## CHAPTER 19

## TRANSITION METALS AND COORDINATION CHEMISTRY

## Transition Metals

6. Transition metal ions lose the s electrons before the d electrons.
a. Ti: $[\mathrm{Ar}] 4 \mathrm{~s}^{2} 3 \mathrm{~d}^{2}$
b. Re: $[X e] 6 s^{2} 4 f^{14} 5 d^{5}$

$$
\begin{aligned}
& \mathrm{Ti}^{2^{+}}:[\mathrm{Ar}] 3 \mathrm{~d}^{2} \\
& \mathrm{Ti}^{4+}:[\mathrm{Ar}] \text { or }[\mathrm{Ne}] 3 \mathrm{~s}^{2} 3 \mathrm{p}^{6}
\end{aligned}
$$

c. Ir: $[\mathrm{Xe}] 6 \mathrm{~s}^{2} 4 \mathrm{f}^{14} 5 \mathrm{~d}^{7}$

$$
\mathrm{Re}^{2+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{5}
$$

$\mathrm{Ir}^{2+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{7}$

$$
\mathrm{Re}^{3+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{4}
$$

$\mathrm{Ir}^{3+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{6}$
7. Cr and Cu are exceptions to the normal filling order of electrons.
a. $\mathrm{Cr}:[\mathrm{Ar}] 4 \mathrm{~s}^{1} 3 \mathrm{~d}^{5}$
b. $\mathrm{Cu}:[\mathrm{Ar}] 4 \mathrm{~s}^{1} 3 \mathrm{~d}^{10}$
c. $\mathrm{V}:[\mathrm{Ar}] 4 \mathrm{~s}^{2} 3 \mathrm{~d}^{3}$
$\mathrm{Cr}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{4}$
$\mathrm{Cu}^{+}:[\mathrm{Ar}] 3 \mathrm{~d}^{10}$
$\mathrm{V}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{3}$
$\mathrm{V}^{3+}:[\mathrm{Ar}] 3 \mathrm{~d}^{2}$
8. Chromium $\left([\operatorname{Ar}] 4 s^{0} 3 d^{5}\right)$ and copper $\left([\operatorname{Ar}] 4 s^{1} 3 d^{10}\right)$ have electron configurations that are different from that predicted from the periodic table. Other exceptions to the predicted filling order are transition metal ions. These all lose the selectrons before they lose the d electrons. In neutral atoms, the $n \mathrm{~s}$ and $(n-1) \mathrm{d}$ orbitals are very close in energy, with the $n$ s orbitals slightly lower in energy. However, for transition metal ions, there is an apparent shifting of energies between the $n \mathrm{~s}$ and $(n-1) \mathrm{d}$ orbitals. For transition metal ions, the energy of the ( $n-1$ )d orbitals are significantly less than that of the $n$ s electrons. So when transition metal ions form, the highest-energy electrons are removed, which are the $n$ s electrons. For example, $\mathrm{Mn}^{2+}$ has the electron configuration $[\mathrm{Ar}] 4 \mathrm{~s}^{0} 3 \mathrm{~d}^{5}$ and not $[\mathrm{Ar}] 4 \mathrm{~s}^{2} 3 \mathrm{~d}^{3}$.

Most transition metals have unfilled d orbitals, which creates a large number of other electrons that can be removed. Stable ions of the representative metals are determined by how many $s$ and $p$ valence electrons can be removed. In general, representative metals lose all of the $s$ and $p$ valence electrons to form their stable ions. Transition metals generally lose the $s$ electron(s) to form +1 and +2 ions, but they can also lose some (or all) of the $d$ electrons to form other oxidation states as well.
9. The lanthanide elements are located just before the 5 d transition metals. The lanthanide contraction is the steady decrease in the atomic radii of the lanthanide elements when going from left to right across the periodic table. As a result of the lanthanide contraction, the sizes of the 4 d and 5 d elements are very similar (see the following exercise). This leads to a greater similarity in the chemistry of the 4 d and 5 d elements in a given vertical group.
10. Size also decreases going across a period. Sc and Ti , and Y and Zr are adjacent elements. There are 14 elements (the lanthanides) between La and Hf, making Hf considerably smaller.
11. a. molybdenum(IV) sulfide; molybdenum(VI) oxide
b. $\mathrm{MoS}_{2},+4 ; \mathrm{MoO}_{3},+6 ;\left(\mathrm{NH}_{4}\right)_{2} \mathrm{Mo}_{2} \mathrm{O}_{7},+6 ;\left(\mathrm{NH}_{4}\right)_{6} \mathrm{Mo}_{7} \mathrm{O}_{24} \bullet 4 \mathrm{H}_{2} \mathrm{O},+6$
12. a. 4 O atoms on faces $\times 1 / 2 \mathrm{O} /$ face $=2 \mathrm{O}$ atoms, 2 O atoms inside body; total: 4 O atoms

8 Ti atoms on corners $\times 1 / 8 \mathrm{Ti} /$ corner +1 Ti atom/body center $=2 \mathrm{Ti}$ atoms
Formula of the unit cell is $\mathrm{Ti}_{2} \mathrm{O}_{4}$. The empirical formula is $\mathrm{TiO}_{2}$.
$+4-2 \quad 0 \quad 0 \quad+4-1 \quad+4-2 \quad+2-2$
b. $2 \mathrm{TiO}_{2}+3 \mathrm{C}+4 \mathrm{Cl}_{2} \rightarrow 2 \mathrm{TiCl}_{4}+\mathrm{CO}_{2}+2 \mathrm{CO} ; \mathrm{Cl}$ is reduced, and C is oxidized. $\mathrm{Cl}_{2}$ is the oxidizing agent, and C is the reducing agent.
$+4-1 \quad 0 \quad+4-2 \quad 0$
$\mathrm{TiCl}_{4}+\mathrm{O}_{2} \rightarrow \mathrm{TiO}_{2}+2 \mathrm{Cl}_{2}$; O is reduced, and Cl is oxidized. $\mathrm{O}_{2}$ is the oxidizing agent, and $\mathrm{TiCl}_{4}$ is the reducing agent.
13. $\mathrm{TiF}_{4}$ : ionic compound containing $\mathrm{Ti}^{4+}$ ions and $\mathrm{F}^{-}$ions. $\mathrm{TiCl}_{4}, \mathrm{TiBr}_{4}$, and $\mathrm{TiI}_{4}$ : covalent compounds containing discrete, tetrahedral $\mathrm{TiX}_{4}$ molecules. As these covalent molecules get larger, the boiling points and melting points increase because the London dispersion forces increase. $\mathrm{TiF}_{4}$ has the highest boiling point because the interparticle forces are stronger in ionic compounds than in covalent compounds.
14. $\mathrm{Fe}_{2} \mathrm{O}_{3}$ : iron has a +3 oxidation state; $\mathrm{Fe}_{3} \mathrm{O}_{4}$ : iron has a $+8 / 3$ oxidation state. The three iron ions in $\mathrm{Fe}_{3} \mathrm{O}_{4}$ must have a total charge of +8 . The only combination that works is to have two $\mathrm{Fe}^{3+}$ ions and one $\mathrm{Fe}^{2+}$ ion per formula unit. This makes sense from the other formula for magnetite, $\mathrm{FeO} \cdot \mathrm{Fe}_{2} \mathrm{O}_{3}$. FeO has an $\mathrm{Fe}^{2+}$ ion, and $\mathrm{Fe}_{2} \mathrm{O}_{3}$ has two $\mathrm{Fe}^{3+}$ ions.
15. $\mathrm{H}^{+}+\mathrm{OH}^{-} \rightarrow \mathrm{H}_{2} \mathrm{O}$; sodium hydroxide $(\mathrm{NaOH})$ will react with the $\mathrm{H}^{+}$on the product side of the reaction. This effectively removes $\mathrm{H}^{+}$from the equilibrium, which will shift the reaction to the right to produce more $\mathrm{H}^{+}$and $\mathrm{CrO}_{4}{ }^{2-}$. As more $\mathrm{CrO}_{4}{ }^{2-}$ is produced, the solution turns yellow.
16. a. Coordination compound: a compound composed of a complex ion (see b) and counter ions (see c) sufficient to give no net charge.
b. Complex ion: a charged species consisting of a metal ion surrounded by ligands (see e).
c. Counter ions: anions or cations that balance the charge on a complex ion in a coordination compound.
d. Coordination number: the number of bonds formed between the metal ion and the ligands (see e) in a complex ion.
e. Ligand: species that donates a pair of electrons to form a covalent bond to a metal ion. Ligands act as Lewis bases (electron pair donors).
f. Chelate: ligand that can form more than one bond to a metal ion.
g. Bidentate: ligand that forms two bonds to a metal ion.
17. Because transition metals form bonds to species that donate lone pairs of electrons, transition metals are Lewis acids (electron pair acceptors). The Lewis bases in coordination compounds are the ligands, all of which have an unshared pair of electrons to donate. The coordinate covalent bond between the ligand and the transition metal just indicates that both electrons in the bond originally came from one of the atoms in the bond. Here, the electrons in the bond come from the ligand.
18. Linear geometry ( $180^{\circ}$ bond angles) is observed when the coordination number is 2 . Tetrahedral geometry ( $109.5^{\circ}$ bond angles) or square planar geometry ( $90^{\circ}$ bond angles) is observed when the coordination number is 4 . Octahedral geometry ( $90^{\circ}$ bond angles) is observed when the coordination number is 6 .

