CHAPTER 23 THE TRANSITION ELEMENTS AND THEIR COORDINATION COMPOUNDS

23.1 It is always one less than the period number.

23.2 a) All transition elements in Period 5 will have a “base” configuration of [Ar]5s², and will differ in the number of d electrons (x) that the configuration contains. Therefore, the general electron configuration is 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰⁴p⁶5s²4dₓ⁴5dₓ.
  b) A general electron configuration for Period 6 transition elements includes f sublevel electrons, which are lower in energy than the d sublevel. The configuration is 1s²2s²2p⁶3s²3p⁶4s²3d¹⁰⁴p⁶5s²4d¹⁰⁵p⁶6s²4f¹⁴5dₓ.

23.3 Electrons with the highest n value are removed first, so the ns electrons are removed before the (n - 1)d. V³⁺ is [Ar] 3d². The ionization energies and the magnetic properties are used to study the electron configurations of atoms.

23.4 The maximum number of unpaired d electrons is five since there are five d orbitals. An example of an atom with five unpaired d electrons is Mn with electron configuration [Ar]4s²3d⁵. An ion with five unpaired electrons is Mn²⁺ with electron configuration [Ar]3d⁵.

23.5 For the main group elements, size decreases as you move to the right. For the transition elements, the size decreases at first and then is fairly constant since inner orbitals are being filled.

23.6 a) One would expect that the elements would increase in size as they increase in mass from Period 5 to 6. Because 14 additional elements lie between Periods 5 and 6, the effective nuclear charge increases significantly. As effective charge increases, the atomic size decreases or “contracts.” This effect is significant enough that Zr⁴⁺ and Hf⁴⁺ are almost the same size but differ greatly in atomic mass.
  b) The size increases from Period 4 to 5, but stays fairly constant from Period 5 to 6.
  c) Atomic mass increases significantly from Period 5 to 6, but atomic radius (and thus volume) hardly increases, so Period 6 elements are very dense.

23.7 a) 1.3-1.9
  b) 0.8-2.8
  c) The range is smaller for the transition elements because the electrons are occupying d orbitals. Since these are inner orbitals, they shield (screen) the nuclear charge, making electrons shared between the transition metal and some bonded atom feel a fairly constant effective nuclear charge.

23.8 a) Transition elements commonly show multiple oxidation states; main-group elements less frequently. Since the outermost s and d electrons are so close in energy, that all of these can become involved in the bonding.
  b) The +2 oxidation state is common because the two ns electrons are more easily removed than the (n-1)d electrons.

23.9 a) A paramagnetic substance is attracted to a magnetic field, while a diamagnetic substance is slightly repelled by one.
  b) Ions of transition elements often have unfilled d-orbitals whose unpaired electrons make the ions paramagnetic. Ions of main group elements usually have a noble gas configuration with no partially filled levels. When orbitals are filled, electrons are paired and the ion is diamagnetic.
  c) The d orbitals in the transition element ions are not filled, which allows an electron from a lower energy d orbital to move to a higher energy d orbital. The energy required for this transition is relatively small and falls in the visible wavelength range. All orbitals are filled in a main-group element ion, so enough energy would have to be added to move an electron to a higher energy level, not just another orbital within the same energy level. This amount of energy is relatively large and outside the visible range of wavelengths.
23.10  a) V: \(1s^22s^22p^63s^23p^64s^23d^3\)  
Check: \(2 + 2 + 6 + 2 + 6 + 2 + 3 = 23\ e^–\)

b) Y: \(1s^22s^22p^63s^23p^64s^23d^{10}4p^6\)  
Check: \(2 + 2 + 6 + 2 + 6 + 2 + 10 + 6 + 2 + 1 = 39\ e^–\)

c) Hg: [Xe]6s^2d^{10}
Check: 54 + 2 + 14 + 10 = 80 e–

23.11  a) [Kr] 5s^2 4d^6  
 b) [Ar] 4s^1 3d^{10}  
c) [Ar] 4s^2 3d^8

23.12  a) Osmium is in row 6 and group 8B(8). Electron configuration of Os is [Xe]6s^24f^{14}5d^6.  
b) Cobalt is in row 4 and group 8B(9). Electron configuration of Co is [Ar]4s^23d^7.  
c) Silver is in row 5 and group 1B(11). Electron configuration of Ag is [Kr]5s^14d^{10}. Note that the filled d orbital is the preferred arrangement, so the configuration is not 5s^24d^9.

23.13  a) [Ar] 4s^23d^{10}  
b) [Ar] 4s^23d^5  
c) [Xe] 6s^24f^{14}5d^6

23.14 Transition metals lose their s orbital electrons first in forming cations.
a) The two 4s electrons and one 3d electron are removed to form Sc^{3+} with electron configuration [Ar] or 1s^22s^22p^63s^23p^6. There are no unpaired electrons.
b) The single 4s electron and one 3d electron are removed to form Cu^{2+} with electron configuration [Ar]3d^9. There is one unpaired electron.
c) The two 4s electrons and one 3d electron are removed to form Fe^{3+} with electron configuration [Ar]3d^5. There are five unpaired electrons.
d) The two 5s electrons and one 4d electron are removed to form Nb^{3+} with electron configuration [Kr]4d^2. There are two unpaired electrons.

