

Self-Assessment Quiz



Q1. What is the electron configuration of the Cu^+ ion?

MISSED THIS? Read Section 26.2

a) $[\text{Ar}]4s^23d^9$
 b) $[\text{Ar}]4s^23d^8$
 c) $[\text{Ar}]4s^13d^9$
 d) $[\text{Ar}]4s^03d^{10}$

Q2. Which metal has the highest first ionization energy?

MISSED THIS? Read Section 26.2

a) Ti b) Mn c) Ru d) Au

Q3. What is the name of the compound $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$?

MISSED THIS? Read Section 26.3

a) pentaamminetrichlorocobalt(III) chloride
 b) pentaamminechlorocobalt(III) chloride
 c) pentaamminechlorocobalt(II) chloride
 d) pentaamminetrichlorocobalt(II) chloride

Q4. What is the formula of hexaaquamanganese(II) sulfate?

MISSED THIS? Read Section 26.3

a) $[\text{Mn}(\text{OH})_6]\text{SO}_4$
 b) $[\text{Mn}(\text{H}_2\text{O})_6]\text{SO}_4$
 c) $[\text{Mn}(\text{H}_2\text{O})_6]^2\text{SO}_4$
 d) $[\text{Mn}_2(\text{H}_2\text{O})_6]\text{SO}_4$

Q5. Which complex ion can exhibit cis-trans isomerism?

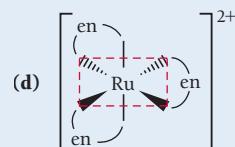
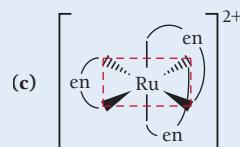
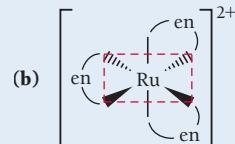
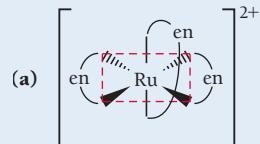
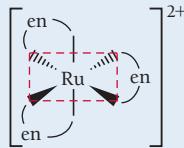
Assume that M is the metal ion, A and B are ligands, and the geometry is octahedral.

MISSED THIS? Read Section 26.4

a) $[\text{MA}_6]^{2+}$
 b) $[\text{MA}_5\text{B}]^{2+}$
 c) $[\text{MA}_4\text{B}_2]^{2+}$
 d) $[\text{MA}_3\text{B}_3]^{2+}$

Q6. Pick the optical isomer of the complex ion represented here:

MISSED THIS? Read Section 26.4



Q7. According to valence bond theory, what is the hybridization of the central metal ion in an octahedral complex ion?

MISSED THIS? Read Section 26.5

a) sp b) sp^3 c) dsp^2 d) d^2sp^3

Q8. Estimate the crystal field splitting energy (in kJ/mol) for a complex ion that is red in solution.

MISSED THIS? Read Section 26.5

a) 228 kJ/mol b) 171 kJ/mol
 c) $2.84 \times 10^{-19} \text{ kJ/mol}$ d) $3.79 \times 10^{-19} \text{ kJ/mol}$

Q9. Use crystal field theory to determine the number of unpaired electrons in the complex ion $[\text{Fe}(\text{CN})_6]^{4-}$.

MISSED THIS? Read Section 26.5

a) 0 b) 2 c) 3 d) 4

a) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ b) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$
 c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ d) $[\text{CoCl}_6]^{3-}$

Answers: 1. (d) 2. (d) 3. (b) 4. (b) 5. (c, d) 6. (b) 7. (d) 8. (a) 9. (a) 10. (c)

CHAPTER 26 IN REVIEW

TERMS

Section 26.1

crystal field theory (1136)

Section 26.2

lanthanide contraction (1138)

Section 26.3

complex ion (1140)

ligand (1140)

coordination compound

(1140)

primary valence (1140)

secondary valence (1140)

coordination number (1140)

coordinate covalent bond

(1141)

monodentate (1142)

bidentate (1142)

polydentate (1142)

chelate (1142)

chelating agent (1142)

geometric isomers (1147)

optical isomers (1148)

Section 26.4

structural isomers (1145)

stereoisomers (1145)

coordination isomers (1145)

linkage isomers (1145)

Section 26.5

strong-field complex (1151)

weak-field complex (1151)

low-spin complex (1154)

high-spin complex (1154)

CONCEPTS

Electron Configurations (26.2)

- As we move across a row of transition elements, electrons add to the $(n-1)d$ orbitals, resulting in a general electron configuration for the first- and second-row transition elements of [noble gas] $ns^2(n-1)d^x$ and for the third and fourth rows of [noble gas] $ns^2(n-2)f^{14}(n-1)d^x$, where x ranges from 1 to 10.
- A transition element forms a cation by losing electrons from the ns orbitals before losing electrons from the $(n-1)d$ orbitals.