For the following complex ions, see Table 19.13 if you don't know the formula, the charge, or the number of bonds the ligands form.
a. $\operatorname{Ag}(\mathrm{CN})_{2}{ }^{-}$
b. $\mathrm{Cu}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}{ }^{+}$
c. $\mathrm{Mn}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}^{2-}$
d. $\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4}{ }^{2+}$
e. $\mathrm{Fe}(\mathrm{EDTA})^{-}$; note: EDTA has an overall $4-$ charge and is a six coordinate ligand.
f. $\mathrm{Co}(\mathrm{Cl})_{6}{ }^{4-}$
g. $\mathrm{Cr}(\mathrm{en})_{3}{ }^{3+}$, where en $=$ ethylenediane $\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)$
19. $\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+6 \mathrm{H}_{2} \mathrm{C}_{2} \mathrm{O}_{4}(\mathrm{aq}) \rightarrow 2 \mathrm{Fe}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}{ }^{3-}(\mathrm{aq})+3 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})+6 \mathrm{H}^{+}(\mathrm{aq})$; the oxalate anion forms a soluble complex ion with iron in rust $\left(\mathrm{Fe}_{2} \mathrm{O}_{3}\right)$, which allows rust stains to be removed.
20. a. With $\mathrm{NH}_{4}{ }^{+}$ions, $\mathrm{Cl}^{-}$ions, and neutral $\mathrm{H}_{2} \mathrm{O}$ molecules present, iron has a +2 charge. $\mathrm{Fe}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{6}$
b. With $\mathrm{I}^{-}$ions and neutral $\mathrm{NH}_{3}$ and $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ molecules present, cobalt has a +2 charge. $\mathrm{Co}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{7}$
c. With $\mathrm{Na}^{+}$and $\mathrm{F}^{-}$ions present, tantalum has a +5 charge. $\mathrm{Ta}^{5+}:[\mathrm{Xe}] 4 \mathrm{f}^{14}$ (expected)
d. Each platinum complex ion must have an overall charge if the two complex ions are counter ions to each other. Knowing that platinum forms +2 and +4 charged ions, we can deduce that the six coordinate complex ion has a +4 charged platinum ion and the four coordinate complex ion has a +2 charged ion. With $\mathrm{I}^{-}$ions and neutral $\mathrm{NH}_{3}$ molecules present, the two complex ions are $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{I}_{2}\right]^{2+}$ and $\left[\mathrm{PtI}_{4}\right]^{2-}$.

$$
\mathrm{Pt}^{2+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{8} ; \quad \mathrm{Pt}^{4+}:[\mathrm{Xe}] 4 \mathrm{f}^{14} 5 \mathrm{~d}^{6}
$$

21. See Section 19.3 for a good summary of the nomenclature rules.
a. The correct name is tetraamminecopper(II) chloride. The complex ion is named incorrectly in several ways.
b. The correct name is bis(ethylenediamine)nickel(II) sulfate. The ethylenediamine ligands are neutral, and sulfate has a $2-$ charge. Therefore, $\mathrm{Ni}^{2+}$ is present, not $\mathrm{Ni}^{4+}$.
c. The correct name is potassium diaquatetrachlorochromate(III). Because the complex ion is an anion, the -ate suffix ending is added to the name of the metal. Also, the ligands were not in alphabetical order ( $a$ in aqua comes before $c$ in chloro).
d. The correct name is sodium tetracyanooxalatocobaltate(II). The only error is that tetra should be omitted in front of sodium. That four sodium ions are needed to balance charge is deduced from the name of the complex ion.
22. 

a. hexaamminecobalt(II) chloride
b. hexaaquacobalt(III) iodide
c. potassium tetrachloroplatinate(II)
d. potassium hexachloroplatinate(II)
e. pentaamminechlorocobalt(III) chloride
f. triamminetrinitrocobalt(III)
23. To determine the oxidation state of the metal, you must know the charges of the various common ligands (see Tables 19.13 and 19.14 of the text).
a. pentaamminechlororuthenium(III) ion
b. hexacyanoferrate(II) ion
c. tris(ethylenediamine)manganese(II) ion
d. pentaamminenitrocobalt(III) ion
24. a. pentaaquabromochromium(III) bromide
b. sodium hexacyanocobaltate(III)
c. bis(ethylenediamine)dinitroiron(III) chloride
d. tetraamminediiodoplatinum(IV) tetraiodoplatinate(II)
25.
a. $\mathrm{K}_{2}\left[\mathrm{CoCl}_{4}\right]$
b. $\left[\mathrm{Pt}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{CO})_{3}\right] \mathrm{Br}_{2}$
c. $\mathrm{Na}_{3}\left[\mathrm{Fe}(\mathrm{CN})_{2}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}\right]$
d. $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{3} \mathrm{Cl}\left(\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}\right)\right] \mathrm{I}_{2}$
26.
a. $\mathrm{FeCl}_{4}^{-}$
b. $\left[\mathrm{Ru}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{H}_{2} \mathrm{O}\right]^{3+}$
c. $\left[\mathrm{Cr}(\mathrm{CO})_{4}(\mathrm{OH})_{2}\right]^{+}$
d. $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right) \mathrm{Cl}_{3}\right]^{-}$
27. $\mathrm{BaCl}_{2}$ gives no precipitate, so $\mathrm{SO}_{4}{ }^{2-}$ must be in the coordination sphere $\left(\mathrm{BaSO}_{4}\right.$ is insoluble). A precipitate with $\mathrm{AgNO}_{3}$ means the $\mathrm{Cl}^{-}$is not in the coordination sphere, that is, $\mathrm{Cl}^{-}$is a counter ion. Because there are only four ammonia molecules in the coordination sphere, $\mathrm{SO}_{4}{ }^{2-}$ must be acting as a bidentate ligand. The structure is:

$\mathrm{Cl}^{-}$
28. $\mathrm{CN}^{-}$is a weak base, so $\mathrm{OH}^{-}$ions are present. When the acid $\mathrm{H}_{2} \mathrm{~S}$ is added, $\mathrm{OH}^{-}$and $\mathrm{CN}^{-}$ions are removed as $\mathrm{H}_{2} \mathrm{O}$ and HCN . The hydrated $\mathrm{Ni}^{2+}$ complex ion forms after the $\mathrm{OH}^{-}$and $\mathrm{CN}^{-}$ ions are removed by addition of $\mathrm{H}_{2} \mathrm{~S}$. The two reactions are:

$$
\begin{aligned}
& \mathrm{Ni}^{2+}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq}) \rightarrow \mathrm{Ni}(\mathrm{OH})_{2}(\mathrm{~s}) ; \text { the precipitate is } \mathrm{Ni}(\mathrm{OH})_{2}(\mathrm{~s}) . \\
& \mathrm{Ni}(\mathrm{OH})_{2}(\mathrm{~s})+4 \mathrm{CN}^{-}(\mathrm{aq}) \rightarrow \mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}(\mathrm{aq})+2 \mathrm{OH}^{-}(\mathrm{aq}) ; \mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-} \text { is a soluble species. } \\
& \mathrm{Ni}(\mathrm{CN})_{4}{ }^{2-}(\mathrm{aq})+4 \mathrm{H}_{2} \mathrm{~S}(\mathrm{aq})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightarrow \mathrm{Ni}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}(\mathrm{aq})+4 \mathrm{HCN}(\mathrm{aq})+4 \mathrm{HS}^{-}(\mathrm{aq})
\end{aligned}
$$

