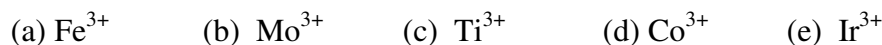


CYL 120 : Tutorial Sheets-Inorganic Chemistry (2012, I SEM)

Week 1: Revision of basic concepts in transition metal complexes

[Importance of metal complexes in catalysis and bioinorganic chemistry; Types of ligands, Shapes of d orbitals, Common geometries of metal complexes (Oh, Td, Sq, Plr), Original work of Alfred Werner (Huheey, 4th edn p 387), nomenclature, isomerism]

1. Write the valence electronic configuration of the following ions (Atomic number of Fe 26; Mo 42; Ti 22; Co 27; Ir 77)

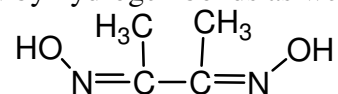


2. Draw the structures of (a) 2, 2' bipyridine (b) 1,10 – phenanthroline (c) glycine (d) ethylenediamine (e) acetylacetonate ion

3. Write examples of (a) bidentate dianionic ligand (b) tridentate dianionic ligand (c) hexadentate tetraanionic ligand

4. Draw the structure of EDTA and show the atoms which would donate electrons so as to form a complex with a metal. Sketch the structure of such a complex anion.

5. Ni^{2+} forms a neutral square planar complex with 2 moles of dimethylglyoxime. The molecule is stabilized by hydrogen bonds as well. Draw its structure.



6. Give an example with structure of a neutral octahedral complex of Cr^{3+} having metal to ligand ratio 1:3

7. Choosing suitable bidentate (neutral and anionic) ligands, draw one structure for each (a) cationic (b) anionic and (c) neutral complex species of Cr(III) with coordination number of six.

8. A. Werner (first Nobel prize in inorganic chemistry) took CoCl_3 and added ammonia solution and obtained four differently colored complexes; green(A), violet(B), yellow(C) and purple(D). Analysis showed that the complexes had varying amounts of ammonia. Reaction of A, B, C and D with excess AgNO_3 gave 1, 1, 3 and 2 moles of AgCl respectively. Given that all of them are octahedral complexes, write the molecular formula arrived for A, B, C and D by Werner.

Did Werner miss any new complex in his studies and why ?

9. Can Xenon, a heavier rare gas act as a ligand in transition metal chemistry? Explain your answer.

10. What is the hybridization of C in (a) CH₄ (b) graphite and (c) C₆₀ (fullerene)
11. Write the specific 3d and 4p orbitals used for the following hybridizations of the central metal ion Cr²⁺ in forming various coordination complexes
 (a) dsp² (b) d²sp³ (c) dsp³
12. Two platinum complexes A and B are prepared by the following reactions.

$$\text{K}_2[\text{PtCl}_4] + 2 \text{NH}_3 \rightarrow \text{A} + \text{side products}$$

$$[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2 + 2\text{KCl} \rightarrow \text{B} + \text{side products}$$
- The molecular formula of A and B are same. A is soluble in polar solvents while B is soluble in non-polar solvents. Sketch the structures of A and B.
13. Write the formula for each of the following compounds
 (a) Diamminesilver(I) hexacyanoferrate(II)
 (b) Tetramminechloronitroplatinum(IV) carbonate
 (c) Chlorocyanonitrotri-aminocobalt(III)
 (d) *mer*-Triamminetrichlorocobalt(III)
 (e) Tetrapyridineplatinum(II) tetrachloroplatinate(II)
 (f) Sulfatotetramminecobalt(III) nitrate
14. Among d orbitals, draw the shape of the orbitals having an “z” component.