Periodic Trends (26.2)

- The variations in atomic size, ionization energy, and electronegativity across a row in the periodic table are similar to those of main-group elements (although the trends are less pronounced and less regular). As we move down a group, however, atomic size increases from the first row to the second but stays roughly constant from the second row to the third because of the lanthanide contraction. This contraction results in ionization energy and electronegativity trends as we move down a column that are opposite of the main-group elements.

Composition and Naming of Coordination Compounds (26.3)

- A coordination compound is composed of a complex ion and a counterion.
- A complex ion contains a central metal ion bound to one or more ligands. The number of ligands directly bound to the metal ion is the coordination number.
- The ligand forms a coordinate covalent bond to the metal ion by donating a pair of electrons to an empty orbital on the metal.
- Ligands that donate a single pair of electrons are monodentate. A ligand that donates two pairs of electrons is bidentate, and a ligand that donates more than two pairs is polydentate.

- In naming coordination compounds, we use the name of the cation followed by the name of the anion. To name a complex ion, we use the guidelines outlined in Section 26.3.

Types of Isomers (26.4)

- We broadly divide the isomerism observed in coordination compounds into two categories: structural isomers, in which atoms are connected differently to one another, and stereoisomers, in which atoms are connected in the same way but the ligands have a different spatial arrangement about the metal atom.
- Structural isomers are either coordination isomers (a coordinated ligand exchanges places with an uncoordinated counterion) or linkage isomers (a particular ligand has the ability to coordinate to the metal in different ways).
- Stereoisomers are either geometric isomers (the ligands bonded to the metal have a different spatial arrangement relative to each other, leading to cis-trans or fac-mer isomers) or optical isomers (nonsuperimposable mirror images).

Crystal Field Theory (26.5)

- Crystal field theory is a bonding model for transition metal complex ions. The model describes how the degeneracy of the d orbitals is broken by the repulsive forces between the electrons on the ligands around the metal ion and the d orbitals in the metal ion.
- The energy difference between the split d orbitals is the crystal field splitting energy (Δ). The magnitude of Δ depends in large part on the ligands bound to the metal.
- Octahedral complexes with a d^4 , d^5 , d^6 , or d^7 metal ion can have two possible electronic configurations with different numbers of unpaired electrons. The first, called high-spin, has the same number of unpaired electrons as the free metal ion and is usually the result of a weak crystal field. The second, called low-spin, has fewer unpaired electrons than the free metal ion and is usually the result of a strong crystal field.

EQUATIONS AND RELATIONSHIPS

Crystal Field Splitting Energy (26.5)

$$\Delta = hc/\lambda \text{ (where } \lambda \text{ is the wavelength of maximum absorption)}$$

LEARNING OUTCOMES

Chapter Objectives

Write electron configurations for transition elements (26.2)

Name and write formulas for complex ions and coordination compounds (26.3)

Identify and draw geometric isomers (26.4)

Identify and draw optical isomers (26.4)

Calculate crystal field splitting energy (26.5)

Predict high-spin and low-spin octahedral complex ions (26.5)

Describe applications of coordination compounds (26.6)