23.15  a) [Ar] 3d^3; 3 unpaired electrons  
b) [Ar]: 0 unpaired electrons  
c) [Ar] 3d^6; 4 unpaired electrons  
d) [Xe] 4f^{14}5d^6; 3 unpaired electrons

23.16 For groups 3B(3) to 7B(7), the highest oxidation state is equal to the group number.
a) Tantalum, Ta, is in group 5B(5), so the highest oxidation state is +5. 
b) Zirconium, Zr, is in group 4B(4), so the highest oxidation state is +4. 
c) Manganese, Mn, is in group 7B(7), so the highest oxidation state is +7.

23.17  a) +5  
b) +3  
c) +7

23.18 The elements in Group 6B(6) exhibit an oxidation state of +6. These elements include Cr, Mo, and W. Sg (Seaborgium) is also in Group 6B(6), but its lifetime is so short that chemical properties, like oxidation states within compounds, are impossible to measure.

23.19 Ti, Zr, and Hf

23.20 Transition elements in their lower oxidation states act more like metals. The oxidation state of chromium in CrF_2 is +2 and in CrF_6 is +6 (use -1 oxidation state of fluorine to find oxidation state of Cr). CrF_2 exhibits greater metallic behavior than CrF_6 because the chromium is in a lower oxidation state in CrF_2 than in CrF_6.

23.21 Due to its lower oxidation state, VF_3 would have greater ionic character, so would be more likely to have a high melting and boiling point.

23.22 While atomic size increases slightly down a group of transition elements, the nuclear charge increases much more, so the first ionization energy generally increases. The reduction potential for Mo is lower, so it is more difficult to oxidize Mo than Cr. In addition, Mo’s ionization energy is higher than that of Cr, so it is more difficult to remove electrons, i.e., oxidize, from Mo.
23.23 Higher oxidation states are more stable for lower transition metals like Re, so ReO$_4^-$ would be a weaker oxidizing agent.

23.24 Oxides of transition metals become less basic (or more acidic) as oxidation state increases. The oxidation state of chromium in CrO$_3$ is +6 and in CrO is +2, based on the -2 oxidation state of oxygen. The oxide of the higher oxidation state, CrO$_3$, produces a more acidic solution.

23.25 Mn$_2$O$_3$, because lower oxidation states form more basic oxides.

23.26 The abnormally small size of Au atoms (due to the lanthanide contraction) means that its electrons are tightly held, giving it low reactivity. The Group 1A(1) elements do not show the lanthanide contraction.

23.27 The “last electron in” is in an f orbital, which is very close to the nucleus. This makes them all very similar from the “outside.”

23.28 a) The f-block contains 7 orbitals, so if one electron occupied each orbital, a maximum of 7 electrons would be unpaired.
   b) This corresponds to a half-filled f subshell.

23.29 All actinides are radioactive.

23.30 a) Lanthanum is a transition element in row 6 with atomic number 57. La: [Xe]6s$^2$5d$^1$
   b) Cerium is in the lanthanide series with atomic number 58. Ce: [Xe]6s$^2$4f$^1$5d$^1$, so Ce$^{3+}$: [Xe]4f$^1$
   c) Einsteinium is in the actinide series with atomic number 99. Es: [Rn]7s$^2$5f$^{11}$
   d) Uranium is in the actinide series with atomic number 92. U: [Rn]7s$^2$5f$^{11}$d$^1$. Removing four electrons gives U$^{4+}$ with configuration [Rn]5f$^1$.

23.31 a) [Xe] 6s$^2$4f$^5$
   b) [Xe] 4f$^{14}$
   c) [Rn] 7s$^2$6d$^2$
   d) [Rn] 5f$^{11}$

23.32 a) Europium is in the lanthanide series with atomic number 63. The configuration of Eu is [Xe]6s$^2$4f$^7$. The stability of the half-filled f sublevel explains why the configuration is not [Xe]6s$^2$4f$^6$5d$^1$. The two 6s electrons are removed to form the Eu$^{2+}$ ion, followed by electron removal in the f-block to form the other two ions:
   Eu$^{2+}$: [Xe]4f$^7$
   Eu$^{3+}$: [Xe]4f$^6$
   Eu$^{4+}$: [Xe]4f$^5$
   The stability of the half-filled f sublevel makes Eu$^{2+}$ most stable.
   b) Terbium is in the lanthanide series with atomic number 65. The configuration of Tb is [Xe]6s$^2$4f$^9$. The two 6s electrons are removed to form the Tb$^{2+}$ ion, followed by electron removal in the f-block to form the other two ions:
   Tb$^{2+}$: [Xe]4f$^9$
   Tb$^{3+}$: [Xe]4f$^8$
   Tb$^{4+}$: [Xe]4f$^7$
   Tb would demonstrate a +4 oxidation state because it has the half-filled sublevel.

23.33 a) Ce$^{2+}$: [Xe] 5d$^1$4f$^1$
   Ce$^{3+}$: [Xe] 4f$^1$
   Ce$^{4+}$: [Xe]
   b) Yb$^{2+}$: [Xe] 4f$^{14}$
   Yb$^{3+}$: [Xe] 4f$^{13}$
   Yb$^{4+}$: [Xe] 4f$^{12}$
   c) Ce$^{3+}$ has a noble-gas configuration and Yb$^{3+}$ has a filled f subshell.

23.34 The lanthanide element gadolinium, Gd, has electron configuration [Xe]6s$^2$4f$^7$5d$^1$ with eight unpaired electrons. The ion Gd$^{3+}$ has seven unpaired electrons: [Xe]4f$^7$.

