

Exercises

Review Questions

1. When a transition metal atom forms an ion, which electrons are lost first?
2. Explain why transition metals exhibit multiple oxidation states instead of a single oxidation state (which most of the main-group metals do).
3. Why is the +2 oxidation state so common for transition metals?
4. Explain why atomic radii of elements in the third row of the transition metals are no larger than those of elements in the second row.
5. Gold is the most electronegative transition metal. Explain.
6. Briefly define each term.
 - a. coordination number
 - b. ligand
 - c. bidentate and polydentate
 - d. complex ion
 - e. chelating agent
7. Using the Lewis acid–base definition, how would you categorize a ligand? How would you categorize a transition metal ion?
8. Explain the differences between each pair of isomer types.
 - a. structural isomer and stereoisomer
 - b. linkage isomer and coordination isomer
 - c. geometric isomer and optical isomer
9. Which complex ion geometry has the potential to exhibit cis–trans isomerism: linear, tetrahedral, square planar, octahedral?
10. How can you tell whether a complex ion is optically active?
11. Explain the differences between weak-field and strong-field metal complexes.
12. Explain why compounds of Sc^{3+} are colorless, but compounds of Ti^{3+} are colored.
13. Explain why compounds of Zn^{2+} are white, but compounds of Cu^{2+} are often blue or green.
14. Explain the differences between high-spin and low-spin metal complexes.
15. Why are almost all tetrahedral complexes high-spin?
16. Many transition metal compounds are colored. How does crystal field theory account for this?

Problems by Topic

Note: Answers to all odd-numbered Problems can be found in [Appendix III](#). Exercises in the Problems by Topic section are paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

Properties of Transition Metals

17. Write the ground state electron configuration for each atom and ion pair.
 - a. Ni, Ni^{2+}
 - b. Mn, Mn^{4+}
 - c. Y, Y^+
 - d. Ta, Ta^{2+}
18. Write the ground state electron configuration for each atom and ion pair.
 - a. Zr, Zr^{2+}

- b. Co, Co^{2+}
 - c. Tc, Tc^{3+}
 - d. Os, Os^{4+}
19. Determine the highest possible oxidation state for each element.
- a. V
 - b. Re
 - c. Pd
20. Which first-row transition metal(s) has the following highest possible oxidation state?
- a. +3
 - b. +7
 - c. +4

Coordination Compounds

21. Determine the oxidation state and coordination number of the metal ion in each complex ion.
- a. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - b. $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^-$
 - c. $[\text{Cu}(\text{CN})_4]^{2-}$
 - d. $[\text{Ag}(\text{NH}_3)_2]^+$
22. Determine the oxidation state and coordination number of the metal ion in each complex ion.
- a. $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$
 - b. $[\text{Fe}(\text{CN})_6]^{4-}$
 - c. $[\text{Co}(\text{ox})_3]^{4-}$
 - d. $[\text{PdCl}_4]^{2-}$
23. Name each complex ion or coordination compound.
- a. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - b. $[\text{Cu}(\text{CN})_4]^{2-}$
 - c. $[\text{Fe}(\text{NH}_3)_5\text{Br}]\text{SO}_4$
 - d. $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)(\text{OH})]\text{Cl}_2$
24. Name each complex ion or coordination compound.
- a. $[\text{Cu}(\text{en})_2]^{2+}$
 - b. $[\text{Mn}(\text{CO})_3(\text{NO}_2)_3]^{2-}$
 - c. $\text{Na}[\text{Cr}(\text{H}_2\text{O})_2(\text{ox})_2]$
 - d. $[\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$
25. Write the formula for each complex ion or coordination compound.
- a. hexaamminechromium(III)
 - b. potassium hexacyanoferrate(III)
 - c. ethylenediaminedithiocyanatocopper(II)
 - d. tetraaquaplatinum(II) hexachloroplatinate(IV)
26. Write the formula for each complex ion or coordination compound.
- a. hexaaquanickel(II) chloride
 - b. pentacarbonylchloromanganese(I)
 - c. ammonium diaquatetrabromovanadate(III)
 - d. tris(ethylenediamine)cobalt(III) trioxalatoferrate(III)
27. Write the formula and the name of each complex ion.
- a. a complex ion with Co^{3+} as the central ion and three NH_3 molecules and three CN^- ions as ligands
 - b. a complex ion with Cr^{3+} as the central ion and a coordination number of 6 with ethylenediamine ligands
28. Write the formula and the name of each complex ion or coordination compound.
- a. a complex ion with four water molecules and two ONO^- ions connected to an iron(III) ion