Week 2: Isomerism, hybridization and Valence Bond theory

1. Indicate the type of isomerism shown by the following pairs of compounds
 (a) [Co(NH₃)₄Cl₂] NO₂ and [Co(NH₃)₄Cl NO₂]Cl
 (b) [Pt(NH₃)₄] [PtCl₆] and [Pt(NH₃)₄Cl₂] [PtCl₄]
2. Write the possible isomers with their structures for the following compounds
 (a) [Co(en)₂Cl₂]⁺ (b) [Co(NH₃)₄NO₂SO₄]
 (c) [Pt(Py)(NH₃)ClBr] (Sq. plr) (d) [Pt(NH₃)₂BrCl]
 (e) [Co(NH₃)₆][Cr(ox)₃] (f) Co(en)₂(NH₃)(NO₂)Cl (Oh)
 (g) [NiCl₂Br₂]²⁻ (tetrahedral) (h) [Co(gly)₃]
 (i) [Pt(NH₃)₄][PtCl₄] (j) [Co(NCS)₂(en)₂]Cl
 (k) [Cr(en)₃]₂(SO₄)₃
3. The compound [Co(en)₂(NO₂)₂Cl] has been prepared in three isomeric forms, A, B and C. A undergoes no reaction with AgNO₃ or en and is optically inactive. B reacts with AgNO₃ but not with en and is optically inactive. The third form, C reacts with AgNO₃ and also with en and is optically active. Sketch the structures of A, B and C.
4. Which of the following complexes does not exhibit optical isomerism?
 (a) [Co(NH₃)₃Cl₃] (b) [Co(NH₃)₂Cl₂(H₂O)₂]
 (c) K₃[Co(C₂O₄)₂Cl₂] (d) K₃[Co(C₂O₄)₃]

- For an octahedral complex of formula $\text{Cr}(\text{en})_2\text{NO}_2\text{Cl}$, draw structures of all optical isomers that do not readily react with AgNO_3
- An octahedral aqua complex of cobalt, A has a magnetic moment of 3.87 B.M. One mole of A when reacts with excess of AgNO_3 gives 2 moles of AgCl precipitate. A, when reacts with excess of ammonia, ammonium chloride and hydrogen peroxide in one pot gives an octahedral diamagnetic complex of cobalt, B. One mole of B, when reacts with excess of AgNO_3 , gives three moles of AgCl precipitate. Find out the hybridization of cobalt in A and B, on the basis of the above data.
- What is the hybridization of the metal in the following compounds ? Indicate the orbitals used. Magnetic moments are given
 (a) $[\text{PtCl}_4]^{2-}$ (0 BM) (b) $[\text{NiCl}_4]^{2-}$ (2.8 B.M) (c) $[\text{Ni}(\text{CN})_5]^{3-}$ (0 B.M)
- Say whether the following statements are true or false
 (a) Diamagnetic character of $[\text{Co}(\text{CN})_6]^{3-}$ can be explained by sp^3d^2 hybridization.
 (b) For the square planar complex $[\text{PdCl}_2(\text{PPh}_3)_2]$, the $\text{d}_{x^2-y^2}$ orbital participates in hybridization
 (c) Trans $[\text{NiCl}_2(\text{en})_2]$ shows optical isomerism.
- Draw box diagram and assign electrons to square planar $[\text{Cu}(\text{NH}_3)_4]^{2+}$. What is the abnormality in this bonding picture ?
- Assuming similarity to the triangular face of a trichelate octahedral complex assign Δ or Λ terminology to a ceiling fan.

Week 3: Crystal Field Theory and its applications to metal complexes

- Draw and label the crystal field splitting diagram (indicating filling of electrons) of an octahedral complex $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$.
- Draw and label the crystal field splitting diagram and calculate the magnetic moment of the complex , $\text{K}_4\text{Fe}(\text{CN})_6$.
- Calculate crystal field stabilization energy (CFSE) for the following complexes
 (a) $[\text{Co}(\text{CN})_6]^{3-}$ (b) $[\text{Fe}(\text{CN})_6]^{3-}$ (c) $[\text{CoCl}_6]^{4-}$
- Explain the following by valence bond theory or crystal field theory
 a. $[\text{NiCl}_4]^{2-}$ is paramagnetic while $[\text{PtCl}_4]^{2-}$ is diamagnetic
 b. Magnetic moment of $[\text{Fe}(\text{CN})_6]^{3-}$ is nearly one third of that of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
- Arrange the following complexes in the ascending order of 10Dq
 $[\text{Co}(\text{CN})_6]^{3-}$ $[\text{FeCl}_6]^{4-}$ $[\text{Fe}(\text{NH}_3)_6]^{2+}$ $[\text{Fe}(\text{ox})_3]^{4-}$ $[\text{Fe}(\text{en})_3]^{2+}$ $[\text{Fe}(\text{EDTA})]^{2-}$
- Arrange the following complex ions in ascending order of Δ_o (10Dq_o) .
 (a) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (b) $[\text{Rh}(\text{NH}_3)_6]^{3+}$ (c) $[\text{Fe}(\text{NH}_3)_6]^{2+}$ (d) $[\text{FeCl}_6]^{4-}$
- Explain the factors on which pairing energies depend.