23.35 Chromium forms a thin, adherent, transparent coating of its oxide which protects the metal from further reaction.
23.36 Valence-state electronegativity refers to the effective electronegativity of an element in a given oxidation state. As manganese is bonded to more oxygen atoms in its different oxides, its oxidation number becomes more positive. In solution a water molecule is attracted to the increasingly positive manganese and one of its protons becomes easier to lose.

23.37 A small amount of Mn makes steel easier to roll, forge, and weld. A larger amount makes it tougher for use as (e.g., armor plate).

23.38 Silver lacks chemical reactivity with oxygen.

23.39 The latent image is not visible but contains defects (scattered atoms of photoreduced Ag) which make the exposed regions more susceptible to reaction.

23.40 Mercury demonstrates an unusual physical property in that it exists in the liquid state at room temperature. There are two reasons for the weaker forces between mercury atoms. First, in its crystal structure each mercury atom is surrounded by 6 nearest neighbors instead of the usual 12. This decreases the forces holding mercury atoms, so they can move more freely than other metal atoms. Second, the bonding between metal atoms is metallic bonding, which involves only the 6s electrons in mercury compared to the s and d electrons in other metals. Mercury occurs in the +1 oxidation state, unusual for its group, because two mercury +1 ions form a dimer, Hg$_2^{2+}$ by sharing their unpaired 6s electrons in a covalent bond.

23.41 \[
\text{Cr(H}_2\text{O)}_2(\text{OH})_4(\text{aq}) + \text{H}^+(\text{aq}) \rightarrow \text{Cr(OH)}(\text{s}) + 3\text{H}_2\text{O(l)}
\]
\[
\text{Cr(OH)}(\text{s}) + 3\text{H}^+(\text{aq}) \rightarrow \text{Cr}^{3+}(\text{aq}) + 3\text{H}_2\text{O(l)}
\]

23.42 A reaction is favorable if the $E^\circ$ for the reaction, as written, is positive. Since Cr$^{3+}(aq)$ is prepared, it must appear on the right side of the equation. Cr(s) and Cr$^{3+}(aq)$ must appear as reactants. The middle equation will result in the cancellation of one of the needed reactants, so it is not included in the reaction summation. Reverse the third equation and multiply the first equation by 2 so that the electron transfer is balanced.

Reduction: \[2(\text{Cr}^{3+}(\text{aq}) + e^- \rightarrow \text{Cr}^{2+}) \]
\[E^\circ = -0.41 \text{ V} \] (changing coefficients does not change $E^\circ$)

Oxidation: \[\text{Cr(s)} \rightarrow \text{Cr}^{2+}(\text{aq}) + 2 e^- \]
\[E^\circ = +0.91 \text{ V} \]

Overall: \[2 \text{Cr}^{3+}(\text{aq}) + \text{Cr(s)} \rightarrow 3 \text{Cr}^{2+} \]
\[E^\circ = +0.50 \text{ V} \]

Since $E^\circ > 0$, the reaction is spontaneous. So, **yes**, Cr$^{2+}$ can be prepared from Cr and Cr$^{3+}$.

23.43 The orange color is characteristic of Cr$_2$O$_7^{2-}$, which is stable only in acidic solution.

23.44 Check reduction standard potentials in Appendix D.

23.45 Donor atoms must have a pair of electrons which can be donated to another atom.
23.47 The coordination number indicates the number of ligand atoms bonded to the central metal ion. The oxidation number represents the number of electrons lost to form the ion. The coordination number is unrelated to the oxidation number.

23.48 Chelates contain two or more donor atoms which can simultaneously bond to a single metal ion.

23.49 Coordination number of two indicates linear geometry. Coordination number of four indicates either tetrahedral or square planar geometry. Coordination number of six indicates octahedral geometry.

23.50 Co(III): 6  Pt(II): 4  Pt(IV): 6

23.51 The metal ion acts as a Lewis acid, accepting one or more electron pairs from the ligand(s), which are acting as Lewis bases.

23.52 The complex ion has a negative charge.

23.53 The ligands are listed first (alphabetically), followed by the metal.

23.54 A constitutional isomer, since the atoms are connected in a different pattern.

23.55 a) The oxidation state of nickel is found from the total charge on the ion (+2 because two Cl\(^-\) charges equals -2) and the charge on ligands:
   \[
   \text{charge on nickel} = +2 - 6(0 \text{ charge on water}) = +2
   \]
   Name nickel as nickel(II) to indicate oxidation state. Ligands are six (hexa-) waters (aqua). Put together with chloride anions to give hexaaquanickel(II) chloride.
   b) The cation is \([\text{Cr(en)}_3]^{n+}\) and the anion is \(\text{ClO}_4^-\), the perchlorate ion (see Chapter 2 for naming polyatomic ions). The charge on the cation is +3 to make a neutral salt in combination with 3 perchlorate ions. The ligand is ethylenediamine, which has 0 charge. The charge of the cation equals the charge on chromium ion, so chromium(III) is included in the name. The three ethylenediamine ligands, abbreviated en, are indicated by the prefix tris because the name of the ligand includes a numerical indicator, di-. The complete name is tris(ethylenediamine)chromium(III) perchlorate.
   c) The cation is \(\text{K}^+\) and the anion is \([\text{Mn(CN)}_6]^{4-}\). The charge of 4- is deduced from the four potassium ions in the formula. The oxidation state of Mn is -4 - \{6(-1)\} = +2. The name of CN\(^-\) ligand is cyano and six ligands are represented by the prefix hexa. The name of manganese anion is manganate(II). The full name of compound is potassium hexacyanomanganate(II).

