: (iii) 3 — $[Co(NH_3)_6]Cl_2$ ionises to give $[Co(NH_3)_6]^{2+}$ and 2 Cl^-, a total of 3 ions.

Q29 Amongst the following ions which one has the highest magnetic moment value?
(i) $[Cr(H_2O)_6]^{3+}$ (ii) $[Fe(H_2O)_6]^{2+}$ (iii) $[Zn(H_2O)_6]^{2+}$

SOLUTION

Spin-only magnetic moment formula: mu = sqrt(n(n+2)) BM, where n = number of unpaired electrons.

(i) $[Cr(H_2O)_6]^{3+}$:
Cr^{3+} = $[Ar]_3d^3$. H_2O is a weak-to-moderate field ligand.
d^3 always gives 3 unpaired electrons (n = 3).
mu = sqrt(3 x 5) = sqrt(15) = 3.87 BM.

(ii) $[Fe(H_2O)_6]^{2+}$:
Fe^{2+} = $[Ar]_3d^6$. H_2O is a weak field ligand -> high spin.
High spin d^6: t_{2g}^{4} e_g^2 -> 4 unpaired electrons (n = 4).
mu = sqrt(4 x 6) = sqrt(24) = 4.90 BM.

(iii) $[Zn(H_2O)_6]^{2+}$:
Zn^{2+} = $[Ar]_3d^{10}$. All d orbitals completely filled.
n = 0 unpaired electrons.
mu = 0 BM (diamagnetic).

Highest magnetic moment: $[Fe(H_2O)_6]^{2+}$ with mu = 4.90 BM.
Answer: (ii) $[Fe(H_2O)_6]^{2+}$

Answer: (ii) $[Fe(H_2O)_6]^{2+}$. Fe^{2+} is d^6; H_2O (weak field) gives high-spin t_2g^4 eg^2 with 4 unpaired electrons; mu = sqrt(24) = 4.90 BM. This exceeds $[Cr(H_2O)_6]^{3+}$ (3.87 BM, d^3) and $[Zn(H_2O)_6]^{2+}$ (0 BM, d^{10}).

Q30 Amongst the following, the most stable complex is:
(i) $[Fe(H_2O)_6]^{3+}$ (ii) $[Fe(NH_3)_6]^{3+}$ (iii) $[Fe(C_2O_4)_3]^{3-}$ (iv) $[FeCl_6]^{3-}$

SOLUTION

Stability of coordination complexes depends on the nature of the metal-ligand interaction, the ligand field strength, and particularly the chelate effect.

(i) $[Fe(H_2O)_6]^{3+}$: H_2O is a weak unidentate ligand. Low stability constant.
(ii) $[Fe(NH_3)_6]^{3+}$: NH_3 is a stronger unidentate ligand than H_2O. Moderate stability constant. (Note: Fe^{3+} + NH_3 complexes are not very stable due to Fe^{3+} preference for hard ligands.)
(iii) $[Fe(C_2O_4)_3]^{3-}$: $C_2O_4^{2-}$ (oxalate) is a chelating didentate ligand. Forms three 5-membered chelate rings with Fe^{3+}. The chelate effect greatly enhances stability. Very high stability constant.
(iv) $[FeCl_6]^{3-}$: Cl^- is a weak unidentate ligand. Low stability constant.

The chelate effect makes $[Fe(C_2O_4)_3]^{3-}$ by far the most stable of the four.
Answer: (iii) $[Fe(C_2O_4)_3]^{3-}$

Answer: (iii) $[Fe(C_2O_4)_3]^{3-}$ is the most stable because oxalate ($C_2O_4^{2-}$) is a chelating didentate ligand; the chelate effect (entropy gain from ring formation) greatly enhances stability over unidentate H_2O, NH_3, or Cl^- complexes.

Q31 What will be the correct order for the wavelengths of absorption in the visible region for the following: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$?

SOLUTION

All three are octahedral Ni(II) complexes (d^8).

The wavelength of absorbed light is inversely proportional to the crystal field splitting energy Do.

Larger Do -> higher energy absorbed -> shorter wavelength.

Field strengths from spectrochemical series (increasing order):

$H_2O < NH_3 < NO_2^-$

Therefore Do increases in the order:

$Do([Ni(H_2O)_6]^{2+}) < Do([Ni(NH_3)_6]^{2+}) < Do([Ni(NO_2)_6]^{4-})$

Since wavelength is inversely proportional to Do (lambda = hc/E = hc/(Do * hc/$lambda_0$)):

$lambda([Ni(NO_2)_6]^{4-}) < lambda([Ni(NH_3)_6]^{2+}) < lambda([Ni(H_2O)_6]^{2+})$

Correct order of absorbed wavelengths (increasing):

$[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$

Answer: The order of absorbed wavelengths (lambda) is: $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$. NO_2^- produces the largest Do (absorbs at shortest wavelength); H_2O produces the smallest Do (absorbs at longest wavelength). This follows directly from the spectrochemical series: $H_2O < NH_3 < NO_2^-$.