29. Because each compound contains an octahedral complex ion, the formulas for the compounds are $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{I}_{3},\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{I}_{2}\right] \mathrm{I}_{2}, \mathrm{Na}_{2}\left[\mathrm{PtI}_{6}\right]$, and $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{I}_{2}\right]$. Note that in some cases the $\mathrm{I}^{-}$ ions are ligands bound to the transition metal ion as required for a coordination number of 6 , whereas in other cases the $\mathrm{I}^{-}$ions are counter ions required to balance the charge of the complex ion. The $\mathrm{AgNO}_{3}$ solution will only precipitate the $\mathrm{I}^{-}$counter ions and will not precipitate the I- ligands. Therefore, 3 mol AgI will precipitate per mole of $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}\right]_{3}, 2$ mol AgI will precipitate per mole of $\left[\mathrm{Pt}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{I}_{2}\right] \mathrm{I}_{2}, 0 \mathrm{~mol}$ AgI will precipitate per mole of $\mathrm{Na}_{2}\left[\mathrm{PtI}_{6}\right]$, and 1 mol AgI will precipitate per mole of $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{I}_{2}\right] \mathrm{I}$.
30. Test tube 1: Added $\mathrm{Cl}^{-}$reacts with $\mathrm{Ag}^{+}$to form a silver chloride precipitate. The net ionic equation is $\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \rightarrow \mathrm{AgCl}(\mathrm{s})$. Test tube 2: Added $\mathrm{NH}_{3}$ reacts with $\mathrm{Ag}^{+}$ions to form a soluble complex ion $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$. As this complex ion forms, $\mathrm{Ag}^{+}$is removed from solution, which causes the $\mathrm{AgCl}(\mathrm{s})$ to dissolve. When enough $\mathrm{NH}_{3}$ is added, all the silver chloride precipitate will dissolve. The equation is $\mathrm{AgCl}(\mathrm{s})+2 \mathrm{NH}_{3}(\mathrm{aq}) \rightarrow \mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}(\mathrm{aq})+$ $\mathrm{Cl}^{-}(\mathrm{aq})$. Test tube 3: Added $\mathrm{H}^{+}$reacts with the weak base $\mathrm{NH}_{3}$ to form $\mathrm{NH}_{4}{ }^{+}$. As $\mathrm{NH}_{3}$ is removed from the $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$complex ion, $\mathrm{Ag}^{+}$ions are released to solution and can then react with $\mathrm{Cl}^{-}$to reform $\mathrm{AgCl}(\mathrm{s})$. The equations are $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}(\mathrm{aq})+2 \mathrm{H}^{+}(\mathrm{aq}) \rightarrow \mathrm{Ag}^{+}(\mathrm{aq})$ $+2 \mathrm{NH}_{4}^{+}(\mathrm{aq})$ and $\mathrm{Ag}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq}) \rightarrow \mathrm{AgCl}(\mathrm{s})$.
31. a. Isomers: species with the same formulas but different properties; they are different compounds. See the text for examples of the following types of isomers.
b. Structural isomers: isomers that have one or more bonds that are different.
c. Steroisomers: isomers that contain the same bonds but differ in how the atoms are arranged in space.
d. Coordination isomers: structural isomers that differ in the atoms that make up the complex ion.
e. Linkage isomers: structural isomers that differ in how one or more ligands are attached to the transition metal.
f. Geometric isomers: (cis-trans isomerism); steroisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other.
g. Optical isomers: steroisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different.
32. a. 2; forms bonds through the lone pairs on the two oxygen atoms.
b. 3; forms bonds through the lone pairs on the three nitrogen atoms.
c. 4 ; forms bonds through the two nitrogen atoms and the two oxygen atoms.
d. 4 ; forms bonds through the four nitrogen atoms.
33. a.

cis


trans

Note: $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ is a bidentate ligand. Bidentate ligands bond to the metal at two positions that are $90^{\circ}$ apart from each other in octahedral complexes. Bidentate ligands do not bond to the metal at positions $180^{\circ}$ apart from each other.
b.

cis

trans
c.

cis

trans
d.




Note:

is an abbreviation for the bidentate en ligand (ethylenediamine, $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ ).
34.
a.

b.

c.

d.

e.

35.


mirror
trans
(mirror image is
superimposable)

The mirror image of the cis isomer is also superimposable.

No ; both the trans and the cis forms of $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}^{+}$have mirror images that are superimposable. For the cis form, the mirror image only needs a $90^{\circ}$ rotation to produce the original structure. Hence neither the trans nor cis form is optically active.
36.


To form the trans isomer, $\mathrm{Cl}^{-}$would replace the $\mathrm{NH}_{3}$ ligand that is bold in the structure above. If any of the other four $\mathrm{NH}_{3}$ molecules are replaced by $\mathrm{Cl}^{-}$, the cis isomer results. Therefore, the expected ratio of the cis:trans isomer in the product is $4: 1$.
37.

$M=$ transition metal ion


38.
monodentate

bidentate

bridging

39. Linkage isomers differ in the way that the ligand bonds to the metal. $\mathrm{SCN}^{-}$can bond through the sulfur or through the nitrogen atom. $\mathrm{NO}_{2}{ }^{-}$can bond through the nitrogen or through the oxygen atom. $\mathrm{OCN}^{-}$can bond through the oxygen or through the nitrogen atom. $\mathrm{N}_{3}{ }^{-}$, $\mathrm{NH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NH}_{2}$ and $\mathrm{I}^{-}$are not capable of linkage isomerism.
40.






41. Similar to the molecules discussed in Figures 19.16 and 19.17 of the text, $\mathrm{Cr}(\mathrm{acac})_{3}$ and cis$\mathrm{Cr}(\mathrm{acac})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$ are optically active. The mirror images of these two complexes are nonsuperimposable. There is a plane of symmetry in trans- $\mathrm{Cr}(\mathrm{acac})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}$, so it is not optically active. A molecule with a plane of symmetry is never optically active because the mirror images are always superimposable. A plane of symmetry is a plane through a molecule where one side exactly reflects the other side of the molecule.
42. There are five geometric isomers (labeled i-v). Only isomer v , where the $\mathrm{CN}^{-}, \mathrm{Br}^{-}$, and $\mathrm{H}_{2} \mathrm{O}$ ligands are cis to each other, is optically active. The nonsuperimposable mirror image is shown for isomer v .
i

ii

iii

iv

V



## Bonding, Color, and Magnetism in Coordination Compounds

43. a. Ligand that will give complex ions with the maximum number of unpaired electrons.
b. Ligand that will give complex ions with the minimum number of unpaired electrons.
c. Complex with a minimum number of unpaired electrons (low spin $=$ strong field).
d. Complex with a maximum number of unpaired electrons (high spin $=$ weak field).
44. $\quad \mathrm{Cu}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{9} ; \mathrm{Cu}^{+}:[\mathrm{Ar}] 3 \mathrm{~d}^{10} ; \mathrm{Cu}(\mathrm{II})$ is $\mathrm{d}^{9}$ and $\mathrm{Cu}(\mathrm{I})$ is $\mathrm{d}^{10}$. Color is a result of the electron transfer between split $d$ orbitals. This cannot occur for the filled $d$ orbitals in $\mathrm{Cu}(\mathrm{I}) \cdot \mathrm{Cd}^{2+}$, like $\mathrm{Cu}^{+}$, is also $\mathrm{d}^{10}$. We would not expect $\mathrm{Cd}\left(\mathrm{NH}_{3}\right)_{4} \mathrm{Cl}_{2}$ to be colored since the d orbitals are filled in this $\mathrm{Cd}^{2+}$ complex.
45. $\mathrm{Sc}^{3+}$ has no electrons in d orbitals. $\mathrm{Ti}^{3+}$ and $\mathrm{V}^{3+}$ have d electrons present. The color of transition metal complexes results from electron transfer between split d orbitals. If no d electrons are present, no electron transfer can occur, and the compounds are not colored.
46. All these complex ions contain $\mathrm{Co}^{3+}$ bound to different ligands, so the difference in d-orbital splitting for each complex ion is due to the difference in ligands. The spectrochemical series indicates that $\mathrm{CN}^{-}$is a stronger field ligand than $\mathrm{NH}_{3}$, which is a stronger field ligand than $\mathrm{F}^{-}$. Therefore, $\mathrm{Co}(\mathrm{CN})_{6}{ }^{3-}$ will have the largest d-orbital splitting and will absorb the lowestwavelength electromagnetic radiation ( $\lambda=290 \mathrm{~nm}$ ) because energy and wavelength are inversely related $(\lambda=\mathrm{hc} / \mathrm{E}) . \quad \mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ will absorb $440-\mathrm{nm}$ electromagnetic radiation, whereas $\mathrm{CoF}_{6}{ }^{3-}$ will absorb the longest-wavelength electromagnetic radiation ( $\lambda=770 \mathrm{~nm}$ ) because $\mathrm{F}^{-}$is the weakest field ligand present.
47. 

a. $\mathrm{Fe}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{6}$


High spin, small $\Delta$
b. $\mathrm{Fe}^{3+}:[\mathrm{Ar}] 3 \mathrm{~d}^{5}$

c. $\mathrm{Ni}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{8}$


High spin, small $\Delta$
d. $\mathrm{Zn}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{10}$

e. $\mathrm{Co}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{7}$


High spin, small $\Delta$


Low spin, large $\Delta$
48. $\mathrm{NH}_{3}$ and $\mathrm{H}_{2} \mathrm{O}$ are neutral ligands, so the oxidation states of the metals are $\mathrm{Co}^{3+}$ and $\mathrm{Fe}^{2+}$. Both have six d electrons ( $[\mathrm{Ar}] 3 \mathrm{~d}^{6}$ ). To explain the magnetic properties, we must have a strong field for $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ and a weak field for $\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$.


$$
\mathrm{Fe}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{6}
$$



Only this splitting of d orbitals gives a diamagnetic $\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ complex ion (no unpaired electrons) and a paramagnetic $\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ complex ion (unpaired electrons present).
49. To determine the crystal field diagrams, you need to determine the oxidation state of the transition metal, which can only be determined if you know the charges of the ligands (see Table 19.13). The electron configurations and the crystal field diagrams follow.
a. $\quad \mathrm{Ru}^{2+}:[\mathrm{Kr}] 4 \mathrm{~d}^{6}$, no unpaired $\mathrm{e}^{-}$
b. $\mathrm{Ni}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{8}, 2$ unpaired $\mathrm{e}^{-}$