23.56 a) tetraamminedinitrocobalt(III) chloride
   b) hexaamminechromium(III) hexacyanochromate(III)
   c) potassium tetrachlorocuprate(II)

23.57 The charge of the central metal atom was determined in 23.55 because the roman numeral indicating oxidation state is part of the name. The coordination number, or number of ligand atoms bonded to the metal ion, is found by examining the bonded entities inside the square brackets to determine if they are unidentate, bidentate, or polydentate.
   a) The roman numeral “II” indicates a +2 oxidation state. There are 6 water molecules bonded to Ni and each ligand is unidentate, so the coordination number is 6.
   b) The roman numeral “III” indicates a +3 oxidation state. There are 3 ethylenediamine molecules bonded to Cr, but each ethylenediamine molecule contains two donor N atoms (bidentate). Therefore, the coordination number is 6.
   c) The roman numeral “II” indicates a +2 oxidation state. There are 6 unidentate cyano molecules bonded to Mn, so the coordination number is 6.

23.58 a) +3, 6  b) +3, 6; +3, 6  c) +2, 4
23.59  
a) The cation is K\(^+\), potassium. The anion is \([Ag(CN)\_2]\)\(^-\) with the name dicyanoargentate ion for the two cyanide ligands and the name of silver in anions, argentate(I). The complete name is \textbf{potassium dicyanoargentate(I)}.  
b) The cation is Na\(^+\), sodium. The anion is \([CdCl\_4]\)\(^2-\) with the name tetrachlorocadmate(II) ion. With four chloride ligands, the oxidation state of cadmium is +2 and the name of cadmium in anions is cadmate. The complete name is \textbf{sodium tetrachlorocadmate(II)}.  
c) The cation is \([Co(NH\_3\_4)(H\_2O)Br]\)\(^2+\) with the name tetraamineaquabromocobalt(III) ion, with four ammonia ligands (tetraamine), one water ligand (aqua) and one bromide ligand (bromo). The oxidation state of cobalt is +3, indicated by (III), following cobalt in the name. The anion is Br\(^-\), bromide. The complete name is \textbf{tetraammineaquabromocobalt(III) bromide}.  

23.60  
a) \textbf{potassium amminepentachloroplatinate(IV)}  
b) \textbf{diammine(ethylenediamine)copper(II) tetrachloro(ethylenediamine)cobaltate(II)}  
c) \textbf{dibromobis(ethylenediamine)platinum(IV) perchlorate}  

23.61  
a) The counter ion is K\(^+\), so the complex ion is \([Ag(CN)\_2]\)\(^-\). Each cyano ligand has a -1 charge, so silver has a +1 charge: +1 + 2(-1) = -1. Each cyano ligand is unidentate, so the coordination number is \textbf{2}.  
b) The counter ion is Na\(^+\), so the complex ion is \([CdCl\_4]\)\(^2-\). Each chloride ligand has a -1 charge, so Cd has a +2 charge: +2 + 4(-1) = -2. Each chloride ligand is unidentate, so the coordination number is \textbf{4}.  
c) The counter ion is Br\(^-\), so the complex ion is \([Co(NH\_3\_4)(H\_2O)Br]\)\(^2+\). Both the ammine and aqua ligands are neutral. The bromide ligand has a -1 charge, so Co has a +3 charge: +3 + 4(0) + 0 + (-1) = +2. Each ligand is unidentate, so the coordination number is \textbf{6}.  

23.62  
a) +4, 6  
b) +2, 6; +2, 6  
c) +4, 6  

23.63  
a) The cation is tetramminezinc ion. The tetraammine indicate four NH\_3 ligands. Zinc has an oxidation state of +2, so the charge on the cation is +2. The anion is SO\_4\(^2-\), only one sulfate is needed to make a neutral salt. The formula of the compound is \[Zn(NH\_3\_4)SO\_4\].  
b) The cation is pentaamminechlorochromium(III) ion. The ligands are 5 NH\_3 from pentaammine, and one chloride from chloro. The chromium ion has a charge of +3, so the complex ion has a charge equal to +3 from chromium, plus 0 from ammonia, plus -1 from chloride for a total of +2. The anion is chloride, Cl\(^-\). Two chloride ions are needed to make a neutral salt. The formula of compound is \[Cr(NH\_3\_5)Cl\]Cl\(_2\).  
c) The anion is bis(thiosulfato)argentate(I). Argentate(I) indicates silver in the +1 oxidation state, and bis(thiosulfato) indicates 2 thiosulfate ligands, S\(_2\)O\_3\(^2-\). The total charge on the anion is +1 plus 2(-2) to equal -3. The cation is sodium, Na\(^+\). Three sodium ions are needed to make a neutral salt. The formula of compound is \[Na_3[Ag(S\_2O\_3\_2)]\].  