- a. a complex ion with four water molecules and two ONO^- ions connected to an iron(III) ion
- b. a coordination compound made of two complex ions: one a complex of vanadium(III) with two ethylenediamine molecules and two Cl^- ions as ligands and the other a complex of nickel(II) having a coordination number of 4 with Cl^- ions as ligands

Structure and Isomerism

29. Draw two linkage isomers of $\left[\text{Mn}(\text{NH}_3)_5(\text{NO}_2)\right]^{2+}$.
30. Draw two linkage isomers of $\left[\text{PtCl}_3(\text{SCN})\right]^{2-}$.
31. Write the formulas and names for the coordination isomers of $\left[\text{Fe}(\text{H}_2\text{O})_6\right]\text{Cl}_2$.
32. Write the formulas and names for the coordination isomers of $\left[\text{Co}(\text{en})_3\right]\left[\text{Cr}(\text{ox})_3\right]$.
33. Which complexes exhibit geometric isomerism?
 - a. $\left[\text{Cr}(\text{NH}_3)_5(\text{OH})\right]^{2+}$
 - b. $\left[\text{Cr}(\text{en})_2\text{Cl}_2\right]^+$
 - c. $\left[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cl}_2\right]^+$
 - d. $\left[\text{Pt}(\text{NH}_3)\text{Cl}_3\right]^-$
 - e. $\left[\text{Pt}(\text{H}_2\text{O})_2(\text{CN})_2\right]$
34. Which complexes exhibit geometric isomerism?
 - a. $\left[\text{Co}(\text{H}_2\text{O})_2(\text{ox})_2\right]^-$
 - b. $\left[\text{Co}(\text{en})_3\right]^{3+}$
 - c. $\left[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2(\text{ox})\right]^+$
 - d. $\left[\text{Ni}(\text{NH}_3)_2(\text{en})\right]^{2+}$
 - e. $\left[\text{Ni}(\text{CO})_2\text{Cl}_2\right]$
35. If W, X, Y, and Z are different monodentate ligands, how many geometric isomers are there for each ion?
 - a. square planar $[\text{NiWXYZ}]^{2+}$
 - b. tetrahedral $[\text{ZnWXYZ}]^{2+}$
36. How many geometric isomers are there for each species?
 - a. $\left[\text{Fe}(\text{CO})_3\text{Cl}_3\right]$
 - b. $\left[\text{Mn}(\text{CO})_2\text{Cl}_2\text{Br}_2\right]^+$
37. Draw the structures and label the type for all the isomers of each ion.
 - a. $\left[\text{Cr}(\text{CO})_3(\text{NH}_3)_3\right]^{3+}$
 - b. $\left[\text{Pd}(\text{CO})_2(\text{H}_2\text{O})\text{Cl}\right]^+$
38. Draw the structures and label the type for all the isomers of each species.
 - a. $\left[\text{Fe}(\text{CO})_4\text{Cl}_2\right]^+$
 - b. $\left[\text{Pt}(\text{en})\text{Cl}_2\right]$
39. Determine if either isomer of $\left[\text{Cr}(\text{NH}_3)_2(\text{ox})_2\right]^-$ is optically active.
40. Determine if either isomer of $\left[\text{Fe}(\text{CO})_3\text{Cl}_3\right]$ is optically active.

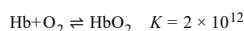
Bonding in Coordination Compounds

41. Draw the octahedral crystal field splitting diagram for each metal ion.
 - a. Zn^{2+}
 - b. Fe^{3+} (high- and low-spin)
 - c. V^{3+}
 - d. Co^{2+} (high-spin)
42. Draw the octahedral crystal field splitting diagram for each metal ion.
 - a. Cr^{3+}
 - b. Cu^{2+}