Low spin, large $\Delta$
c. $\mathrm{V}^{3+}:[\mathrm{Ar}] 3 \mathrm{~d}^{2}, 2$ unpaired $\mathrm{e}^{-}$


Note: $\mathrm{Ni}^{2+}$ must have two unpaired electrons, whether high spin or low spin, and $\mathrm{V}^{3+}$ must have two unpaired electrons, whether high spin or low spin.
50. All have octahedral $\mathrm{Co}^{3+}$ ions, so the difference in d-orbital splitting and the wavelength of light absorbed only depends on the ligands. From the spectrochemical series, the order of the ligands from strongest to weakest field is $\mathrm{CN}^{-}>$en $>\mathrm{H}_{2} \mathrm{O}>\mathrm{I}^{-}$. The strongest-field ligand produces the greatest d-orbital splitting (largest $\Delta$ ) and will absorb light having the smallest wave-length. The weakest-field ligand produces the smallest $\Delta$ and absorbs light having the longest wavelength. The order is:

$$
\begin{array}{ll}
\mathrm{Co}(\mathrm{CN})_{6}{ }_{6}{ }^{3-}<\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}<\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }_{6}^{3+}<\mathrm{CoI}_{6}{ }_{6}^{3-} \\
\text { shortest } \lambda & \text { longest } \lambda \\
\text { absorbed } & \text { absorbed }
\end{array}
$$

51. Replacement of water ligands by ammonia ligands resulted in shorter wavelengths of light being absorbed. Energy and wavelength are inversely related, so the presence of the $\mathrm{NH}_{3}$ ligands resulted in a larger d-orbital splitting (larger $\Delta$ ). Therefore, $\mathrm{NH}_{3}$ is a stronger-field ligand than $\mathrm{H}_{2} \mathrm{O}$.
52. In both compounds, iron is in the +3 oxidation state with an electron configuration of $[\operatorname{Ar}] 3 d^{5}$. $\mathrm{Fe}^{3+}$ complexes have one unpaired electron when a strong-field case and five unpaired electrons when a weak-field case. $\mathrm{Fe}(\mathrm{CN})_{6}{ }^{2-}$ is a strong-field case, and $\mathrm{Fe}(\mathrm{SCN})_{6}{ }^{3-}$ is a weakfield case. Therefore, cyanide $\left(\mathrm{CN}^{-}\right)$is a stronger-field ligand than thiocyanate $\left(\mathrm{SCN}^{-}\right)$.
53. From Table 19.16 of the text, the violet complex ion absorbs yellow-green light ( $\lambda \approx 570$ nm ), the yellow complex ion absorbs blue light ( $\lambda \approx 450 \mathrm{~nm}$ ), and the green complex ion absorbs red light $(\lambda \approx 650 \mathrm{~nm})$. The spectrochemical series shows that $\mathrm{NH}_{3}$ is a stronger-field ligand than $\mathrm{H}_{2} \mathrm{O}$, which is a stronger-field ligand than $\mathrm{Cl}^{-}$. Therefore, $\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ will have
the largest d-orbital splitting and will absorb the lowest wavelength electromagnetic radiation $(\lambda \approx 450 \mathrm{~nm})$ because energy and wavelength are inversely related $(\lambda=\mathrm{hc} / \mathrm{E})$. Thus the yellow solution contains the $\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ complex ion. Similarly, we would expect the $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}^{+}$complex ion to have the smallest d-orbital splitting because it contains the weakest-field ligands. The green solution with the longest wavelength of absorbed light contains the $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}^{+}$complex ion. This leaves the violet solution, which contains the $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ complex ion. This makes sense because we would expect $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ to absorb light of a wavelength between that of $\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}{ }^{3+}$ and $\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}{ }^{+}$.
54. Octahedral $\mathrm{Cr}^{2+}$ complexes should be used. $\mathrm{Cr}^{2+}$ : [Ar]3d ${ }^{4}$; High spin (weak field) $\mathrm{Cr}^{2+}$ complexes have four unpaired electrons, and low spin (strong field) $\mathrm{Cr}^{2+}$ complexes have two unpaired electrons. $\mathrm{Ni}^{2+}$ : [Ar] $3 \mathrm{~d}^{8}$; octahedral $\mathrm{Ni}^{2+}$ complexes will always have two unpaired electrons, whether high or low spin. Therefore, $\mathrm{Ni}^{2+}$ complexes cannot be used to distinguish weak- from strong-field ligands by examining magnetic properties. Alternatively, the ligand field strengths can be measured using visible spectra. Either $\mathrm{Cr}^{2+}$ or $\mathrm{Ni}^{2+}$ complexes can be used for this method.
55. a. $\mathrm{Ru}(\mathrm{phen}) 3^{2+}$ exhibits optical isomerism [similar to $\mathrm{Co}(\mathrm{en}) 3^{3+}$ in Figure 19.16 of the text].
b. $\mathrm{Ru}^{2+}:[\mathrm{Kr}] 4 \mathrm{~d}^{6}$; because there are no unpaired electrons, $\mathrm{Ru}^{2+}$ is a strong-field (low-spin) case.

56. $\mathrm{Co}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{7}$; the corresponding d-orbital splitting diagram for tetrahedral $\mathrm{Co}^{2+}$ complexes is:


All tetrahedral complexes are high spin since the d-orbital splitting is small. Ions with two or seven d electrons should give the most stable tetrahedral complexes because they have the greatest number of electrons in the lower-energy orbitals as compared with the number of electrons in the higher-energy orbitals.
57. The crystal field diagrams are different because the geometries of where the ligands point are different. The tetrahedrally oriented ligands point differently in relationship to the d orbitals than do the octahedrally oriented ligands. Also, we have more ligands in an octahedral complex.

See Figure 19.28 for the tetrahedral crystal field diagram. Notice that the orbitals are reverse of that in the octahedral crystal field diagram. The degenerate $d_{z^{2}}$ and $d_{x^{2}-y^{2}}$ are at a lower energy than the degenerate $\mathrm{d}_{\mathrm{xy}}, \mathrm{d}_{\mathrm{xz}}$, and $\mathrm{d}_{\mathrm{yz}}$ orbitals. Again, the reason for this is that
tetrahedral ligands are oriented differently than octahedral field ligands, so the interactions with specifically oriented d orbitals are different. Also notice that the difference in magnitude of the d-orbital splitting for the two geometries. The d-orbital splitting in tetrahedral complexes is less than one-half the d-orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case; hence all tetrahedral complexes are weak field or high spin.
58. From Table 19.16, the red octahedral $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ complex ion absorbs blue-green light $(\lambda \approx$ 490 mm ), whereas the blue tetrahedral $\mathrm{CoCl}_{4}{ }^{2-}$ complex ion absorbs orange light ( $\lambda \approx 600$ nm ). Because tetrahedral complexes have a d-orbital splitting much less than octahedral complexes, one would expect the tetrahedral complex to have a smaller energy difference between split d orbitals. This translates into longer-wavelength light absorbed ( $\mathrm{E}=\mathrm{hc} / \lambda$ ) for tetrahedral complex ions compared to octahedral complex ions. Information from Table 19.16 confirms this.
59. $\mathrm{CoBr}_{6}{ }^{4-}$ has an octahedral structure, and $\mathrm{CoBr}_{4}{ }^{2-}$ has a tetrahedral structure (as do most $\mathrm{Co}^{2+}$ complexes with four ligands). Coordination complexes absorb electromagnetic radiation (EMR) of energy equal to the energy difference between the split d orbitals. Because the tetrahedral d-orbital splitting is less than one-half the octahedral d-orbital splitting, tetrahedral complexes will absorb lower-energy EMR, which corresponds to longer-wavelength EMR ( $\mathrm{E}=\mathrm{hc} / \lambda$ ). Therefore, $\mathrm{CoBr}_{6}{ }^{4-}$ will absorb EMR having a wavelength shorter than 3.4 $\times 10^{-6} \mathrm{~m}$.
60. Pd is in the +2 oxidation state in $\mathrm{PdCl}_{4}{ }^{2-} ; \mathrm{Pd}^{2+}:[\mathrm{Kr}] 4 \mathrm{~d}^{8}$. If $\mathrm{PdCl}_{4}{ }^{2-}$ were a tetrahedral complex, then it would have two unpaired electrons and would be paramagnetic (see diagram below). Instead, $\mathrm{PdCl}_{4}{ }^{2-}$ has a square planar molecular structure with a d-orbital splitting diagram shown below. Note that all electrons are paired in the square planar diagram, which explains the diamagnetic properties of $\mathrm{PdCl}_{4}{ }^{2-}$.