23.64  
a) \[Co(en)\_2 Br\_2\]SO\_4  
b) \[Cr(NH\_3\_6)\_2[CuCl\_4\]  
c) \[K_4[Fe(CN)\_6]\]  

23.65  
Coordination compounds act like electrolytes, i.e., they dissolve in water to yield charged species. However, the complex ion itself does not dissociate. The “number of individual ions per formula unit” refers to the number of ions that would form per coordination compound upon dissolution in water.  
a) The counter ion is SO\_4\(^2-\), so the complex ion is \[Zn(NH\_3\_4)\]SO\_4\(^2-\). Each ammine ligand is unidentate, so the coordination number is \textbf{4}. Each molecule dissolves in water to form one SO\_4\(^2-\) ion and one \[Zn(NH\_3\_4)\]\(^{2+}\) ion, so \textbf{2 ions} form per formula unit.  
b) The counter ion is Cl\(^-\), so the complex ion is \[Cr(NH\_3\_5)Cl\]\(^2+\). Each ligand is unidentate, so the coordination number is \textbf{6}. Each molecule dissolves in water to form two Cl\(^-\) ions and one \[Cr(NH\_3\_5)Cl\]\(^{2+}\) ion, so \textbf{3 ions} form per formula unit.  
c) The counter ion is Na\(^+\), so the complex ion is \[Ag(S\_2O\_3\_2)\]\(^3-\). Assuming that the thiosulfate ligand is unidentate, the coordination number is \textbf{2}. Each molecule dissolves in water to form 3 Na\(^+\) ions and one \[Ag(S\_2O\_3\_2)\]\(^{3-}\) ion, so \textbf{4 ions} form per formula unit.  

23.66  
a) 6; \textbf{3 ions}  
b) 6 and \textbf{4; 5 ions}  
c) 6; \textbf{5 ions}
a) The cation is hexaaquachromium(III) with the formula \([\text{Cr(H}_2\text{O})_6]\)^{3+}. The total charge of the ion equals the charge on chromium because water is neutral ligand. Six water ligands are indicated by a \textit{hexa} prefix to aqua. The anion is \(\text{SO}_4^{2-}\). To make the neutral salt requires 3 sulfate ions for 2 cations. The compound formula is \([\text{Cr(H}_2\text{O})_6]\)\(_2\)(\text{SO}_4)_3.

b) The anion is tetrabromoferrate(III) with the formula \([\text{FeBr}_4]^-\). The total charge on the ion equals +3 charge on iron plus 4 times -1 charge on each bromide ligand for -1 overall. The cation is barium, \(\text{Ba}^{2+}\). Two anions are needed for each barium ion to make a neutral salt. The compound formula is \(\text{Ba}[\text{FeBr}_4]_2\).

c) The anion is bis(ethylenediamine)platinum(II) ion. Charge on platinum is +2 and this equals the total charge on the complex ion because ethylenediamine is a neutral ligand. The \textit{bis} preceding ethylenediamine indicates two ethylenediamine ligands, which are represented by the abbreviation “en.” The cation is \(\text{CO}_3^{2-}\). One carbonate combines with one cation to produce a neutral salt. The compound formula is \([\text{Pt(en)}_2]\text{CO}_3\).

23.68

a) \(K_2[\text{Cr(C}_2\text{O}_4)_3]\)

b) \([\text{Co(en)}_3]_4[\text{Mn(CN)}_3]\)_3

c) \([\text{Al(H}_2\text{O})_2(\text{NH}_3)_2\text{BrCl}]\text{NO}_3\)

23.69

a) The counter ion is \(\text{SO}_4^{2-}\), so the complex ion is \([\text{Cr(H}_2\text{O})_6]\)^{3+}. Each aqua ligand is unidentate, so the coordination number is 6. Each molecule dissolves in water to form three \(\text{SO}_4^{2-}\) ions and two \([\text{Cr(H}_2\text{O})_6]\)^{3+} ions, so \(5\) ions form per formula unit.

b) The counter ion is \(\text{Ba}^{2+}\), so the complex ion is \([\text{FeBr}_4]^-\). Each bromo ligand is unidentate, so the coordination number is 4. Each molecule dissolves in water to form one \(\text{Ba}^{2+}\) ion and 2 \([\text{FeBr}_4]^-\) ions, so \(3\) ions form per formula unit.

c) The counter ion is \(\text{CO}_3^{2-}\), so the complex ion is \([\text{Pt(en)}_2]\)^{2+}. Each ethylenediamine ligand is bidentate, so the coordination number is 4. Each molecule dissolves in water to form one \(\text{CO}_3^{2-}\) ion and one \([\text{Pt(en)}_2]\)^{2+} ion, so \(2\) ions forms per formula unit.

23.70

a) \(6; 4\) ions

b) \(6\) and \(6; 7\) ions

c) \(6; 2\) ions

23.71

Ligands that form linkage isomers have two different possible donor atoms.

a) The nitrite ion \textbf{forms linkage isomers} because it can bind to the metal ion through either the nitrogen or one of the oxygen atoms – both have a lone pair of electrons. Resonance Lewis structures are

\[
\begin{array}{c}
\overset{\ddots}{\text{O}} - \overset{\ddots}{\text{N}} - \overset{\ddots}{\text{O}}
\end{array}
\]

b) Sulfur dioxide molecules \textbf{form linkage isomers} because both the sulfur and oxygen atoms can bind metal ions because they both have lone pairs.

\[
\overset{\ddots}{\text{O}} - \overset{\ddots}{\text{S}} - \overset{\ddots}{\text{O}}
\]

c) Nitrate ions have three oxygen atoms, all with a lone pair that can bond to the metal ion, but all of the oxygen atoms are equivalent, so there are \textbf{no linkage isomers}.

\[
\begin{array}{c}
\overset{\ddots}{\text{O}} - \overset{\ddots}{\text{N}} - \overset{\ddots}{\text{O}}
\end{array}
\]

23.72

a) The thiocyanate ion can form linkage isomers because both the sulfur and nitrogen ions have lone pairs.

\[
\overset{\ddots}{\text{S}} - \overset{\ddots}{\text{C}} - \overset{\ddots}{\text{N}}
\]

Only one of the resonance forms is shown.
b) The thiosulfate ion can form linkage isomers because either one of the oxygens or the non-central sulfur may serve as a donor atom.

