CLASS 12 CHEMISTRY NCERT SOLUTIONS

NCERT Solutions for Class 12 Chemistry Chapter 5: Coordination Compounds – Free PDF Download

Chapter 5 covers Coordination Compounds — Werner's theory, definitions (ligands, coordination number, coordination polyhedron), IUPAC nomenclature, isomerism (structural and stereoisomerism), Valence Bond Theory, Crystal Field Theory (splitting, spectrochemical series, CFSE, magnetism, colour), bonding in metal ca...

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NCERT Exercise Solutions

5.1 Explain bonding in coordination compounds in terms of Werner's postulates.
Ans: Werner proposed that metals show two types of valence: a **primary valence** (ionisable, satisfied by negative ions, corresponding to the metal's oxidation state) and a **secondary valence** (non-ionisable, satisfied by neutral or negative ligands directly bonded to the metal, corresponding to the coordination number). Secondary valences are directed towards fixed positions in space, giving the complex a definite geometry (e.g. octahedral, tetrahedral, or square planar), which explains the existence of isomers.

5.2 $FeSO_4$ solution mixed with $(NH_4)_2SO_4$ in 1:1 ratio gives the test of Fe^{2+} ion but $CuSO_4$ solution mixed with aqueous ammonia in 1:4 ratio does not give the test of Cu^{2+} ion. Explain why.
Ans: $FeSO_4$+$(NH_4)_2SO_4$ forms **Mohr's salt, a double salt**, which dissociates completely in water into its simple constituent ions (Fe^{2+}, NH_4^+, SO_4^{2-}), so free Fe^{2+} is available to give its characteristic test. $CuSO_4$+excess NH_3 instead forms the **coordination complex $[Cu(NH_3)_4]^{2+}$**, where Cu^{2+} is held by coordinate bonds to NH_3 and is not released as free Cu^{2+} ions in solution, so the usual Cu^{2+} test fails.

5.3 Explain with two examples each of the following: coordination entity, ligand, coordination number, coordination polyhedron, homoleptic and heteroleptic.
Ans: A **coordination entity** is an ion/molecule with a central metal bonded to a fixed number of ligands, e.g. $[Co(NH_3)_6]^{3+}$, $[PtCl_4]^{2-}$. A **ligand** is the ion/molecule bonded to the central metal, e.g. Cl^-, NH_3. The **coordination number** is the number of ligand donor atoms bonded to the metal, e.g. 6 in $[Co(NH_3)_6]^{3+}$, 4 in $[Ni(CN)_4]^{2-}$. The **coordination polyhedron** is the spatial arrangement of ligand atoms around the metal, e.g. octahedral in $[Co(NH_3)_6]^{3+}$, tetrahedral in $[Ni(CO)_4]$. **Homoleptic** complexes have only one kind of ligand, e.g. $[Co(NH_3)_6]^{3+}$, $[Ni(CO)_4]$; **heteroleptic** complexes have more than one kind, e.g. $[Co(NH_3)_4Cl_2]^+$, $[Pt(NH_3)_2Cl_2]$.

5.4 What is meant by unidentate, didentate and ambidentate ligands? Give two examples for each.
Ans: A **unidentate** ligand binds through a single donor atom, e.g. NH_3, Cl^-. A **didentate** ligand binds through two donor atoms, e.g. ethane-1,2-diamine ($H_2NCH_2CH_2NH_2$, "en"), oxalate ion ($C_2O_4^{2-}$). An **ambidentate** ligand has two different donor atoms but binds through only one at a time, e.g. NO_2^- (binds via N as nitrito-N, or via O as nitrito-O), SCN^- (binds via S as thiocyanato, or via N as isothiocyanato).

5.5 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) $[Cr(NH_3)_3Cl_3]$.
Ans: (i) H_2O and en are neutral, CN is –1: Co**+3**. (ii) Br is –1 each, en neutral: Co**+3**. (iii) Cl is –1 each: Pt**+2**. (iv) complex ion is –3 ($3K^+$), CN is –1 each: Fe**+3**. (v) neutral complex, Cl is –1 each: Cr**+3**.