## Additional Exercises

61. $\mathrm{Hg}^{2+}(\mathrm{aq})+2 \mathrm{I}^{-}(\mathrm{aq}) \rightarrow \operatorname{HgI}_{2}(\mathrm{~s})$, orange precipitate
$\mathrm{HgI}_{2}(\mathrm{~s})+2 \mathrm{I}^{-}(\mathrm{aq}) \rightarrow \mathrm{HgI}_{4}{ }^{2-}(\mathrm{aq})$, soluble complex ion
$\mathrm{Hg}^{2+}$ is a $\mathrm{d}^{10}$ ion. Color is the result of electron transfer between split d orbitals. This cannot occur for the filled d orbitals in $\mathrm{Hg}^{2+}$. Therefore, we would not expect $\mathrm{Hg}^{2+}$ complex ions to form colored solutions.
62. The transition metal ion must form octahedral complex ions; only with the octahedral geometry are two different arrangements of d electrons possible in the split d orbitals. These two arrangements depend on whether a weak field or a strong field is present. For four unpaired electrons in the first row, the two possible weak-field cases are for transition metal ions having either a $3 \mathrm{~d}^{4}$ or a $3 \mathrm{~d}^{6}$ electron configuration:


Of these two, only $\mathrm{d}^{6}$ ions have no unpaired electron in the strong-field case.


Therefore, the transition metal ion has a $3 \mathrm{~d}^{6}$ valence electron configuration. $\mathrm{Fe}^{2+}$ and $\mathrm{Co}^{3+}$ are two possible metal ions that are $3 \mathrm{~d}^{6}$. Thus one of these ions is probably present in the four coordination compounds, with each complex ion having a coordination number of 6 due to the octahedral geometry.

The colors of the compounds are related to the magnitude of $\Delta$ (the d-orbital splitting value). The weak-field compounds will have the smallest $\Delta$, so the wavelength of light absorbed will be longest. Using Table 19.16, the green solution (absorbs $650-\mathrm{nm}$ light) and the blue solution (absorbs $600-\mathrm{nm}$ light) absorb the longest-wavelength light; these solutions contain the complex ions that are the weak-field cases with four unpaired electrons. The red solution (absorbs $490-\mathrm{nm}$ light) and yellow solution (absorbs $450-\mathrm{nm}$ light) contain the two strongfield case complex ions because they absorb the shortest-wavelength (highest-energy) light. These complex ions are diamagnetic.
63. $\mathrm{Ni}(\mathrm{CO})_{4}$ is composed of 4 CO molecules and Ni . Thus nickel has an oxidation state of zero.
64. $\mathrm{CN}^{-}$and CO form much stronger complexes with $\mathrm{Fe}^{2+}$ than $\mathrm{O}_{2}$. Thus $\mathrm{O}_{2}$ cannot be transported by hemoglobin in the presence of $\mathrm{CN}^{-}$or CO because the binding sites prefer the toxic $\mathrm{CN}^{-}$and CO ligands.
65. i. $0.0203 \mathrm{~g} \mathrm{CrO}_{3} \times \frac{52.00 \mathrm{~g} \mathrm{Cr}}{100.0 \mathrm{~g} \mathrm{CrO}_{3}}=0.0106 \mathrm{~g} \mathrm{Cr} ; \% \mathrm{Cr}=\frac{0.0106 \mathrm{~g}}{0.105 \mathrm{~g}} \times 100=10.1 \% \mathrm{Cr}$
ii. $\quad 32.93 \mathrm{~mL} \mathrm{HCl} \times \frac{0.100 \mathrm{mmol} \mathrm{HCl}}{\mathrm{mL}} \times \frac{1 \mathrm{mmol} \mathrm{NH}_{3}}{\mathrm{mmol} \mathrm{HCl}} \times \frac{17.03 \mathrm{mg} \mathrm{NH}_{3}}{\mathrm{mmol}}=56.1 \mathrm{mg} \mathrm{NH}_{3}$
$\% \mathrm{NH}_{3}=\frac{56.1 \mathrm{mg}}{341 \mathrm{mg}} \times 100=16.5 \% \mathrm{NH}_{3}$
iii. $73.53 \%+16.5 \%+10.1 \%=100.1 \%$; the compound must be composed of only $\mathrm{Cr}, \mathrm{NH}_{3}$, and I.

Out of 100.00 g of compound:

$$
\begin{array}{ll}
10.1 \mathrm{~g} \mathrm{Cr} \times \frac{1 \mathrm{~mol}}{52.00 \mathrm{~g}}=0.194 \mathrm{~mol} ; & \frac{0.194}{0.194}=1.00 \\
16.5 \mathrm{~g} \mathrm{NH}_{3} \times \frac{1 \mathrm{~mol}}{17.03 \mathrm{~g}}=0.969 \mathrm{~mol} ; & \frac{0.969}{0.194}=4.99 \\
73.53 \mathrm{~g} \mathrm{I} \times \frac{1 \mathrm{~mol}}{126.9 \mathrm{~g}}=0.5794 \mathrm{~mol} ; & \frac{0.5794}{0.194}=2.99
\end{array}
$$

$\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{I}_{3}$ is the empirical formula. $\mathrm{Cr}^{3+}$ forms octahedral complexes. So compound A is made of the octahedral $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{I}\right]^{2+}$ complex ion and two I- ions as counter ions; the formula is $\left.\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5}\right]\right] \mathrm{I}_{2}$. Lets check this proposed formula using the freezing-point data.
iv. $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{i} \mathrm{K}_{\mathrm{f}} m$; for $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5}\right] \mathrm{I}_{2}, \mathrm{i}=3.0$ (assuming complete dissociation).

Molality $=m=\frac{0.601 \mathrm{~g} \text { complex }}{1.000 \times 10^{-2} \mathrm{~kg} \mathrm{H}_{2} \mathrm{O}} \times \frac{1 \mathrm{~mol} \text { complex }}{517.9 \mathrm{~g} \text { complex }}=0.116 \mathrm{~mol} / \mathrm{kg}$
$\Delta \mathrm{T}_{\mathrm{f}}=3.0 \times 1.86^{\circ} \mathrm{C} \mathrm{kg} / \mathrm{mol} \times 0.116 \mathrm{~mol} / \mathrm{kg}=0.65^{\circ} \mathrm{C}$
Because $\Delta \mathrm{T}_{\mathrm{f}}$ is close to the measured value, this is consistent with the formula $\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{I}\right] \mathrm{I}_{2}$.
66. a. Copper is both oxidized and reduced in this reaction, so, yes, this reaction is an oxidationreduction reaction. The oxidation state of copper in $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}$ is +2 , the oxidation state of copper in Cu is zero, and the oxidation state of copper in $\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}$ is +1 .
b. Total mass of copper used:

$$
10,000 \text { boards } \times \frac{(8.0 \mathrm{~cm} \times 16.0 \mathrm{~cm} \times 0.060 \mathrm{~cm})}{\text { board }} \times \frac{8.96 \mathrm{~g}}{\mathrm{~cm}^{3}}=6.9 \times 10^{5} \mathrm{~g} \mathrm{Cu}
$$

Amount of Cu to be recovered $=0.80\left(6.9 \times 10^{5} \mathrm{~g}\right)=5.5 \times 10^{5} \mathrm{~g} \mathrm{Cu}$

$$
\begin{aligned}
& 5.5 \times 10^{5} \mathrm{~g} \mathrm{Cu} \times \frac{1 \mathrm{~mol} \mathrm{Cu}}{63.55 \mathrm{~g} \mathrm{Cu}} \times \frac{1 \mathrm{~mol}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}}{\mathrm{~mol} \mathrm{Cu}} \times \frac{202.59 \mathrm{~g}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}}{\operatorname{mol}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}} \\
&= 1.8 \times 10^{6} \mathrm{~g}\left[\mathrm{Cu}\left(\mathrm{NH}_{3}\right)_{4}\right] \mathrm{Cl}_{2}
\end{aligned}
$$

$5.5 \times 10^{5} \mathrm{~g} \mathrm{Cu} \times \frac{1 \mathrm{~mol} \mathrm{Cu}}{63.55 \mathrm{~g} \mathrm{Cu}} \times \frac{4 \mathrm{~mol} \mathrm{NH}_{3}}{\mathrm{~mol} \mathrm{Cu}} \times \frac{17.03 \mathrm{~g} \mathrm{NH}_{3}}{\mathrm{~mol} \mathrm{NH}_{3}}=5.9 \times 10^{5} \mathrm{~g} \mathrm{NH}_{3}$
67. $\mathrm{M}=$ metal ion



68. a. The optical isomers of this compound are similar to the ones discussed in Figure 19.16 of the text. In the following structures we omitted the $4 \mathrm{NH}_{3}$ ligands coordinated to the outside cobalt atoms.

mirror
b. All are $\mathrm{Co}(\mathrm{III})$. The three "ligands" each contain $2 \mathrm{OH}^{-}$and $4 \mathrm{NH}_{3}$ groups. If each cobalt is in the +3 oxidation state, then each ligand has a +1 overall charge. The +3 charge from the three ligands, along with the +3 charge of the central cobalt atom, gives the overall complex a +6 charge. This is balanced by the -6 charge of the six $\mathrm{Cl}^{-}$ions.
c. $\mathrm{Co}^{3+}:[\mathrm{Ar}] 3 \mathrm{~d}^{6}$; There are zero unpaired electrons if a low-spin (strong-field) case.