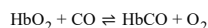
- c. Mn^{3+} (high- and low-spin)
d. Fe^{2+} (low-spin)
43. The $[\text{CrCl}_6]^{3-}$ ion has a maximum absorbance in its absorption spectrum at 735 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
44. The absorption spectrum of the complex ion $[\text{Rh}(\text{NH}_3)_6]^{3+}$ has maximum absorbance at 295 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion.
45. Three complex ions of cobalt(III), $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, and $[\text{CoF}_6]^{3-}$, absorb light at wavelengths of (in no particular order) 290 nm, 440 nm, and 770 nm. Match each complex ion to the appropriate wavelength absorbed. What color would you expect each solution to be?
46. Three bottles of aqueous solutions are discovered in an abandoned lab. The solutions are green, yellow, and purple. It is known that three complex ions of chromium(III) were commonly used in that lab: $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$, and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. Determine the likely identity of each of the colored solutions.
47. The $[\text{Mn}(\text{NH}_3)_6]^{2+}$ ion is paramagnetic with five unpaired electrons. The NH_3 ligand is usually a strong-field ligand. Is NH_3 acting as a strong-field in this case?
48. The complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is paramagnetic. Is the H_2O ligand inducing a strong or weak field?
49. How many unpaired electrons do you expect each complex ion to have?
- a. $[\text{RhCl}_6]^{3-}$
b. $[\text{Co}(\text{OH})_6]^{4-}$
c. $\text{cis-}[\text{Fe}(\text{en})_2(\text{NO}_2)_2]^+$
50. How many unpaired electrons do you expect each complex ion to have?
- a. $[\text{Cr}(\text{CN})_6]^{4-}$
b. $[\text{MnF}_6]^{4-}$
c. $[\text{Ru}(\text{en})_3]^{2+}$
51. How many unpaired electrons do you expect the complex ion $[\text{CoCl}_4]^{2-}$ to have if it is a tetrahedral shape?
52. The complex ion $[\text{PdCl}_4]^{2-}$ is known to be diamagnetic. Use this information to determine if it is a tetrahedral or square planar structure.

Applications of Coordination Compounds

53. What structural feature do hemoglobin, cytochrome c, and chlorophyll have in common?
54. Identify the central metal atom in each complex.
- a. hemoglobin
b. carbonic anhydrase
c. chlorophyll
d. iron blue
55. Hemoglobin exists in two predominant forms in our bodies. One form, known as oxyhemoglobin, has O_2 bound to the iron and the other, known as deoxyhemoglobin, has a water molecule bound instead. Oxyhemoglobin is a low-spin complex that gives arterial blood its red color, and deoxyhemoglobin is a high-spin complex that gives venous blood its darker color. Explain these observations in terms of crystal field splitting. Would you categorize O_2 as a strong- or weak-field ligand?
56. Carbon monoxide and the cyanide ion are both toxic because they bind more strongly than oxygen to the iron in hemoglobin (Hb).



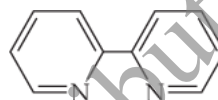
Calculate the equilibrium constant value for this reaction.



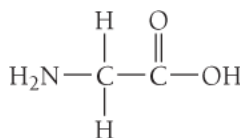
Does the equilibrium favor reactants or products?

Cumulative Problems

57. Recall from Chapter 3 that Cr and Cu are exceptions to the normal orbital filling, resulting in a $[\text{Ar}]4s^13d^5$ configuration. Write the ground state electron configuration for each species.
- Cr, Cr^+ , Cr^{2+} , Cr^{3+}
 - Cu, Cu^+ , Cu^{2+}
58. Most of the second-row transition metals do not follow the normal orbital filling pattern. Five of them—Nb, Mo, Ru, Rh, and Ag—have a $[\text{Kr}]5s^14d^5$ configuration and Pd has a $[\text{Kr}] 4d^{10}$ configuration. Write the ground state electron configuration for each species.
- Mo, Mo^+ , Ag, Ag^+
 - Ru, Ru^{3+}
 - Rh, Rh^{2+}
 - Pd, Pd^+ , Pd^{2+}
59. Draw the Lewis diagrams for each ligand. Indicate the lone pair(s) that may be donated to the metal. Indicate any you expect to be bidentate or polydentate.
- NH_3
 - SCN^-
 - H_2O
60. Draw the Lewis diagrams for each ligand. Indicate the lone pair(s) that may be donated to the metal. Indicate any you expect to be bidentate or polydentate.
- CN^-
 - bipyridyl (bipy), which has the following structure:



- NO_2^-
61. List all the different formulas for an octahedral complex made from a metal (M) and three different ligands (A, B, and C). Describe any isomers for each complex.
62. Amino acids, such as glycine (gly), form complexes with the trace metal ions found in the bloodstream. Glycine, whose structure is shown here, acts as a bidentate ligand coordinating with the nitrogen atom and one of the oxygen atoms.