Assessment

Examples 26.1, 26.2 For Practice 26.1, 26.2 Exercises 17–20

Examples 26.3, 26.4 For Practice 26.3, 26.4 Exercises 21–28

Examples 26.5, 26.6 For Practice 26.5, 26.6 Exercises 29–36

Example 26.7 For Practice 26.7 Exercises 37–40

Example 26.8 For Practice 26.8 Exercises 43–46

Examples 26.9, 26.10 For Practice 26.9, 26.10 Exercises 41–42, 47–52

Exercises 53–56

EXERCISES

Mastering Chemistry provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

REVIEW QUESTIONS

- When a transition metal atom forms an ion, which electrons are lost first?
- Explain why transition metals exhibit multiple oxidation states instead of a single oxidation state (like most of the main-group metals).
- Why is the +2 oxidation state so common for transition metals?
- 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.
- Gold is the most electronegative transition metal. Explain.
- Briefly define each term.
 - coordination number
 - ligand
 - bidentate and polydentate
 - complex ion
 - chelating agent
- Using the Lewis acid-base definition, how would you categorize a ligand? How would you categorize a transition metal ion?
- Explain the differences between each pair of isomer types.
 - structural isomer and stereoisomer
 - linkage isomer and coordination isomer
 - geometric isomer and optical isomer
- Which complex ion geometry has the potential to exhibit cis-trans isomerism: linear, tetrahedral, square planar, octahedral?
- How can you tell whether a complex ion is optically active?
- Explain the differences between weak-field and strong-field metal complexes.
- Explain why compounds of Sc^{3+} are colorless, but compounds of Ti^{3+} are colored.
- Explain why compounds of Zn^{2+} are colorless, but compounds of Cu^{2+} are often blue or green.
- Explain the differences between high-spin and low-spin metal complexes.
- Why are almost all tetrahedral complexes high-spin?
- Many transition metal compounds are colored. How does crystal field theory account for this?

PROBLEMS BY TOPIC

Properties of Transition Metals

- Write the ground state electron configuration for each atom and ion pair. **MISSED THIS? Read Section 26.2**
 - Ni , Ni^{2+}
 - Mn , Mn^{4+}
 - Y , Y^+
 - Ta , Ta^{2+}
- Write the ground state electron configuration for each atom and ion pair.
 - Zr , Zr^{2+}
 - Co , Co^{2+}
 - Tc , Tc^{3+}
 - Os , Os^{4+}
- Determine the highest possible oxidation state for each element. **MISSED THIS? Read Section 26.2**
 - V
 - Re
 - Pd
- Which first-row transition metal(s) has the following highest possible oxidation state?
 - +3
 - +7
 - +4

Coordination Compounds

- Determine the oxidation state and coordination number of the metal ion in each complex ion. **MISSED THIS? Read Section 26.3**
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^-$
 - $[\text{Cu}(\text{CN})_4]^{2-}$
 - $[\text{Ag}(\text{NH}_3)_2]^+$
- Determine the oxidation state and coordination number of the metal ion in each complex ion.
 - $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$
 - $[\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{Co}(\text{ox})_3]^{4-}$
 - $[\text{PdCl}_4]^{2-}$
- Name each complex ion or coordination compound. **MISSED THIS? Read Section 26.3**
 - $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Cu}(\text{CN})_4]^{2-}$
 - $[\text{Fe}(\text{NH}_3)_5\text{Br}]^{2-}$
 - $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)(\text{OH})]\text{Cl}_2$
- Name each complex ion or coordination compound.
 - $[\text{Mn}(\text{CO})_3(\text{NO}_2)_3]^{2+}$
 - $\text{Na}[\text{Cr}(\text{H}_2\text{O})_2(\text{ox})_2]$
 - $[\text{Co}(\text{en})_3][\text{Fe}(\text{CN})_6]$
- Write the formula for each complex ion or coordination compound. **MISSED THIS? Read Section 26.3**
 - hexaamminechromium(III)
 - potassium hexacyanoferrate(III)
 - ethylenediaminedithiocyanatocupper(II)
 - tetraqua platinum(II) hexachloroplatinate(IV)
- Write the formula for each complex ion or coordination compound.
 - hexaaquanickel(II) chloride
 - pentacarbonylchloromanganese(I)
 - ammonium diaquatetrabromovanadate(III)
 - tris(ethylenediamine)cobalt(III) trioxalatoferrate(III)
- Write the formula and the name of each complex ion. **MISSED THIS? Read Section 26.3**
 - a complex ion with Co^{3+} as the central ion and three NH_3 molecules and three CN^- ions as ligands
 - a complex ion with Cr^{3+} as the central ion and a coordination number of 6 with ethylenediamine ligands
- Write the formula and the name of each complex ion or coordination compound.
 - a complex ion with four water molecules and two ONO^- ions connected to an $\text{Fe}(\text{III})$ ion
 - a coordination compound made of two complex ions: one a complex of $\text{V}(\text{III})$ with two ethylenediamine molecules and two Cl^- ions as ligands and the other a complex of $\text{Ni}(\text{II})$ having a coordination number of 4 with Cl^- ions as ligands

Structure and Isomerism

29. Draw two linkage isomers of $[\text{Mn}(\text{NH}_3)_5(\text{NO}_2)]^{2+}$.

MISSED THIS? Read Section 26.4

30. Draw two linkage isomers of $[\text{PtCl}_3(\text{SCN})]^{2-}$.

31. Write the formulas and names for the coordination isomers of $[\text{Fe}(\text{H}_2\text{O})_6]\text{Cl}_2$. **MISSED THIS? Read Section 26.4**