69. No; in all three cases, six bonds are formed between $\mathrm{Ni}^{2+}$ and nitrogen, so $\Delta \mathrm{H}$ values should be similar. $\Delta \mathrm{S}^{\circ}$ for formation of the complex ion is most negative for $6 \mathrm{NH}_{3}$ molecules reacting with a metal ion (seven independent species become one). For penten reacting with a metal ion, two independent species become one, so $\Delta \mathrm{S}^{\circ}$ is least negative for this reaction compared to the other reactions. Thus the chelate effect occurs because the more bonds a chelating agent can form to the metal, the more favorable $\Delta \mathrm{S}^{\circ}$ is for the formation of the complex ion, and the larger is the formation constant.
70. $\mathrm{CrCl}_{3} \bullet 6 \mathrm{H}_{2} \mathrm{O}$ contains nine possible ligands, only six of which are used to form the octahedral complex ion. The three species not present in the complex ion will either be counter ions to balance the charge of the complex ion and/or waters of hydration. The number of counter ions for each compound can be determined from the silver chloride precipitate data, and the number of waters of hydration can be determined from the dehydration data. In all experiments, the ligands in the complex ion do not react.

Compound I:

$$
\begin{aligned}
& \mathrm{mol} \mathrm{CrCl}_{3} \bullet 6 \mathrm{H}_{2} \mathrm{O}=0.27 \mathrm{~g} \times \frac{1 \mathrm{~mol}}{266.5 \mathrm{~g}}=1.0 \times 10^{-3} \mathrm{~mol} \mathrm{CrCl}_{3} \bullet 6 \mathrm{H}_{2} \mathrm{O} \\
& \text { mol waters of hydration }=0.036 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol}}{18.02 \mathrm{~g}}=2.0 \times 10^{-3} \mathrm{~mol} \mathrm{H}_{2} \mathrm{O} \\
& \frac{\text { mol waters of hydration }}{\text { mol compound }}=\frac{2.0 \times 10^{-3} \mathrm{~mol}}{1.0 \times 10^{-3} \mathrm{~mol}}=2.0
\end{aligned}
$$

In compound I, two of the $\mathrm{H}_{2} \mathrm{O}$ molecules are waters of hydration, so the other four water molecules are present in the complex ion. Therefore, the formula for compound I must be $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}\right] \mathrm{Cl} \bullet 2 \mathrm{H}_{2} \mathrm{O}$. Two of the $\mathrm{Cl}^{-}$ions are present as ligands in the octahedral complex ion, and one $\mathrm{Cl}^{-}$ion is present as a counter ion. The AgCl precipitate data that refer to this compound are the one that produces 1430 mg AgCl :

$$
\begin{aligned}
\mathrm{mol} \mathrm{Cl}
\end{aligned}{ }^{-} \text {from compound } \mathrm{I}=0.1000 \mathrm{~L} \times \frac{0.100 \mathrm{~mol}\left[\mathrm{Cr}_{\mathrm{l}}\left(\mathrm{H}_{2} \mathrm{O}\right)_{4} \mathrm{Cl}_{2}\right] \mathrm{Cl} \bullet 2 \mathrm{H}_{2} \mathrm{O}}{\mathrm{~L}}
$$

$$
\begin{aligned}
& \text { mass } \mathrm{AgCl} \text { produced }=0.0100 \mathrm{~mol} \mathrm{Cl}^{-} \times \frac{1 \mathrm{~mol} \mathrm{AgCl}^{\mathrm{mol} \mathrm{Cl}^{-}} \times \frac{143.4 \mathrm{~g} \mathrm{AgCl}}{\mathrm{~mol} \mathrm{AgCl}}}{}=1.43 \mathrm{~g} \\
&=1430 \mathrm{mg} \mathrm{AgCl}
\end{aligned}
$$

Compound II:

$$
\frac{\text { mol waters of hydration }}{\text { mol compound }}=\frac{0.018 \mathrm{~g} \mathrm{H}_{2} \mathrm{O} \times \frac{1 \mathrm{~mol}}{18.02 \mathrm{~g}}}{1.0 \times 10^{-3} \mathrm{~mol} \text { compound }}=1.0
$$

The formula for compound II must be $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5} \mathrm{Cl}^{2} \mathrm{Cl}_{2} \bullet \mathrm{H}_{2} \mathrm{O}\right.$. The $2870-\mathrm{mg} \mathrm{AgCl}$ precipitate data refer to this compound. For 0.0100 mol of compound II, $0.0200 \mathrm{~mol} \mathrm{Cl}^{-}$is present as counter ions:

$$
\text { mass } \begin{aligned}
\mathrm{AgCl} \text { produced }=0.0200 \mathrm{~mol} \mathrm{Cl}^{-} \times \frac{1 \mathrm{~mol} \mathrm{AgCl}^{2}}{\mathrm{~mol} \mathrm{Cl}^{-}} \times \frac{143.4 \mathrm{~g}}{\mathrm{~mol}} & =2.87 \mathrm{~g} \\
& =2870 \mathrm{mg} \mathrm{AgCl}
\end{aligned}
$$

Compound III:
This compound has no mass loss on dehydration, so there are no waters of hydration present. The formula for compound III must be $\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{Cl}_{3}$. 0.0100 mol of this compound produces 4300 mg of $\mathrm{AgCl}(\mathrm{s})$ when treated with $\mathrm{AgNO}_{3}$.

$$
0.0300 \mathrm{~mol} \mathrm{Cl}^{-} \times \frac{1 \mathrm{~mol} \mathrm{AgCl}}{\mathrm{~mol} \mathrm{Cl}^{-}} \times \frac{143.4 \mathrm{~g} \mathrm{AgCl}}{\mathrm{~mol} \mathrm{AgCl}}=4.30 \mathrm{~g}=4.30 \times 10^{3} \mathrm{mg} \mathrm{AgCl}
$$

The structural formulas for the compounds are:
Compound I


Compound II


Compound III


From Table 19.16 of the text, the violet compound will be the one that absorbs light with the shortest wavelength (highest energy). This should be compound III. $\mathrm{H}_{2} \mathrm{O}$ is a stronger field ligand than $\mathrm{Cl}^{-}$; compound III with the most coordinated $\mathrm{H}_{2} \mathrm{O}$ molecules will have the largest d-orbital splitting and will absorb the higher-energy light.


Yes; this is consistent. After the oxidation, the ligands on $\mathrm{Cr}(\mathrm{III})$ won't exchange. Because $\mathrm{Cl}^{-}$is in the coordination sphere, it must have formed a bond to $\mathrm{Cr}(\mathrm{II})$ before the electron transfer occurred (as proposed through the formation of the intermediate).
72. a. $\mathrm{Be}(\mathrm{tfa})_{2}$ exhibits optical isomerism. Representations for the tetrahedral optical isomers are:


mirror

Note: The dotted line indicates a bond pointing into the plane of the paper, and the wedge indicates a bond pointing out of the plane of the paper. Also note that the placement of the double bonds in the tfa isomer is not important. The two double bonds can resonate between adjacent carbon or oxygen atoms. Therefore, multiple resonance structures can be drawn. Resonance structures are not different isomers.
b. Square planar $\mathrm{Cu}(\mathrm{tfa})_{2}$ molecules exhibit geometric isomerism. In one geometric isomer, the $\mathrm{CF}_{3}$ groups are cis to each other, and in the other isomer, the $\mathrm{CF}_{3}$ groups are trans.


cis
trans
73. a.

$$
\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}(\mathrm{OH})^{2+}+\mathrm{H}_{3} \mathrm{O}^{+}
$$

| Initial | $0.10 M$ | 0 | $\sim 0$ |
| :--- | :--- | :--- | :---: |
| Equil. | $0.10-x$ | $x$ | $x$ |

$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}(\mathrm{OH})^{2+}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}^{3+}\right]}=6.0 \times 10^{-3}=\frac{x^{2}}{0.10-x} \approx \frac{x^{2}}{0.10}$
$x=2.4 \times 10^{-2}$; assumption is poor ( $x$ is $24 \%$ of 0.10 ). Using successive approximations:

$$
\begin{aligned}
& \frac{x^{2}}{0.10-0.024}=6.0 \times 10^{-3}, x=0.021 \\
& \frac{x^{2}}{0.10-0.021}=6.0 \times 10^{-3}, x=0.022 ; \frac{x^{2}}{0.10-0.022}=6.0 \times 10^{-3}, x=0.022
\end{aligned}
$$

$x=\left[\mathrm{H}^{+}\right]=0.022 \mathrm{M} ; \mathrm{pH}=1.66$
b. Because of the lower charge, $\mathrm{Fe}^{2+}(\mathrm{aq})$ will not be as strong an acid as $\mathrm{Fe}^{3+}(\mathrm{aq})$. A solution of iron(II) nitrate will be less acidic (have a higher pH ) than a solution with the same concentration of iron(III) nitrate.
74. We need to calculate the $\mathrm{Pb}^{2+}$ concentration in equilibrium with EDTA ${ }^{4-}$. Because K is large for the formation of $\mathrm{PbEDTA}^{2-}$, let the reaction go to completion; then solve an equilibrium problem to get the $\mathrm{Pb}^{2+}$ concentration.