5.6 Using IUPAC norms, write the formulas for the following: (i) Tetrahydroxozincate(II) (ii) Potassium tetrachloridopalladate(II) (iii) Diamminedichloridoplatinum(II) (iv) Potassium tetracyanidonickelate(II) (v) Pentaamminenitrito-O-cobalt(III) ion (vi) Hexaamminecobalt(III) sulphate (vii) Potassium tris(oxalato)chromate(III) (viii) Hexaammineplatinum(IV) ion (ix)

Tetrabromidocuprate(II) ion (x) Pentaamminenitrito-N-cobalt(III) ion.
Ans: (i) **$[Zn(OH)_4]^{2-}$**. (ii) **$K_2[PdCl_4]$**. (iii) **$[Pt(NH_3)_2Cl_2]$**. (iv) **$K_2[Ni(CN)_4]$**. (v) **$[Co(ONO)(NH_3)_5]^{2+}$**. (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) **$[Co(NO_2)(NH_3)_5]^{2+}$**.

5.7 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) $[Ni(CO)_4]$.
Ans: Ligands are always named alphabetically (ignoring multiplying prefixes), anionic ligands end in "-o," and the metal's oxidation state is given in Roman numerals. (i) **Hexaamminecobalt(III) chloride**. (ii) **Amminechloridomethanaminoplatinum(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)**.

5.8 List various types of isomerism possible for coordination compounds, giving an example of each.
Ans: **Structural isomerism:** (a) linkage isomerism, e.g. $[Co(NH_3)_5(NO_2)]^{2+}$ vs $[Co(NH_3)_5(ONO)]^{2+}$; (b) ionisation isomerism, e.g. $[Co(NH_3)_5Br]SO_4$ vs $[Co(NH_3)_5SO_4]Br$; (c) coordination isomerism, e.g. $[Co(NH_3)_6][Cr(CN)_6]$ vs $[Cr(NH_3)_6][Co(CN)_6]$; (d) solvate (hydrate) isomerism, e.g. $[Cr(H_2O)_6]Cl_3$ vs $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$. **Stereoisomerism:** (a) geometrical isomerism (cis-trans, fac-mer), e.g. cis-/trans-$[Pt(NH_3)_2Cl_2]$; (b) optical isomerism, e.g. the d- and l-forms of $[Cr(C_2O_4)_3]^{3-}$.

5.9 How many geometrical isomers are possible for the following complexes? (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[Co(NH_3)_3Cl_3]$.
Ans: (i) **No geometrical isomers** — being a tris-chelate of an identical bidentate ligand, $[Cr(C_2O_4)_3]^{3-}$ shows only optical isomerism. (ii) **2 geometrical isomers** — the **facial (fac)** form (three Cl on one triangular face) and the **meridional (mer)** form (three Cl in a plane through the metal).

5.10 Draw the structures of optical isomers of: (i) $[Cr(C_2O_4)_3]^{3-}$ (ii) $[PtCl_2(en)_2]^{2+}$ (iii) $[Cr(NH_3)_2Cl_2(en)]^{+}$.
Ans: Each of these is a chiral octahedral complex that exists as a pair of non-superimposable mirror images (enantiomers), conventionally labelled d- and l- (or Δ- and Λ-). (i) The tris-chelate $[Cr(C_2O_4)_3]^{3-}$ forms a propeller-shaped pair of enantiomers. (ii) The cis form of $[PtCl_2(en)_2]^{2+}$ is chiral and gives an enantiomeric pair (the trans form is achiral). (iii) cis-$[Cr(NH_3)_2Cl_2(en)]^{+}$ is likewise chiral, giving an enantiomeric pair.

5.11 Draw all the isomers (geometrical and optical) of: (i) $[CoCl_2(en)_2]^{+}$ (ii) $[Co(NH_3)Cl(en)_2]^{2+}$ (iii) $[Co(NH_3)_2Cl_2(en)]^{+}$.
Ans: Each of these $[M(AA)_2B_2]$-type octahedral complexes (two bidentate "en" ligands plus two different unidentate ligands) gives **3 total isomers**: a **trans** geometrical isomer, which is optically inactive (has a plane of symmetry), and a **cis** geometrical isomer, which is chiral and exists as a pair of optical isomers (d- and l-forms). This pattern applies identically to all three complexes listed.