Draw all the possible isomers of:

- square planar $[\text{Ni}(\text{gly})_2]$
 - tetrahedral $[\text{Zn}(\text{gly})_2]$
 - octahedral $[\text{Fe}(\text{gly})_3]$
63. Oxalic acid solutions remove rust stains. Draw a complex ion that is likely responsible for this effect. Does it have any isomers?
64. W, X, Y, and Z are different monodentate ligands.
- Is the square planar $[\text{NiWXYZ}]^{2+}$ optically active?
 - Is the tetrahedral $[\text{ZnWXYZ}]^{2+}$ optically active?
65. Hexacyanomanganate(III) ion is a low-spin complex. Draw the crystal field splitting diagram with electrons filled in appropriately. Is this complex paramagnetic or diamagnetic?
66. Determine the color and approximate wavelength absorbed most strongly by each solution.
- blue solution
 - red solution

c. yellow solution

67. Draw the structures of all the geometric isomers of $[\text{Ru}(\text{H}_2\text{O})_2(\text{NH}_3)_2\text{Cl}_2]^+$. Draw the mirror images of any that are chiral.
68. A 0.32 mol amount of NH_3 is dissolved in 0.47 L of a 0.38 M silver nitrate solution. Calculate the equilibrium concentrations of all species in the solution.

Challenge Problems

69. When a solution of PtCl_2 reacts with the ligand trimethylphosphine, $\text{P}(\text{CH}_3)_3$, two compounds are produced. The compounds share the same elemental analysis: 46.7% Pt; 17.0% Cl; 14.8% P; 17.2% C; 4.34% H. Determine the formula, draw the structure, and give the systematic name for each compound.
70. Draw a crystal field splitting diagram for a trigonal planar complex ion. Assume the plane of the molecule is perpendicular to the z axis.
71. Draw a crystal field splitting diagram for a trigonal bipyramidal complex ion. Assume the axial positions are on the z axis.
72. Explain why $[\text{Ni}(\text{NH}_3)_4]^{2+}$ is paramagnetic, while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.
73. Sulfide (S^{2-}) salts are notoriously insoluble in aqueous solution.
- a. Calculate the molar solubility of nickel(II) sulfide in water. $K_{\text{sp}}(\text{NiS}) = 3 \times 10^{-16}$
- b. Nickel(II) ions form a complex ion in the presence of ammonia with a formation constant K_f of 2.0×10^8 :
- $$\text{Ni}^{2+} + 6 \text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$$
- Calculate the molar solubility of NiS in 3.0 M NH_3 .
- c. Explain any differences between the answers to parts a and b.
74. Calculate the solubility of $\text{Zn}(\text{OH})_2(\text{s})$ in 2.0 M NaOH solution. (*Hint:* You must take into account the formation of $\text{Zn}(\text{OH})_4^{2-}$, which has a $K_f = 2 \times 10^{15}$.)
75. Halide complexes of metal M of the form $[\text{MX}_6]^{3-}$ are found to be stable in aqueous solution. But it is possible that they undergo rapid ligand exchange with water (or other ligands) that is not detectable because the complexes are less stable. This property is referred to as their *lability*. Suggest an experiment to measure the lability of these complexes that does not employ radioactive labels.
76. The K_f for $[\text{Cu}(\text{en})_2]^{2+}$ is much larger than the one for $[\text{Cu}(\text{NH}_3)_4]^{2+}$. This difference is primarily an entropy effect. Explain why and calculate the difference between the ΔS° values at 298 K for the complete dissociation of the two complex ions. (*Hint:* The value of ΔH is about the same for both systems.)
77. When solid $\text{Cd}(\text{OH})_2$ is added to a solution of 0.10 M NaI, some of it dissolves. Calculate the pH of the solution at equilibrium.

Conceptual Problems

78. Two ligands, A and B, both form complexes with a particular metal ion. When the metal ion complexes with ligand A, the solution is green. When the metal ion complexes with ligand B, the solution is violet. Which of the two ligands results in the larger Δ ?
79. Which element has the higher first ionization energy, Cu or Au?
80. The complexes of Fe^{3+} have magnetic properties that depend on whether the ligands are strong or weak field. Explain why this observation supports the idea that electrons are lost from the 4s orbital before the 3d orbitals in the transition metals.