$$
\mathrm{Pb}^{2+}+\mathrm{EDTA}^{4-} \rightleftharpoons \mathrm{PbEDTA}^{2-} \quad \mathrm{K}=1.1 \times 10^{18}
$$

| Before | 0.010 M | 0.050 M | 0 |  |
| :--- | :---: | :---: | :---: | :--- |
|  | $0.010 \mathrm{~mol} / \mathrm{L} \mathrm{Pb}$ |  |  |  |
| 2+ reacts completely (large K) |  |  |  |  |
| Change | -0.010 | -0.010 | +0.010 | Reacts completely |
| After | 0 | 0.040 | 0.010 | New initial condition |
|  | $x \mathrm{~mol} / \mathrm{L} \mathrm{PbEDTA}$ |  |  |  |
| Equil. | $x$ | $0.040+x$ | $0.010-x$ |  |
|  |  |  |  |  |
| $1.1 \times 10^{18}=$ | $\frac{(0.010-x)}{(x)(0.040+x)} \approx \frac{(0.010)}{x(0.040)}$, | $x=\left[\mathrm{Pb}^{2+}\right]=2.3 \times 10^{-19} \mathrm{M} ;$ | assumptions good. |  |

Now calculate the solubility quotient for $\mathrm{Pb}(\mathrm{OH})_{2}$ to see if precipitation occurs. The concentration of $\mathrm{OH}^{-}$is 0.10 M because we have a solution buffered at $\mathrm{pH}=13.00$.
$\mathrm{Q}=\left[\mathrm{Pb}^{2+}\right]_{0}\left[\mathrm{OH}^{-}\right]_{0}^{2}=\left(2.3 \times 10^{-19}\right)(0.10)^{2}=2.3 \times 10^{-21}<\mathrm{K}_{\text {sp }}\left(1.2 \times 10^{-15}\right)$
$\mathrm{Pb}(\mathrm{OH})_{2}(\mathrm{~s})$ will not form because Q is less than $\mathrm{K}_{\text {sp }}$.
75. a. In the lungs, there is a lot of $\mathrm{O}_{2}$, and the equilibrium favors $\mathrm{Hb}\left(\mathrm{O}_{2}\right)_{4}$. In the cells, there is a deficiency of $\mathrm{O}_{2}$, and the equilibrium favors $\mathrm{HbH}_{4}{ }^{4+}$.
b. $\mathrm{CO}_{2}$ is a weak acid in water, $\mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{HCO}_{3}^{-}+\mathrm{H}^{+}$. Removing $\mathrm{CO}_{2}$ essentially decreases $\mathrm{H}^{+} . \mathrm{Hb}\left(\mathrm{O}_{2}\right)_{4}$ is then favored, and $\mathrm{O}_{2}$ is not released by hemoglobin in the cells. Breathing into a paper bag increases $\left[\mathrm{CO}_{2}\right]$ in the blood, thus increasing $\left[\mathrm{H}^{+}\right]$, which shifts the reaction left.
c. $\mathrm{CO}_{2}$ builds up in the blood, and it becomes too acidic, driving the equilibrium to the left. Hemoglobin can't bind $\mathrm{O}_{2}$ as strongly in the lungs. Bicarbonate ion acts as a base in water and neutralizes the excess acidity.
76.

$$
\begin{array}{cl}
\mathrm{HbO}_{2} \rightarrow \mathrm{Hb}+\mathrm{O}_{2} & \Delta \mathrm{G}^{\circ}=-(-70 \mathrm{~kJ}) \\
\mathrm{Hb}+\mathrm{CO} \rightarrow \mathrm{HbCO} & \Delta \mathrm{G}^{\circ}=-80 \mathrm{~kJ} \\
\hline \mathrm{HbO}_{2}+\mathrm{CO} \rightarrow \mathrm{HbCO}+\mathrm{O}_{2} & \Delta \mathrm{G}^{\circ}=-10 \mathrm{~kJ} \\
\Delta \mathrm{G}^{\circ}=-\mathrm{RT} \ln \mathrm{~K}, & \mathrm{~K}=\left(\frac{-\Delta \mathrm{G}^{\mathrm{o}}}{\mathrm{RT}}\right)=\exp \left[\frac{-\left(-10 \times 10^{3} \mathrm{~J}\right)}{\left(8.3145 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right)(298 \mathrm{~kJ})}\right]=60
\end{array}
$$

## Challenge Problems

77. 



The $d_{x^{2}-y^{2}}$ and $d_{x y}$ orbitals are in the plane of the three ligands and should be destabilized the most. The amount of destabilization should be about equal when all the possible interactions are considered. The $d_{z^{2}}$ orbital has some electron density in the $x y$ plane (the doughnut) and should be destabilized a lesser amount than the $d_{x^{2}-y^{2}}$ and $d_{x y}$ orbitals. The $\mathrm{d}_{\mathrm{xz}}$ and $\mathrm{d}_{\mathrm{yz}}$ orbitals have no electron density in the plane and should be lowest in energy.
78. $\mathrm{Ni}^{2+}=\mathrm{d}^{8}$; if ligands A and B produced very similar crystal fields, the trans- $\left[\mathrm{NiA}_{2} \mathrm{~B}_{4}\right]^{2+}$ complex ion would give the following octahedral crystal field diagram for a $\mathrm{d}^{8}$ ion:

11 This is paramagnetic.

Because it is given that the complex ion is diamagnetic, the A and B ligands must produce different crystal fields, giving a unique d-orbital splitting diagram that would result in a diamagnetic species.
79.

z axis (pointing out of the plane of the paper)
$\qquad$ $\mathrm{d}_{\mathrm{z}^{2}}$
$\qquad$

$$
d_{x^{2}-y^{2}}, d_{x y}
$$

$\qquad$ $\mathrm{d}_{\mathrm{xz}}, \mathrm{d}_{\mathrm{yz}}$

The $\mathrm{d}_{\mathrm{z}^{2}}$ orbital will be destabilized much more than in the trigonal planar case (see Exercise 19.77). The $\mathrm{d}_{\mathrm{z}^{2}}$ orbital has electron density on the z axis directed at the two axial ligands. The $d_{x^{2}-y^{2}}$ and $d_{x y}$ orbitals are in the plane of the three trigonal planar ligands and should be destabilized a lesser amount than the $\mathrm{d}_{\mathrm{z}^{2}}$ orbital; only a portion of the electron density in the $d_{x^{2}-y^{2}}$ and $d_{x y}$ orbitals is directed at the ligands. The $d_{x z}$ and $d_{y z}$ orbitals will be destabilized the least since the electron density is directed between the ligands.
80. $\quad \mathrm{Ni}^{2+}:[\mathrm{Ar}] 3 \mathrm{~d}^{8}$; the coordinate system for trans- $\left[\mathrm{Ni}\left(\mathrm{NH}_{3}\right)_{2}(\mathrm{CN})_{4}\right]^{2-}$ is shown below. Because $\mathrm{CN}^{-}$produces a much stronger crystal field, it will dominate the d-orbital splitting. From the coordinate system, the $\mathrm{CN}^{-}$ligands are in a square planar arrangement. Therefore, the diagram will most resemble the square planar diagram given in Figure 19.29. Note that the relative position of $\mathrm{d}_{\mathrm{z}^{2}}$ orbital is hard to predict; it could switch positions with the $\mathrm{d}_{\mathrm{xy}}$ orbital.


81. a. Consider the following electrochemical cell:

$$
\begin{array}{cl}
\mathrm{Co}^{3+}+\mathrm{e}^{-} \rightarrow \mathrm{Co}^{2+} & \mathrm{E}_{\mathrm{c}}^{\mathrm{o}}=1.82 \mathrm{~V} \\
\mathrm{Co}(\mathrm{en})_{3}{ }^{2+} \rightarrow \mathrm{Co}(\mathrm{en})_{3}{ }^{3+}+\mathrm{e}^{-} & -\mathrm{E}_{\mathrm{a}}^{\mathrm{o}}=? \\
\hline \mathrm{Co}^{3+}+\mathrm{Co}(\mathrm{en})_{3}{ }^{2+} \rightarrow \mathrm{Co}^{2+}+\mathrm{Co}(\mathrm{en})_{3}{ }^{3+} & \mathrm{E}_{\mathrm{cell}}^{\mathrm{o}}=1.82-\mathrm{E}_{\mathrm{a}}^{\mathrm{o}}
\end{array}
$$

The equilibrium constant for this overall reaction is:

$$
\begin{array}{cl}
\mathrm{Co}^{3+}+3 \mathrm{en} \rightarrow \mathrm{Co}(\mathrm{en})_{3}^{3+} & \mathrm{K}_{1}=2.0 \times 10^{47} \\
\mathrm{Co}(\mathrm{en})_{3}^{2+} \rightarrow \mathrm{Co}^{2+}+3 \mathrm{en} & \mathrm{~K}_{2}=1 / 1.5 \times 10^{12} \\
\hline \mathrm{Co}^{3+}+\mathrm{Co}(\mathrm{en})_{3}^{2+} \rightarrow \mathrm{Co}(\mathrm{en})_{3}^{3+}+\mathrm{Co}^{2+} & \mathrm{K}=\mathrm{K}_{1} \mathrm{~K}_{2}=\frac{2.0 \times 10^{47}}{1.5 \times 10^{12}}=1.3 \times 10^{35}
\end{array}
$$