5.12 Draw the structures of geometrical isomers of $[Pt(NH_3)(Br)(Cl)(py)]$.
Ans: This is a square-planar complex with four different unidentate ligands (formula type Mabcd), which gives **3 geometrical isomers**, depending on which pair of ligands occupies mutually trans positions: (NH_3, Cl) trans with (Br, py) trans; (NH_3, Br) trans with (Cl, py) trans; and (NH_3, py) trans with (Br, Cl) trans.

5.13 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 observations.
Ans: Both observations arise from **ligand-dependent crystal field splitting**. (i) With excess F^-, the green complex **$[CuF_4]^{2-}$** (or its hydrate) forms. (ii) With excess Cl^-, the bright green complex **$[CuCl_4]^{2-}$** forms.

Since F^- and Cl^- are different-field-strength ligands compared to water, they produce a different crystal field splitting (Δ) than $[Cu(H_2O)_4]^{2+}$, shifting the wavelength of light absorbed and hence changing the observed colour from blue to green.

5.14 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?
Ans: Excess CN^- first reduces Cu^{2+} to Cu^+ (with the release of cyanogen gas, $(CN)_2$), forming the very stable complex **$[Cu(CN)_4]^{3-}$**. Since this complex is so stable, the concentration of free Cu^{2+}/Cu^+ ions in solution is far too low for the ionic product of CuS to be exceeded when H_2S is passed, so no CuS precipitate forms.

5.15 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) $[CoF_6]^{3-}$.
Ans: (i) Fe^{2+} (d^6); CN^- is a strong-field ligand, forcing pairing: **d^2sp^3 hybridisation, low spin, diamagnetic (0 unpaired electrons)**. (ii) Fe^{3+} (d^5); F^- is a weak-field ligand: **sp^3d^2 hybridisation, high spin, paramagnetic (5 unpaired electrons)**. (iii) Co^{3+} (d^6); oxalate favours the inner-orbital arrangement typical of Co^{3+}: **d^2sp^3 hybridisation, low spin, diamagnetic**. (iv) Co^{3+} (d^6); F^- is weak-field: **sp^3d^2 hybridisation, high spin, paramagnetic (4 unpaired electrons)**.

5.16 Draw figures to show the splitting of d-orbitals in an octahedral crystal field.
Ans: In an octahedral field, the five degenerate d-orbitals split into two sets: the higher-energy **e_g set** (d_{z^2} and $d_{x^2-y^2}$, orbitals pointing directly at the approaching ligands) and the lower-energy **t_{2g} set** (d_{xy}, d_{yz}, d_{xz}, orbitals pointing between the ligands), separated by the crystal field splitting energy Δ_o.

5.17 What is the spectrochemical series? Explain the difference between a weak field ligand and a strong field ligand.
Ans: The **spectrochemical series** arranges ligands in order of increasing crystal field splitting strength: **$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} \approx H_2O < NCS^- < py \approx NH_3 < en < NO_2^- < CN^- \approx CO$**. **Weak field ligands** (left of the series) produce a small Δ_o, favouring high-spin complexes; **strong field ligands** (right of the series) produce a large Δ_o, favouring low-spin complexes.

5.18 What is crystal field splitting energy? How does the magnitude of Δ_o decide the actual configuration of d-orbitals in a coordination entity?
Ans: **Crystal field splitting energy (Δ_o)** is the energy gap created between the t_{2g} and e_g sets of d-orbitals when ligands approach the metal in an octahedral field. If Δ_o is **greater than** the pairing energy P (strong-field ligands), electrons preferentially pair up in the lower t_{2g} orbitals first, giving a **low-spin** configuration. If Δ_o is **less than** P (weak-field ligands), electrons follow Hund's rule and singly occupy all five d-orbitals before any pairing occurs, giving a **high-spin** configuration.