\[
\begin{array}{c}
\text{O} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{S} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{O} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{O} \\
\text{\vdots}
\end{array}
\end{array}
\]^{2-}

\[2-\]

c) The hydrogen sulfide ion cannot form linkage isomers, because the hydrogen does not have a lone-pair.

\[\text{H} \quad \text{\vdots} \quad \text{S} \quad \text{\vdots} \quad \text{H}\]

23.73 a) Platinum ion, Pt\(^{2+}\), is a \(d^8\) ion so the ligand arrangement is square planar. A \textit{cis} and \textit{trans} geometric isomer exist for this complex ion:

\[\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Br} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Pt} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Br} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{\vdots}
\end{array}
\end{array}\]

\[\text{cis isomer} \quad \text{trans isomer}\]

No optical isomers exist because the mirror images of both compounds are superimposable on the original molecules. In general, a square planar molecule is superimposable on its mirror image.

b) A \textit{cis} and \textit{trans} geometric isomer exist for this complex ion. No optical isomers exist because the mirror images of both compounds are superimposable on the original molecules.

\[\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{F} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Pt} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{F} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{\vdots}
\end{array}
\end{array}\]

\[\text{cis isomer} \quad \text{trans isomer}\]

c) Three geometric isomers exist for this molecule, although they are not named \textit{cis} or \textit{trans} because all the ligands are different. A different naming system is used to indicate the relation of one ligand to another.

\[\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{F} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Pt} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{N} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{F} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{O} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{O} \\
\text{\vdots}
\end{array}
\begin{array}{c}
\text{H} \\
\text{\vdots}
\end{array}
\end{array}\]
23.74 a) No isomers
b) Optical isomers

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{Zn} & \quad \text{F} \\
\text{Cl} & \quad \text{N} & \quad \text{H} \\
\text{Cl} & \quad \text{H} & \quad \text{H} & \quad \text{N} & \quad \text{Zn} & \quad \text{F} \\
\end{align*}
\]

c) geometric isomers

\[
\begin{align*}
\left[ \begin{array}{c}
\text{H} \\
\text{O} \\
\text{Pd} \\
\text{C} \\
\text{C} \\
\text{N}
\end{array} \right] & \quad \text{2}^{-} \\
\text{H} & \quad \text{O} & \quad \text{Pd} & \quad \text{C} & \quad \text{C} & \quad \text{N} & \quad \text{2}^{-}
\end{align*}
\]

23.75 Types of isomers for coordination compounds are coordination isomers with different arrangements of ligands and counterions, linkage isomers with different donor atoms from the same ligand bound to the metal ion, geometric isomers with differences in ligand arrangement relative to other ligands, and optical isomers with mirror images that are not superimposable.

a) Platinum ion, Pt\(^{2+}\), is a d\(^8\) ion, so the ligand arrangement is square planar. The ligands are 2 Cl\(^-\) and 2 Br\(^-\), so the arrangement can be either both ligands \textit{trans} or both ligands \textit{cis} to form geometric isomers.

\[
\begin{align*}
\left[ \begin{array}{c}
\text{Br} \\
\text{Cl} \\
\text{Pt} \\
\text{Cl} \\
\text{Br}
\end{array} \right] & \quad \text{2}^{-} \\
\left[ \begin{array}{c}
\text{Br} \\
\text{Cl} \\
\text{Pt} \\
\text{Br} \\
\text{Cl}
\end{array} \right] & \quad \text{2}^{-}
\end{align*}
\]

b) The complex ion can form linkage isomers with the NO\(_2\) ligand. Either the N or an O may be the donor.

\[
\begin{align*}
\left[ \begin{array}{c}
\text{NH}_3 \\
\text{H}_3\text{N} \\
\text{Cr} \\
\text{ONO}
\end{array} \right] & \quad \text{2}^{-} \\
\left[ \begin{array}{c}
\text{NH}_3 \\
\text{H}_3\text{N} \\
\text{Cr} \\
\text{NO}_2
\end{array} \right] & \quad \text{2}^{-}
\end{align*}
\]

c) In the octahedral arrangement, the two iodide ligands can be either \textit{trans} to each other, \textit{cis} to each other, or \textit{cis} to each other, 90° apart.

\[
\begin{align*}
\left[ \begin{array}{c}
\text{NH}_3 \\
\text{H}_3\text{N} \\
\text{Pt} \\
\text{I}
\end{array} \right] & \quad \text{2}^{+} \\
\left[ \begin{array}{c}
\text{NH}_3 \\
\text{H}_3\text{N} \\
\text{Pt} \\
\text{I}
\end{array} \right] & \quad \text{2}^{+}
\end{align*}
\]
23.76 a) Coordination isomers:

\[
\begin{align*}
\text{NH}_3 & \quad \text{Co} \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\end{align*}
\]

\[\text{Br}^- \quad 2^+ \]

\[
\begin{align*}
\text{NH}_3 & \quad \text{Co} \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{Br} \\
\end{align*}
\]

\[\text{Br}^- \quad \text{Cl}^- \quad 2^+ \]

b) Coordination isomers:

\[
\begin{align*}
\text{H} & \quad \text{CH}_3 \\
\text{H} & \quad \text{N} \quad \text{Pr} \\
\text{N} & \quad \text{N} \quad \text{Pr} \\
\text{H} & \quad \text{H} \quad \text{CH}_3 \\
\end{align*}
\]

\[\text{Br} \quad \text{Cl} \]

c) Geometric isomers:

\[
\begin{align*}
\text{NH}_3 & \quad \text{Fe} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{OH}_2 & \quad \text{OH}_2 \\
\end{align*}
\]

\[2^+ \]

\[
\begin{align*}
\text{NH}_3 & \quad \text{Fe} \\
\text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{OH}_2 & \quad \text{OH}_2 \\
\end{align*}
\]

\[2^+ \]