Questions for Group Work

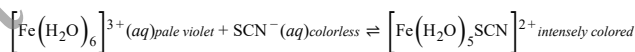
Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

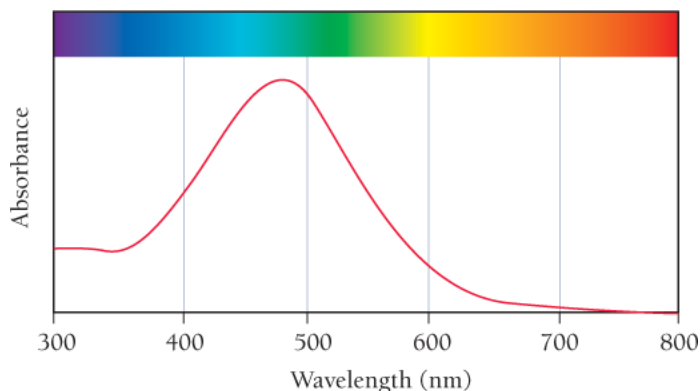
81. Have each group member choose a row of the transition metals in the periodic table and ask each to look up and graph (where appropriate) a trend, choosing from the following: electron configuration, atomic size, ionization energy, or electronegativity. Present your graph to the group. Describe the general trend and any notable exceptions. If possible, form new groups with individuals who researched the same property for a different row of the periodic table.
82. Have each group member write down the names and formulas for two coordination compounds. Taking turns, show the formula to the group, and have the rest of the group members name the compound, with each member contributing one step in the process. Once each group member has had his or her formula named, repeat the process by showing only names to the group and having group members determine the correct formula.
83. Working individually, draw a pair of coordination compounds that are isomers. Take turns showing your drawings to the group and having them identify the type of isomerism and the reasons that your drawing demonstrates that type of isomerism. If your group misidentifies your type of isomerism, rather than telling them the correct answer right away, point out the part of the structure that prevents it from being the type of isomerism they identified.
84. Divide the electron configurations d^1 through d^{10} among the group members such that every configuration is assigned to at least two group members. Working individually, draw the orbital diagram for the configurations assigned to you, including both high-spin and low-spin diagrams where possible. Present your diagrams to your group. Combine all diagrams into one set for the group.
85. Working individually, review one of the applications of coordination complexes. Without you or your group members referring to the text, describe the application you reviewed without mentioning the key words in the heading of the subsection. As each group member describes the application they reviewed, take turns attempting to identify the key words from the heading of the subsection they are describing.

Data Interpretation and Analysis

86. Many aqueous solutions of complex ions display brilliant colors that depend on the identities of the metal ion and ligand(s). Some ligands bind selectively to certain metal ions and produce a complex ion with characteristic colors. These distinctive complex ions serve as qualitative indicators of the presence of particular metal ions. For example, Fe^{3+} is identified by the rapid formation of the intensely colored pentaquathiocyanatoiron(III) complex ion, $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$, when thiocyanate, SCN^- , is added to a solution containing hexaaquairon(III), $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, according to the balanced chemical equation shown here:



Examine the absorption spectrum of an aqueous solution of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ shown here and answer the questions.





Absorption Spectrum of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$

absorption spectrum of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$

- Based on the spectrum, what is the color of an $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ solution?
- Calculate the crystal field splitting energy, Δ , of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ in kJ/mol.
- The hexaaquairon(III) complex ion, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, produces a pale violet aqueous solution. Is the crystal field splitting energy, Δ , of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ smaller or larger than the Δ of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$?
- On the basis of your answers to parts b and c, compare the crystal field strengths of water and thiocyanate ligands.
- The complex ion hexacyanoferrate(III), $[\text{Fe}(\text{CN})_6]^{3-}$, is red in aqueous solution. What can you conclude about the relative crystal field splitting energies of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$?

Answers to Conceptual Connections

Cc 22.1  The element W has the larger radius because it is in the third transition row and Fe is in the first. Atomic radii increase from the first to the second transition row and stay roughly constant from the second to the third.

Cc 22.2  Ligand B forms a yellow solution, which means that the complex absorbs in the violet region. Ligand A forms a red solution, which means that the complex absorbs in the green. Since the violet region of the electromagnetic spectrum is of shorter wavelength (higher energy) than the green region, ligand B produces a higher Δ .

Not for Distribution

Not for Distribution

Not for Distribution