5.19 $[Cr(NH_3)_6]^{3+}$ is paramagnetic while $[Ni(CN)_4]^{2-}$ is diamagnetic. Explain why.
Ans: Cr^{3+} is **$3d^3$**: regardless of field strength, all three electrons singly occupy the t_{2g} orbitals (no pairing possible either way), so $[Cr(NH_3)_6]^{3+}$ is always **paramagnetic (3 unpaired electrons)**. Ni^{2+} is **$3d^8$**; with the strong-field ligand CN^-, the complex adopts a square-planar geometry with **dsp^2 hybridisation**, forcing all electrons to pair up, making $[Ni(CN)_4]^{2-}$ **diamagnetic**.

5.20 $[Ni(H_2O)_6]^{2+}$ is green in colour while $[Ni(CN)_4]^{2-}$ is colourless. Explain.
Ans: In $[Ni(H_2O)_6]^{2+}$, the weak-field ligand H_2O gives a small Δ_o, allowing a d-d transition in the visible region, producing the observed **green** colour. In $[Ni(CN)_4]^{2-}$, the strong-field ligand CN^- pairs all electrons (square planar, diamagnetic, no partially-filled d-orbital transition available in the visible range) and shifts any absorption into the UV region, so the complex appears **colourless**.

5.21 $[Fe(CN)_6]^{4-}$ and $[Fe(H_2O)_6]^{2+}$ are of different colours in dilute solutions. Why?
Ans: Both contain Fe^{2+} ($3d^6$), but CN^- is a much stronger-field ligand than H_2O, so $[Fe(CN)_6]^{4-}$ has a much larger Δ_o than $[Fe(H_2O)_6]^{2+}$. Since the energy (and hence wavelength) of the d-d transition absorbed depends directly on Δ_o, the two complexes absorb different wavelengths of visible light and consequently show different colours.

5.22 Discuss the nature of bonding in metal carbonyls.
Ans: Bonding in metal carbonyls is **synergic**: CO donates a lone pair from its carbon atom into a vacant metal orbital (σ-donation), while the metal simultaneously donates electron density from a filled d-orbital back into the empty π* antibonding orbital of CO (π-backdonation). This mutual, reinforcing donation strengthens the metal–carbon bond while weakening the carbon–oxygen bond, compared to free CO.

5.23 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) $[Mn(H_2O)_6]SO_4$.
Ans: (i) Co**+3**, **$3d^6$** (high spin, $t_{2g}^4e_g^2$, 4 unpaired), CN=**6**. (ii) Cr**+3**, **$3d^3$** (t_{2g}^3, 3 unpaired), CN=**6**. (iii) Co**+2**, **$3d^7$** (tetrahedral, high spin, 3 unpaired), CN=**4**. (iv) Mn**+2**, **$3d^5$** (high spin, $t_{2g}^3e_g^2$, 5 unpaired), CN=**6**.

5.24 Write down the IUPAC name for each of the following complexes and indicate the oxidation state, electronic configuration and coordination number: (i) $K[Cr(H_2O)_2(C_2O_4)_2]\cdot 3H_2O$ (ii) $[Co(NH_3)_5Cl]Cl_2$ (iii) $CrCl_3(py)_3$ (iv) $Cs[FeCl_4]$ (v) $K_4[Mn(CN)_6]$.
Ans: (i) **Potassium diaquabis(oxalato)chromate(III) trihydrate**; Cr**+3**, $3d^3$, CN=**6**. (ii) **Pentaamminechloridocobalt(III) chloride**; Co**+3**, $3d^6$, CN=**6**. (iii) **Trichloridotris(pyridine)chromium(III)**; Cr**+3**, $3d^3$, CN=**6**. (iv) **Caesium tetrachloridoferrate(III)**; Fe**+3**, $3d^5$, CN=**4**. (v) **Potassium hexacyanidomanganate(II)**; Mn**+2**, $3d^5$, CN=**6**.