32. Write the formulas and names for the coordination isomers of $[\text{Co}(\text{en})_3][\text{Cr}(\text{ox})_3]$.

33. Which complexes exhibit geometric isomerism?

MISSED THIS? Read Section 26.4

a. $[\text{Cr}(\text{NH}_3)_5(\text{OH})]^{2+}$ b. $[\text{Cr}(\text{en})_2\text{Cl}_2]^{+}$

c. $[\text{Cr}(\text{H}_2\text{O})(\text{NH}_3)_3\text{Cl}_2]^{+}$ d. $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{2-}$

e. $[\text{Pt}(\text{H}_2\text{O})_2(\text{CN})_2]$

34. Which complexes exhibit geometric isomerism?

a. $[\text{Co}(\text{H}_2\text{O})_2(\text{ox})_2]^{2-}$ b. $[\text{Co}(\text{en})_3]^{3+}$

c. $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_2(\text{ox})]^{+}$ d. $[\text{Ni}(\text{NH}_3)_2(\text{en})]^{2+}$

e. $[\text{Ni}(\text{CO})_2\text{Cl}_2]$

35. If W, X, Y, and Z are different monodentate ligands, how many geometric isomers are there for each ion?

MISSED THIS? Read Section 26.4

a. square planar $[\text{NiWXYZ}]^{2+}$

b. tetrahedral $[\text{ZnWXYZ}]^{2+}$

36. How many geometric isomers are there for each species?

a. $[\text{Fe}(\text{CO})_3\text{Cl}_3]$ b. $[\text{Mn}(\text{CO})_2\text{Cl}_2\text{Br}_2]^{+}$

37. Draw the structures and label the type for all the isomers of each ion. **MISSED THIS? Read Section 26.4**

a. $[\text{Cr}(\text{CO})_3(\text{NH}_3)_3]^{3+}$ b. $[\text{Pd}(\text{CO})_2(\text{H}_2\text{O})\text{Cl}]^{+}$

38. Draw the structures and label the type for all the isomers of each species.

a. $[\text{Fe}(\text{CO})_4\text{Cl}_2]^{+}$ b. $[\text{Pt}(\text{en})\text{Cl}_2]$

39. Determine if either isomer of $[\text{Cr}(\text{NH}_3)_2(\text{ox})_2]^{2-}$ is optically active. **MISSED THIS? Read Section 26.4**

40. Determine if either isomer of $[\text{Fe}(\text{CO})_3\text{Cl}_3]$ is optically active.

Bonding in Coordination Compounds

41. Draw the octahedral crystal field splitting diagram for each metal ion. **MISSED THIS? Read Section 26.5**

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 in its absorption spectrum at 735 nm. Calculate the crystal field splitting energy (in kJ/mol) for this ion. **MISSED THIS? Read Section 26.5**

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? **MISSED THIS? Read Section 26.5**

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 ligand in this case?

MISSED THIS? Read Section 26.5

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 would you expect for each complex ion? **MISSED THIS? Read Section 26.5**

a. $[\text{RhCl}_6]^{3-}$
b. $[\text{Co}(\text{OH})_6]^{4-}$
c. $cis-[\text{Fe}(\text{en})_2(\text{NO}_2)_2]^{2+}$

50. How many unpaired electrons would you expect for each complex ion?

a. $[\text{Cr}(\text{CN})_6]^{4-}$
b. $[\text{MnF}_6]^{4-}$
c. $[\text{Ru}(\text{en})_3]^{2+}$

51. How many unpaired electrons would you expect for the complex ion $[\text{CoCl}_4]^{2-}$ if it is a tetrahedral shape?

MISSED THIS? Read Section 26.5

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?

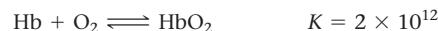
MISSED THIS? Read Section 26.6

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? **MISSED THIS? Read Section 26.6**

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 9 that Cr and Cu are exceptions to the normal orbital filling, resulting in a $[\text{Ar}] 4s^1 3d^x$ configuration. Write the ground state electron configuration for each species.

- $\text{Cr, Cr}^+, \text{Cr}^{2+}, \text{Cr}^{3+}$
- $\text{Cu, Cu}^+, \text{Cu}^{2+}$

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 $[\text{Kr}] 5s^1 4d^x$ configuration and Pd has a $[\text{Kr}] 4d^{10}$ configuration. Write the ground state electron configuration for each species.

