Self Study Concepts

1. How can you account for the series of compounds with the formulas: CrCl₃, CrCl₃ · 3NH₃, CrCl₃ · 4NH₃, CrCl₃ · 5NH₃, and CrCl₃ · 6NH₃? Why would you not expect to find the missing members of the series: CrCl₃ · 2NH₃ and CrCl₃ · NH₃?

2. If you found the compound CrCl₃ · NaCl · xNH₃, what would you expect x to be?

3. How many different isomers of this compound, CrCl₃ · NaCl · xNH₃, would you expect to find?

4. What assumption about the geometry of bonding around the Cr molecule did you make in answering Question 3?

5. How does the number of isomers of a compound distinguish between the possible geometrical arrangements around the central metal ion? Illustrate with tetrahedral and square planar geometry.

6. What is the difference between paramagnetic and diamagnetic compounds? How are these distinguished from one another by experiment?

7. What is the difference between stability and inertness? Can a chemical system be stable yet not be inert? Can it be inert yet not be stable?

8. Why are complexes with electronic configuration of d⁵ or d¹⁰ on the central metal atom stable? Why are complexes with d⁴ and d⁶ arrangements stable? Which configurations would you predict to be more important for stability in complexes with ligands of large splitting energies? Of small splitting energies?

9. How would you name the following compounds in a systematic way:
   • Ir(NH₃)₃Cl₃
   • Rh(en)₂Cl₂Ir(en)Cl₄
   • Co(NH₃)₆Cl₃
   • Rh(en)Cl₄Ir(en)₂Cl₂
   • Rh(en)₃IrCl₆
   • RhCl₆Ir(en)₃

10. Sketch each of the four Rh-Ir complexes of Question 9.
11. Sketch each of the following complex ions or molecules:
   - cis-dichlorotetraamminechromium(III) ion
   - trans-dichlorotetraamminechromium(III) ion

Indicate the charge on each complex.

12. What is the difference between structural, geometrical, and optical isomers? Find examples in Questions 9 and 11 of structural and geometrical isomers.

13. Why do complexes in which the central metal ion has the d8 electronic configuration exist with square planar geometry?

14. What will be the number of unpaired electrons in FeCl$_6^{3-}$? In Fe(CN)$_6^{3-}$?

15. All octahedral complexes of vanadium(III) have the same number of unpaired electrons, no matter what the nature of the ligand. Why is this so?

16. What is the difference in the way that valence bond theory and crystal Held theory explain the magnetic properties of complex ions?

17. How does ligand field theory account for the observed order of ligands in terms of the sizes of their splitting energies?

18. Why, in the crystal Field theory, are the five d orbitals on the metal atom divided into two energy levels in the way they are? Where do the corresponding energy levels come from in the molecular orbital theory of complex ion structure?

19. Why are the same groupings of the five d orbitals made in tetrahedral coordination as in octahedral, but with the relative energies of these two groups reversed?

20. What is a chelate? If porphyrin is a tetradeutate chelating group, and ethylenediamine is a bidentate chelating group, how would triethylenetetraamine, diethylenetriamine, and EDTA be described?

21. What is a heme group? How does it function in hemoglobin and in cytochrome c?

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**Exercises**

**Stoichiometry**

1. A student was given 1.00 g of ammonium dichromate for the preparation of a coordination compound. The sample was ignited, thereby producing chromium(III) oxide, water, and nitrogen gas. The chromium(III) oxide was allowed to react at 600°C with carbon tetrachloride to yield chromium(III) chloride and phosgene (COCl$_2$). Upon treatment with excess liquid ammonia, the chromium(III) chloride reacted to produce hexaamminechromium(III) chloride. Calculate the maximum
amount of hexaamminechromium(III) chloride that the student could prepare from the 1.00-g sample of ammonium dichromate.

2. When silver nitrate is added to a solution of a substance with the empirical formula \( \text{CoCl}_3 \cdot 5\text{NH}_3 \), how many moles of AgCl will be precipitated per mole of cobalt present? Why?

3. \( \text{Co(III)} \) occurs in octahedral complexes with the general empirical formula \( \text{CoCl}_m \cdot n\text{NH}_3 \). What values of \( n \) and \( m \) are possible? What are the values of \( n \) and \( m \) for the complex that precipitates 1 mole of AgCl for every mole of Co present?

4. How many ions per mole will you expect to find in solution when a compound with the empirical formula \( \text{PtCl}_4^- \cdot 3\text{NH}_3 \) is dissolved in water? What about \( \text{PtCl}_2 \cdot 3\text{NH}_3 \)? Draw diagrams of each of the complex cations.