8. Determine (in terms of Dq) the change in CFSE when the following reaction occurs
- $$[\text{Fe}(\text{CN})_6]^{4-} + \text{H}_3\text{O}^+ \longrightarrow \frac{1}{2} \text{H}_2 + \text{H}_2\text{O} + [\text{Fe}(\text{CN})_6]^{3-}.$$
9. Magnetic moments of some complexes are as follows. Predict on the basis of this data whether they are high spin or low spin complexes
- (a) $\text{K}_3[\text{Mn}(\text{NO}_2)_6]$ 2.87 BM
 (b) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ 1.73 BM
 (c) $\text{K}_4[\text{Fe}(\text{CN})_6]$ 0 BM
10. The magnetic moment of an octahedral complex of cobalt $[\text{CoL}_6]\text{SO}_4$ is 3.8 BM. Draw the CFT diagram of the complex and choose the correct ligand L from the list provided. [CN^- , NH_3 , H_2O , Cl^-]
11. Calculate the approximate magnetic moments of the following octahedral complexes using crystal field theory
- (a) $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, (b) $[\text{Co}(\text{Phen})_3]^{2+}$ (c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
 (d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ (e) $[\text{Cr}(\text{CN})_6]^{4-}$ (f) $[\text{CoCl}_6]^{4-}$
12. Cobalt form three octahedral complexes, $[\text{MCl}_6]^{4-}$, $[\text{M}(\text{R}_2\text{NCS}_2)_3]$ and $[\text{M}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$. These have magnetic moments 0, 1.73 and 3.9 BM (not in the order). Assign the moments to the complexes and predict the relative strength of the dithiocarbamate ligand.
13. What are the basic differences between the CFT diagrams of an octahedral complex and a tetrahedral complex ?
14. Calculate the CFSE (in cm^{-1}) of $[\text{CoCl}_4]^{2-}$ if $10 Dq$ for $[\text{CoCl}_6]^{4-}$ is 18600 cm^{-1}
15. Draw the crystal field splitting diagram of d orbitals in a linear complex MX_2 , assuming the ligands (X) to be along the z axis.
16. In NiFe_2O_4 (inverse spinel) the Ni^{2+} ions are in octahedral sites while the Fe^{3+} ions are in tetrahedral sites. Why?

Week 4, CFT (Contd); Color, Magnetism, Jahn-Teller distortion

- Show diagrammatically the variation of ionic radii of 3d series M^{2+} ions in $\text{M}(\text{CN})_6$.
- Arrange $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ in decreasing order of metal ion radii with justification.
- Which of the two complexes $[\text{CoCl}_4]^{2-}$ and $[\text{CoCl}_6]^{4-}$ would absorb at lower wavelength ?
- $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ solution is pink while $[\text{CoCl}_4]^{2-}$ is blue in colour. Explain.