5.25 What is the coordination entity formed when excess ammonia reacts with copper sulphate in aqueous solution? What is its colour, and why does $[Ti(H_2O)_6]^{3+}$ appear violet in colour?
Ans: Excess aqueous ammonia with $CuSO_4$ forms the deep blue coordination entity **$[Cu(NH_3)_4]^{2+}$**. For **$[Ti(H_2O)_6]^{3+}$**: Ti^{3+} is $3d^1$, and this single t_{2g} electron absorbs light in the yellow-green region of the visible spectrum, exciting it to the e_g level (a d-d transition); the complementary colour transmitted/reflected is **violet**, which is the colour observed.

5.26 What is meant by stability of a coordination compound in solution? State the factors that govern the stability of complexes.
Ans: **Stability** in solution refers to the degree of association/resistance to dissociation of a complex into its constituent metal ion and ligands, measured by its formation (stability) constant. Key factors include: the **charge and size of the metal ion** (higher charge and smaller size generally give greater stability), the **nature of the ligand** (donor atom basicity/field strength), and especially the **chelate effect** — complexes with polydentate (ring-forming) ligands are markedly more stable than comparable complexes with unidentate ligands, e.g. $[Ni(en)_3]^{2+}$ is more stable than $[Ni(NH_3)_6]^{2+}$.

5.27 What is the basis of formation of coordination compounds in the biological system? Give an example of a coordination compound used in medicine.
Ans: Coordination compounds occur widely in biological systems because metal ions bind to polydentate, often nitrogen/oxygen-donor natural ligands (porphyrins, proteins), forming stable functional complexes — e.g. **chlorophyll (Mg complex, essential for photosynthesis), haemoglobin (Fe complex, oxygen transport), and vitamin B_{12} (Co complex)**. In medicine, **cis-platin, cis-$[PtCl_2(NH_3)_2]$**, is a well-known coordination compound used as an anticancer drug, and **EDTA complexes** are used to treat heavy-metal (e.g. lead) poisoning. Coordination compounds are also central to analytical chemistry (EDTA titrations for water hardness, coloured complexes for qualitative tests) and metallurgy (extraction of Ag/Au as cyanide complexes, purification of Ni via the Mond process, $[Ni(CO)_4]$).

5.28 What number of ions are produced from the complex $[Co(NH_3)_6]Cl_2$ in solution? (i) 6 (ii) 4 (iii) 3 (iv) 2.
Ans: **(iii) 3** — the complex dissociates into **$[Co(NH_3)_6]^{2+}$ and $2Cl^-$**, giving 3 ions in total (the NH_3 ligands remain coordinated and do not ionise).

5.29 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) $[Zn(H_2O)_6]^{2+}$.
Ans: **(ii) $[Fe(H_2O)_6]^{2+}$**. Cr^{3+} ($3d^3$): 3 unpaired electrons, $\mu=\sqrt{(3\times5)}\approx3.87$ BM. Fe^{2+} ($3d^6$, high spin with weak-field H_2O): 4 unpaired electrons, $\mu=\sqrt{(4\times6)}\approx$**4.90 BM (highest)**. Zn^{2+} ($3d^{10}$): 0 unpaired electrons, $\mu=0$.

5.30 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) $[FeCl_6]^{3-}$.
Ans: **(iii) $[Fe(C_2O_4)_3]^{3-}$**, by the **chelate effect** — the bidentate oxalate ligand forms three stable five-membered chelate rings with Fe^{3+}, making this complex significantly more stable than the comparable complexes with unidentate ligands (H_2O, NH_3, Cl^-).

5.31 The correct order of the wavelength of absorption of light in the visible region for the complexes of Ni^{2+} is: $[Ni(NO_2)_6]^{4-}$, $[Ni(NH_3)_6]^{2+}$, $[Ni(H_2O)_6]^{2+}$.
Ans: By the spectrochemical series, field strength decreases as **$NO_2^->NH_3>H_2O$**, so Δ_o (and hence the energy of the d-d transition) decreases in the same order; since wavelength is inversely proportional to energy ($E\propto1/\lambda$), the order of **increasing wavelength absorbed** is: **$[Ni(NO_2)_6]^{4-}<[Ni(NH_3)_6]^{2+}<[Ni(H_2O)_6]^{2+}$**.

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