5. Each of the following is dissolved in water to make a 0.001 M solution. Rank the compounds in order of decreasing conductivity of their solutions: \( \text{K}_2\text{PtCl}_6 \), \( \text{Co(NH}_3)_6\text{Cl}_3 \), \( \text{Cr(NH}_3)_4\text{Cl}_3 \), \( \text{Pt(NH}_3)_6\text{Cl}_4 \). Rewrite each compound by using brackets to distinguish the complex ion present in aqueous solution.

Formulas and nomenclature

6. Give the systematic names of \( \text{[Co(NH}_3)_4\text{Cl}_2]Br \), \( \text{K}_3\text{Cr(CN)}_5 \), and \( \text{Na}_2\text{CoCl}_4 \).

7. Write the formulas for each of the following compounds by using brackets to distinguish the complex ion from the other ions: (1) \( \text{hexaaquonickel(II) perchlorate} \) (2) \( \text{trichlorotriammineplatinum(IV) bromide} \) (3) \( \text{dichlorotetraammineplatinum(IV) sulfate} \) (4) \( \text{potassium monochloropentacyanoferrate (III)} \)

8. Write the formula for each of the following by using brackets to distinguish the complex ion: (1) \( \text{hydroxopentaaquoaluminum(III) chloride} \) (2) \( \text{sodium tricarbonatocobaltate(III)} \) (3) \( \text{sodium hexacyanoferrate(II)} \) (4) \( \text{ammonium hexanitrocobaltate(III)} \)

Isomers

9. How many isomers are there of the compound \( \text{[Cr(NH}_3)_4\text{Cl}_2]Cl} \)? Sketch them.

10. Sketch all the geometrical and optical isomers of \( \text{PtCl}_2\text{Cl}_2(\text{NH}_3)_2 \).

11. How many geometrical and optical isomers are there of the complex ion \( \text{Co(en)}_2\text{Cl}_2 \)? Of these, how many pairs of isomers are there differing only by a mirror reflection? How many isomers have a plane of symmetry and hence do not exist in pairs of optical isomers?
12. Repeat Problem 11 with propylenediamine substituted for ethylenediamine. Ignore optical isomers from the propylene carbon.

13. How many different structural isomers are there of a substance with the empirical formula FeBrCl · 3NH₃ · 2H₂O? For each different structural isomer, how many different geometrical isomers exist? How many of these can be grouped into right-handed and left-handed pairs of optical isomers?

Electronic structure

14. The Co²⁺ ion in aqueous solution is octahedrally coordinated and paramagnetic, with three unpaired electrons. Which one or ones of the following statements follow from this observation:

1. Co(H₂O)₄²⁺ is square planar
2. Co(H₂O)₄²⁺ is tetrahedral
3. Co(H₂O)₄²⁺ has a Δ₀ that is larger than the electron—pairing energy;
4. the d levels are split in energy and filled as follows: (t₂g)⁵(eg)²
5. the d levels are split in energy and filled as follows: (t₂g)⁶(eg)¹

15. The coordination compound potassium hexafluorochromate(III) is paramagnetic. What is the formula for this compound? What is the configuration of the Cr d electrons?

16. How many unpaired electrons are there in Cr³⁺, Cr²⁺, Mn²⁺, Fe²⁺, Co³⁺, Co²⁺ in

1. a strong octahedral ligand field and
2. a very weak octahedral field?

17. A low-spin tetrahedral complex has never been reported, although numerous high-spin complexes of this geometry have been prepared. What conclusion may be drawn regarding the magnitude of Δ₁ from this fact?

18. Certain platinum complexes have been found to be active antitumor agents. Among these are cis-Pt(NH₃)₂Cl₂, cis-Pt(NH₃)₂Cl₂, and cis-Pt(en)Cl₂ (none of the trans isomers are effective). Use valence bond theory to account for the diamagnetism of these complexes. Are these inner or outer complexes? What kinds of hybrid orbitals are used in bonding?

19. What is the d-orbital electronic configuration of Cr(NH₃)₆³⁺? How many unpaired electrons are present? If six Br⁻ groups were substituted for the six NH₃ groups to give CrBr₆³⁻, would you expect Δ₀ to increase or decrease?

20. Diagram the electronic arrangements in Fe(H₂O)₆²⁺ and Fe(CN)₆⁴⁻ for both the valence bond and crystal field models. Briefly compare these models.

21. For each of the following, sketch the d-orbital energy levels and the distribution of d electrons among them:

1. Ni(CN)₄²⁻ (square planar)
2. Ti(H₂O)₆²⁺ (octahedral)
3. NiCl⁴⁻ (tetrahedral)
4. CoF₆³⁻ (high-spin complex)
5. Co(NH₃)₆³⁺ (low—spin complex)

22. Co(III) can occur in the complex ion Co(NH₃)₆³⁺.

1. What is the geometry of this ion? In the valence bond theory, what Co orbitals are used in making bonds to the ligands?
2. What is the systematic name for the chloride salt of this ion?
3. Using crystal Field theory, draw two possible d—electron configurations for this ion. Assign to them the labels high spin, low spin, paramagnetic, diamagnetic. Which two labels are correct for the ammine complex?
4. Co(NH₃)₆³⁺ can be reduced to Co(NH₃)₆²⁺ by adding an electron. Draw the preferred d-electron configuration for this reduced ion. Why is it preferred?