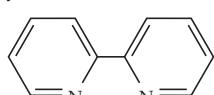
- $\text{Mo, Mo}^+, \text{Ag, Ag}^+$
- Ru, Ru^{3+}
- Rh, Rh^{2+}
- $\text{Pd, Pd}^+, \text{Pd}^{2+}$

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.

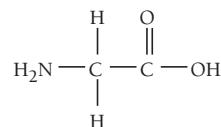
- CN^-
- bipyridine (bipy), which has the following structure:



c. 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
- 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.

- Calculate the molar solubility of nickel(II) sulfide in water. $K_{\text{sp}}(\text{NiS}) = 3 \times 10^{-16}$

- 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 .

- Explain any differences between the answers to parts a and b.

74. Calculate the solubility of $\text{Zn}(\text{OH})_2(s)$ 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 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

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

81. Choose a row of the transition metals in the periodic table. Have each group member look up and graph (where appropriate) a separate trend for the elements in that row, choosing from electron configuration, atomic size, ionization energy, and electronegativity. Each member should present a graph to the group and describe the general trend and any notable exceptions. If possible, form new groups made up of individuals who researched the same property for different rows of the periodic table.
82. Have each group member write down the names and formulas for two coordination compounds. Taking turns, show each formula to the group and have the rest of the group name the compound, with each member contributing one step in the process. Once all group members have had their formulas named, repeat the process by showing each formula name 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

Active Classroom Learning

and have them identify the type of isomerism and the reasons 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 thought it was.

84. Divide the electron configurations d^1 through d^{10} among the group members so 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 everyone's diagrams into one set for the group.

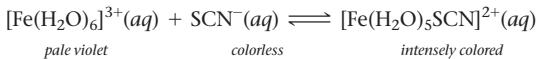
85. Working individually, review one of the applications of coordination complexes. Without referring to the text or mentioning the key words in the heading of the subsection, describe the application you reviewed. As group members each describe the application they reviewed, take turns attempting to identify the key words from the heading of the subsection they are describing.



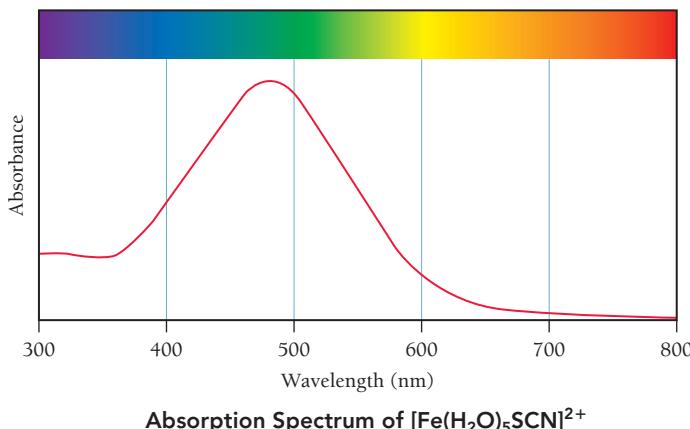
DATA INTERPRETATION AND ANALYSIS

Qualitative Test for Fe^{3+} Ions in Solution

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, producing complex ions with characteristic colors. These distinctive complex ions serve as qualitative indicators for the presence of particular metal ions. For example, Fe^{3+} is identified by the rapid formation of the intensely colored penta aqua thio-cyanato iron(III) complex ion, $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$, when thiocyanate, SCN^- , is added to a solution containing hexa aqua iron(III), $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, according to the following chemical equation:



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 that follow.



- a. What is the color of the aqueous solution of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$ based on the spectrum?
- b. Calculate the crystal field splitting energy, Δ , of $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$, in kJ/mol .
- c. 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 $[\text{Fe}(\text{H}_2\text{O})_5\text{SCN}]^{2+}$?

- d. On the basis of your answers to parts b and c, compare the crystal field strengths of water and thiocyanate ligands.
- e. 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

Atomic Size

26.1 (b) 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.

Isomerism

26.2 (c) Geometric isomers are two molecules in which the atoms are bonded together in the same way, but with different overall orientations in space. Therefore, geometric isomers are *not* structural isomers.

Weak- and Strong-Field Ligands

26.3 (b) 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 region. Since the violet region of the electromagnetic spectrum is of shorter wavelength (higher energy) than the green region, ligand B produces a higher Δ .

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