23.77 The traditional formula does not correctly indicate that at least some of the chloride ions serve as counter ions. The \text{NH}_3 molecules serve as ligands, so \(n\) could equal 6 to satisfy the coordination number requirement. This complex has the formula \([\text{Cr(NH}_3)_6]\text{Cl}_3\). This is a correct formula because the name “chromium(III)” means that the chromium has a +3 charge, and this balances with the -3 charge provided by the three chloride counter ions. However, when this compound dissociates in water, it produces 4 ions (\([\text{Cr(NH}_3)_6]\text{Cl}_3^2^-\) and 3 \text{Cl}^-), whereas \text{NaCl} only produces two ions. Other possible compounds are \(n=5\), \(\text{CrCl}_3\cdot5\text{NH}_3\), with formula \([\text{Cr(NH}_3)_5\text{Cl}]\text{Cl}_2\); \(n=4\), \(\text{CrCl}_3\cdot4\text{NH}_3\), with formula \([\text{Cr(NH}_3)_4\text{Cl}_2]\text{Cl}\); \(n=3\), \(\text{CrCl}_3\cdot3\text{NH}_3\), with formula \([\text{Cr(NH}_3)_3\text{Cl}_3]\). The compound \([\text{Cr(NH}_3)_4\text{Cl}_2]\text{Cl}\) has a coordination number equal to 6 and produces two ions when dissociated in water, so it has an electrical conductivity similar to an equimolar solution of \text{NaCl}.

23.78 4 (Corresponding to \([\text{M(NH}_3)_2\text{Cl}_2]\text{Cl}_2\))

23.79 First find the charge on the palladium ion, then arrange ligands and counter ions to form the complex.

a) Charge on palladium = \(-[(+1 \text{ on K}^+) + (0 \text{ on NH}_3) + 3(-1 \text{ on Cl}^-)]\) = +2

Palladium(II) forms four-coordinate complexes. The four ligands in the formula are one \text{NH}_3 and three \text{Cl}^- ions.

The formula of the complex ion is \([\text{Pd(NH}_3]\text{Cl}_3]^-.\) Combined with the potassium cation, the compound formula is \(\text{K}[\text{Pd(NH}_3]\text{Cl}_3].\)

b) Charge on palladium = \(-[2(-1 \text{ on Cl}^-) + 2(0 \text{ on NH}_3)]\) = +2

Palladium(II) forms four-coordinate complexes. The four ligands are 2 chloride ions and 2 ammonia molecules.

The formula is \([\text{PdCl}_2(\text{NH}_3)_2].\)
c) Charge on palladium = \([-2(\text{on K}) + 6(-1 \text{ on Cl})]\) = +4
Palladium(IV) forms six-coordinate complexes. The six ligands are the 6 chloride ions. The formula is $K_2[PdCl_6]$.

d) Charge on palladium = \([-4(0 \text{ on NH}_3) + 4(-1 \text{ on Cl})]\) = +4
Palladium(IV) forms six-coordinate complexes. The ammonia molecules have to be ligands. The other two ligand bonds are formed with two of the chloride ions. The remaining two chloride ions are the counter ions. The formula is $[Pd(NH_3)_4Cl_2]Cl_2$.

23.80  
a) A bond formed when both electrons came from one atom.
b) Yes. $H_2O$ molecules act as donors to $Fe^{3+}$, forming $Fe(H_2O)_6^{3+}$.
c) Yes. $H_2O$ molecules act as donors to $H^+$, forming $H_3O^+$.  

23.81  
a) Four empty orbitals of equal energy are “created” to receive the donated electron pairs from four ligands. The four orbitals are hybridized from an $s$, two $p$, and one $d$ orbital from the previous $n$ level to form 4 $dsp^3$ orbitals.
b) One $s$ and three $p$ orbitals become four $sp^3$ hybrid orbitals.

23.82  
6: octahedral

23.83  
Purple (red + violet/blue)

23.84  
Absorption of orange or yellow light gives a blue solution.

23.85  
a) The crystal field splitting energy is the energy difference between the two sets of $d$ orbitals that result from the bonding of ligands to a central transition metal atom.  
b) In an octahedral field of ligands, the ligands approach along the $x$, $y$, and $z$ axes. The $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are located along the $x$, $y$, and $z$ axes, so ligand interaction is higher in energy than the other orbital-ligand interactions. The other orbital-ligand interactions are lower in energy because the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals are located between the $x$, $y$, and $z$ axes.
c) In a tetrahedral field of ligands, the ligands do not approach along the $x$, $y$, and $z$ axes. The ligand interaction is greater for the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals and lesser for the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals. The crystal field splitting is reversed, and the $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals are higher in energy than the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals.

23.86  
A strong-field ligand causes a greater crystal-field splitting (a greater $\Delta$) than a weak-field ligand. $CN^-$ is a strong-field ligand, and $F^-$ is a weak-field ligand.

23.87  
High-spin.

23.88  
If $\Delta$ is greater than $E_{\text{pairing}}$, electrons will preferentially pair spins in the lower energy $d$ orbitals before adding as unpaired electrons to the higher energy $d$ orbitals. If $\Delta$ is less than $E_{\text{pairing}}$, electrons will preferentially add as unpaired electrons to the higher $d$ orbitals before pairing spins in the lower energy $d$ orbitals. The first case gives a complex that is low-spin and less paramagnetic than the high-spin complex formed in the latter case.