5. $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ is dark pink whereas $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ is pale pink. Explain
6. $\text{K}_3[\text{Co}(\text{CN})_6]$ is colorless while $\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)]$ is colored. Why ?
7. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic and orange yellow. $[\text{CoF}_6]^{3-}$ on the other hand is paramagnetic and blue . Why ?
8. Two of the following octahedral complexes are colorless. Identify them and give reasons
 $[\text{VCl}_6]$, $[\text{V}(\text{CN})_6]^{2-}$ and $[\text{V}(\text{NH}_3)_6]^{3+}$
9. Why is a dilute aqueous solution of $[\text{CrO}_4]^{2-}$ or $[\text{Cr}_2\text{O}_7]^{2-}$ ion intensely colored ?
10. Compare qualitatively (a) color of complexes (in frequency): $[\text{FeF}_6]^{3-}$ and $[\text{FeF}_6]^{4-}$ and (b) Size of the metal ions in $[\text{FeF}_6]^{4-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$
11. Calculate the magnetic moments of only those complexes which have significant tetragonal distortion: $\text{K}_2[\text{PdCl}_6]$, $[\text{Co}(\text{Phen})_3]^{2+}$, $[\text{MnBr}_6]^{4-}$, $[\text{Cu}(\text{NH}_3)_6]^{2+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$
12. Explain whether the d – d transition in the following complex will follow the selection rules. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_2$
13. In the crystal structure of CuF_2 , the Cu^{2+} ion is six coordinate with four F^- ions at a distance of 1.93 Å and two F^- ions at a distance of 2.27 Å. Explain.
14. Which of the following ligands F^- , CN^- , H_2O and NO_2 will form significantly distorted octahedral complexes with cobalt (II) ? Explain.
15. Which of the following complex ions are expected to show **very weak** tetragonal distortion and why?
 (a) $[\text{Cr}(\text{CN})_6]^{4-}$ (b) $[\text{Co}(\text{Cl})_6]^{4-}$ (c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (d) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$
16. Which of the following is easily reduced and why ? Explain using crystal field theory. (a) $[\text{Cu}(\text{CN})_4]^{1-}$ (b) $[\text{Au}(\text{CN})_4]^{1-}$

Week 5 : INORGANIC SOLIDS

1. Draw the structure of the unit cell generated by a ccp –packing of spheres of equal size. Shade the atoms corresponding to A, B, C layers .
2. Why we have only two types of close packing ABAB.... and ABCABC.....?
3. State True or False for the following statements
 - a. In hcp and ccp closest packing arrangement of atoms in a metal the coordination number of a metal atom will be 12 .

- b. The hcp closest packing is identical to an FCC arrangement of atoms
 - c. In ionic crystals a radius ratio r^+/r^- of 0.60 will result in a tetrahedral arrangement of ions
 - d. The total space occupied by an hcp arrangement of atoms will be 76% while the space occupied by a ccp arrangement will be 68 %.
 - e. In a cubic close packing structure if there are N atoms there will be N tetrahedral voids and 2N octahedral voids.
4. Calculate the formula of NaCl, if every alternate Na^+ is removed from the cell-edge. (Given that the corners of the unit cell are occupied by Na^+).
 5. Write down the coordination numbers of Na^+ , Cl^- and Cs^+ in the NaCl and CsCl structures.
 6. Describe the structure of ZnS (Sphalerite) and compare the same with diamond and fluorite structures
 7. Show that the formula for an infinite layered lattice of edge-shared octahedra is AB_3 where A is at the center of each octahedron.
 8. $\text{Na}_{0.99}\text{Cl}_{0.99}$ will have Schottky or Frenkel defects. Explain.
 9. At high temperatures the defect concentration increases. Is there a thermodynamic basis for the above statement ? Explain.
 10. In the ABO_3 (perovskite) structure, what is the coordination number of 'A' and 'B' ions. What is the resultant formula if every alternate cell (in all three directions) has a empty A-site.
 11. The lattice parameter decreases in Fe_{1-x}O , as x increases. Explain.
 12. Describe the two types of acid sites in Zeolites
 13. The zeolite, ZSM -5 has the molecular formula, $\text{Na}_3\text{Al}_3\text{Si}_{93}\text{O}_{192}$. The synthesis is carried out in the presence of $[(n\text{-Propyl})_4\text{N}]\text{OH}$ as template. Write the chemical equation for its synthesis.
 14. Draw the plots of variation of resistivity as a function of temperature for metal, semiconductor, insulator and superconductor.
 15. Why does the resistance of a metal increase with temperature?
 16. Calculate the average oxidation state of copper in the compounds $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$.