From the Nernst equation for the overall reaction:

$$
\begin{aligned}
& \mathrm{E}_{\text {cell }}^{\mathrm{o}}=\frac{0.0591}{\mathrm{n}} \log \mathrm{~K}=\frac{0.0591}{1} \log \left(1.3 \times 10^{35}\right), \quad \mathrm{E}_{\text {cell }}^{\mathrm{o}}=2.08 \mathrm{~V} \\
& \mathrm{E}_{\text {cell }}^{\mathrm{o}}=1.82-\mathrm{E}_{\mathrm{a}}^{\mathrm{o}}=2.08 \mathrm{~V},-\mathrm{E}_{\mathrm{a}}^{\mathrm{o}}=2.08 \mathrm{~V}-1.82 \mathrm{~V}=0.26 \mathrm{~V}, \text { so } \mathrm{E}_{\mathrm{c}}^{\mathrm{o}}=-0.26 \mathrm{~V}
\end{aligned}
$$

b. The stronger oxidizing agent will be the more easily reduced species and will have the more positive standard reduction potential. From the reduction potentials, $\mathrm{Co}^{3+}\left(\mathrm{E}^{\circ}=\right.$ $1.82 \mathrm{~V})$ is a much stronger oxidizing agent than $\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}\left(\mathrm{E}^{\circ}=-0.26 \mathrm{~V}\right)$.
c. In aqueous solution, $\mathrm{Co}^{3+}$ forms the hydrated transition metal complex $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$. In both complexes, $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ and $\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}$, cobalt exists as $\mathrm{Co}^{3+}$, which has six d electrons. Assuming a strong-field case for each complex ion, the d-orbital splitting diagram for each is:


When each complex gains an electron, the electron enters a higher-energy $\mathrm{e}_{\mathrm{g}}$ orbital. Because en is a stronger-field ligand than $\mathrm{H}_{2} \mathrm{O}$, the d-orbital splitting is larger for $\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}$, and it takes more energy to add an electron to $\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}$ than to $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$. Therefore, it is more favorable for $\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{3+}$ to gain an electron than for $\mathrm{Co}(\mathrm{en})_{3}{ }^{3+}$ to gain an electron.
82. a. $\mathrm{Cr}^{3+}:[\mathrm{Ar}] 3 \mathrm{~d}^{3}$; we will assume the A ligands lie on the z axis.

b.

c. The major difference in the two diagrams involves the $\mathrm{d}_{\mathrm{xy}}, \mathrm{d}_{\mathrm{xz}}$, and $\mathrm{d}_{\mathrm{yz}}$ orbitals. These are degenerate in the MO diagram (only $\sigma$ bonding assumed) but are not degenerate in the crystal field diagram. If the $d$ orbitals were involved in $\pi$ bonding, this might reconcile the differences between the two diagrams. One expects involvement of $\mathrm{d}_{\mathrm{xy}}$ to be different from $d_{x z}$ and $d_{y z}$ because of the symmetry of the complex. This would remove the degeneracy of these orbitals in the MO picture.
83.
a.

$$
\mathrm{AgBr}(\mathrm{~s}) \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-} \quad \mathrm{K}_{\mathrm{sp}}=\left[\mathrm{Ag}^{+}\right][\mathrm{Br}]=5.0 \times 10^{-13}
$$

Initial $s=$ solubility $(\mathrm{mol} / \mathrm{L}) \quad 0 \quad 0$
Equil. $s \quad s$

$$
\mathrm{K}_{\mathrm{sp}}=5.0 \times 10^{-13}=s^{2}, s=7.1 \times 10^{-7} \mathrm{~mol} / \mathrm{L}
$$

b.

$$
\begin{array}{rll}
\mathrm{AgBr}(\mathrm{~s}) \rightleftharpoons \mathrm{Ag}^{+}+\mathrm{Br}^{-} & \begin{array}{l}
\mathrm{K}_{\mathrm{sp}}=5.0 \times 10^{-13} \\
\mathrm{Ag}^{+}+2 \mathrm{NH}_{3} \rightleftharpoons \mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}
\end{array} & \mathrm{K}_{\mathrm{f}}=1.7 \times 10^{7} \\
\hline \mathrm{AgBr}(\mathrm{~s})+2 \mathrm{NH}_{3}(\mathrm{aq}) \rightleftharpoons \mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}(\mathrm{aq})+\mathrm{Br}^{-}(\mathrm{aq}) & \mathrm{K}=\mathrm{K}_{\mathrm{sp}} \times \mathrm{K}_{\mathrm{f}}=8.5 \times 10^{-6} \\
\mathrm{AgBr}(\mathrm{~s}) & +2 \mathrm{NH}_{3} \rightleftharpoons & \mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}+\mathrm{Br}^{-}
\end{array}
$$

Initial $3.0 \mathrm{M} \quad 0 \quad 0$
$s \mathrm{~mol} / \mathrm{L}$ of $\mathrm{AgBr}(\mathrm{s})$ dissolves to reach equilibrium = molar solubility
Equil.

$$
3.0-2 s
$$

$s \quad s$

$$
\mathrm{K}=\frac{\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}^{+}\right]\left[\mathrm{Br}^{-}\right]}{\left[\mathrm{NH}_{3}\right]^{2}}=\frac{s^{2}}{(3.0-2 s)^{2}}, 8.5 \times 10^{-6} \approx \frac{s^{2}}{(3.0)^{2}}, s=8.7 \times 10^{-3} \mathrm{~mol} / \mathrm{L}
$$

Assumption good.
c. The presence of $\mathrm{NH}_{3}$ increases the solubility of AgBr . Added $\mathrm{NH}_{3}$ removes $\mathrm{Ag}^{+}$from solution by forming the complex ion $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$. $\mathrm{As}_{\mathrm{Ag}}{ }^{+}$is removed, more $\mathrm{AgBr}(\mathrm{s})$ will dissolve to replenish the $\mathrm{Ag}^{+}$concentration.
d. Mass $\mathrm{AgBr}=0.2500 \mathrm{~L} \times \frac{8.7 \times 10^{-3} \mathrm{~mol} \mathrm{AgBr}}{\mathrm{L}} \times \frac{187.8 \mathrm{~g} \mathrm{AgBr}}{\mathrm{mol} \mathrm{AgBr}}=0.41 \mathrm{~g} \mathrm{AgBr}$
e. Added $\mathrm{HNO}_{3}$ will have no effect on the $\mathrm{AgBr}(\mathrm{s})$ solubility in pure water. Neither $\mathrm{H}^{+}$nor $\mathrm{NO}_{3}^{-}$reacts with $\mathrm{Ag}^{+}$or $\mathrm{Br}^{-}$ions. $\mathrm{Br}^{-}$is the conjugate base of the strong acid HBr , so it is a terrible base. Added $\mathrm{H}^{+}$will not react with $\mathrm{Br}^{-}$to any great extent. However, added $\mathrm{HNO}_{3}$ will reduce the solubility of $\mathrm{AgBr}(\mathrm{s})$ in the ammonia solution. $\mathrm{NH}_{3}$ is a weak base $\left(\mathrm{K}_{\mathrm{b}}=1.8 \times 10^{-5}\right)$. Added $\mathrm{H}^{+}$will react with $\mathrm{NH}_{3}$ to form $\mathrm{NH}_{4}^{+}$. As $\mathrm{NH}_{3}$ is removed, a smaller amount of the $\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}{ }^{+}$complex ion will form, resulting in a smaller amount of $\mathrm{AgBr}(\mathrm{s})$ that will dissolve.
84. For a linear complex ion with ligands on the $x$ axis, the $d_{x^{2}-y^{2}}$ will be destabilized the most, with the lobes pointing directly at the ligands. The $\mathrm{d}_{\mathrm{yz}}$ orbital has the fewest interactions with x -axis ligands, so it is destabilized the least. The $\mathrm{d}_{\mathrm{xy}}$ and $\mathrm{d}_{\mathrm{xz}}$ orbitals will have similar destabilization but will have more interactions with x -axis ligands than the $\mathrm{d}_{\mathrm{yz}}$ orbital. Finally, the $\mathrm{d}_{\mathrm{z}^{2}}$ orbital with the doughnut of electron density in the xy plane will probably be destabilized more than the $\mathrm{d}_{\mathrm{xy}}$ and $\mathrm{d}_{\mathrm{xz}}$ orbitals but will have nowhere near the amount of destabilization that occurs with the $d_{x^{2}-y^{2}}$ orbital. The only difference that would occur in the diagram if the ligands were on the y axis is the relative positions of the $\mathrm{d}_{\mathrm{xy}}$, $\mathrm{d}_{\mathrm{xz}}$, and $\mathrm{d}_{\mathrm{yz}}$ orbitals. The $\mathrm{d}_{\mathrm{xz}}$ will have the smallest destabilization of all these orbitals, whereas the $d_{\mathrm{xy}}$ and $\mathrm{d}_{\mathrm{yz}}$ orbitals will be degenerate since we expect both to be destabilized equivalently from $y$-axis ligands. The d-orbital splitting diagrams are:
a.

linear x -axis ligands
b.

linear $y$-axis ligands