23. Pt(II) can occur in the complex ion PtCl⁴⁻.

1. What is the geometry of this ion? In the valence bond theory, what Pt orbitals are used in making bonds to the Cl⁻ ions?
2. What is the systematic name for the sodium salt of this ion?
3. Using crystal field theory, draw the d-electron configuration for this ion. Is the ion paramagnetic or diamagnetic?
4. Pt(II) can be oxidized to Pt(IV). Draw the d-electron configuration for the chloride complex ion of Pt(IV). Explain the difference between this configuration and that of Pt(II). Is the Pt(IV) chloride complex ion paramagnetic or diamagnetic?

Formation constants

24. A solution is prepared that is 0.025M in tetraamminecopper(IIl), Cu(NH₃)₄⁴⁺. What will be the concentration of Cu²⁺ hydrated copper ion if the ammonia concentration is 0.10, 0.50, 1.00, and 3.00 M respectively? What ammonia concentration is needed to keep the Cu²⁺ concentration less than 10⁻¹⁵ M?

25. From the data in Table 20-8, calculate the pH of a 0.10M solution of Cr³⁺ ion. Hint: Consider the reactions

\[
Cr^{3+} + H₂O \leftrightarrow Cr(OH)^{2+} + H^+ \quad K = ? \\
Cr^{3+} + OH^- \leftrightarrow Cr(OH)^{2+} \quad K_f = 1 \times 10^{10} \\
H^+ + OH^- \leftrightarrow H₂O \quad K_w = ?
\]

26. From the data in Table 20-8, calculate the pH of 0.10M solutions of Mn²⁺, Fe²⁺, and Ag⁺. See Problem 25 if you need help. From the results of these two problems, can you correlate the “acidity” of positive ions with their charge?
27. The ion \( \text{Co(NH}_3\text{)}_6^{3+} \) is very stable, with \( K_f = 2.3 \times 10^{34} \). If the hydrolysis constant for the ammonium ion, \( K_b \), is \( 5 \times 10^{-10} \), show that the equilibrium in the reaction

\[
\text{Co(NH}_3\text{)}_6^{3+} + 6\text{H}^+ \leftrightarrow \text{Co}^{3+} + 6\text{NH}_4^+
\]

lies far to the right. Then why does \( \text{Co(NH}_3\text{)}_6^{3+} \) remain intact in hot concentrated sulfuric acid?

28. What is the concentration of chromate ion, \( \text{CrO}_4^{2-} \) when solid BaCrO\(_4\) is placed in contact with water? What is the chromate ion concentration when solid BaCrO\(_4\) is placed in contact with a solution of 0.2M Ba\(^{2+}\)? BaCrO\(_4\) can be dissolved in a solution of pyridine (py), producing the complex Ba(py)_2\(^{2+}\), with a formation constant of \( 4 \times 10^{-12} \). If 0.10M BaCrO\(_4\) is dissolved in a solution with a constant pyridine concentration of 1.0 mole liter\(^{-1}\), what is the concentration of Ba\(^{2+}\) ion?

29. What is the solubility of Cu(OH)\(_2\) in pure water? In buffer at pH 6? Copper(II) forms a complex with NH\(_3\), Cu(NH\(_3\))\(_4^{2+}\), with \( K_f = 1.0 \times 10^{12} \). What concentration of ammonia must be maintained in a solution to dissolve 0.10 mole of Cu(OH)\(_2\) per liter of solution?

30. Calculate the silver ion concentration in a saturated solution of AgCl in water. Silver ions react with an excess of Cl\(^-\) as follows:

\[
\text{Ag}^+ + 2\text{Cl}^- \leftrightarrow \text{AgCl}_2 \quad K_f : 1 \times 10^2
\]

Calculate the concentration of AgCl\(_2\); and show that you were justified in ignoring the complex ion formation in calculating the silver ion concentration at the beginning of the problem.

31. The formation constant for the pyridine complex of silver

\[
\text{Ag}^+ + 2\text{py} \leftrightarrow 2\text{Ag(py)}^2+
\]

is \( K_f : 1 \times 10^{10} \). If a solution is initially 0.10M in AgNO\(_3\) and 1.0M in pyridine, what are the equilibrium concentrations of silver ion, pyridine, and the complex ion?

32. In 0.10M NaCl, the concentration of silver ions cannot exceed \( 10^{-9} \) mole liter\(^{-1}\) because AgCl is so slightly soluble. What concentration of pyridine must be added to dissolve 0.10 mole of AgCl per liter of solution?