23.89  
The $\Delta$ values for tetrahedral complexes are smaller than for octahedral, so $\Delta$ is always $E_{\text{pairing}}$.

23.90  
To determine the number of $d$ electrons in a central metal ion, first write the electron configuration for the metal atom. Examine the formula of the complex to determine the charge on the central metal ion, and then write the ion’s configuration.
a) Electron configuration of Ti: $[Ar]4s^23d^2$
Charge on Ti: Each chloride ligand has a -1 charge, so Ti has a +4 charge.
Electron configuration of Ti$^{4+}$: $[Ar]$
Ti$^{4+}$ has no $d$ electrons.
b) Electron configuration of Au: [Xe]6s¹4f¹⁴5d¹⁰
Charge on Au: The complex ion has a -1 charge ([AuCl₄]⁻) and each chloride ligand has a -1 charge, so Au has a +3 charge.

   Electron configuration of Au³⁺: [Xe]4f¹⁴5d⁸
   Au³⁺ has 8 d electrons.

c) Electron configuration of Rh: [Kr]5s²4d⁷
Charge on Rh: Each chloride ligand has a -1 charge, so Rh has a +3 charge.

   Electron configuration of Rh³⁺: [Kr]4d⁶
   Rh³⁺ has 6 d electrons.

23.91 a) 4 d electrons  b) 3 d electrons  c) 6 d electrons

23.92 a) Charge on iridium = -(+2 on Ca²⁺) + 6(-1 on F⁻) = +4
   Configuration of Ir⁴⁺ is [Xe]⁴f¹⁴5d⁸.  5 d electrons in Ir⁴⁺.

b) Charge on mercury = [4(-1 on I⁻)] - 2 = +2
   Configuration of Hg²⁺ is [Xe]⁴f¹⁴5d¹⁰.  10 d electrons in Hg²⁺.

c) Charge on cobalt = [-4 on EDTA] - 2 = +2
   Configuration of Co²⁺ is [Ar]³d⁷.  7 d electrons in Co²⁺.

23.93 a) 5  b) 4  c) 6

23.94

The unequal shading of the lobes of the d orbitals is a consequence of the quantum mechanical derivation of these orbitals, and does not affect the current discussion.

In an octahedral field of ligands, the ligands approach along the x, y, and z axes. The \( d_{x^2-y^2} \) orbital is located along the x and y axes, so ligand interaction is greater. The \( d_{xy} \) orbital is offset from the x and y axes by 90°, so ligand interaction is not less. The greater interaction of the \( d_{x^2-y^2} \) orbital results in its higher energy.
The unequal shading of the lobes of the $d$ orbitals is a consequence of the quantum mechanical derivation of these orbitals, and does not affect the current discussion. In an octahedral complex, the ligands “point” directly at the electrons in both of these orbitals. In a square planar complex, there are no ligands along the $z$ axis, so the $d_{z^2}$ is a very favorable (i.e., low-energy) place for the electrons.

23.96  

a) The electron configuration of Ti$^{3+}$ is [Ar]$3d^1$. With only one electron in the $d$ orbitals, the titanium(III) ion cannot form high and low spin complexes – all complexes will contain one unpaired electron and have the same spin.  
b) Co$^{2+}$ will form high and low spin complexes with 7 electrons in the $d$ orbital.  
c) Fe$^{2+}$ will form high and low spin complexes with 6 electrons in the $d$ orbital.  
d) The electron configuration of Cu$^{2+}$ is [Ar]$3d^9$, so in complexes with both strong and weak field ligands, one electron will be unpaired and the spin in both types of complexes is identical. Cu$^{2+}$ cannot form high and low spin complexes.

23.97  

b and d

23.98  

To draw the orbital-energy splitting diagram, first determine the number of $d$ electrons in the transition metal ion. Examine the formula of the complex ion to determine the electron configuration of the metal ion, remembering that the ns electrons are lost first. Determine the coordination number from the number of ligands, recognizing that 6 ligands result in an octahedral arrangement and 4 ligands result in a tetrahedral or square planar arrangement. Weak-field ligands give the maximum number of unpaired electrons (high spin) while strong-field ligands lead to electron pairing (low spin).

a) Electron configuration of Cr: [Ar]$4s^13d^5$  
Charge on Cr: The aqua ligands are neutral, so the charge on Cr is +3.  
Electron configuration of Cr$^{3+}$: [Ar]$3d^3$  
Six ligands indicate an octahedral arrangement. Using Hund’s rule, fill the lower energy $t_{2g}$ orbitals first, filling empty orbitals before pairing electrons within an orbital.

b) Electron configuration of Cu: [Ar]$4s^13d^{10}$  
Charge on Cu: The aqua ligands are neutral, so Cu has a +2 charge.  
Electron configuration of Cu$^{2+}$: [Ar]$3d^9$  
Four ligands and a $d^9$ configuration indicate a square planar geometry (only filled $d$ sublevel ions exhibit tetrahedral geometry). Use Hund’s rule to fill in the 9 $d$ electrons. Therefore, the correct orbital-energy splitting diagram shows one unpaired electron.
c) Electron configuration of Fe: [Ar]4s^23d^6
Charge on Fe: Each fluoride ligand has a -1 charge, so Fe has a +3 charge to make the overall complex charge equal to -3.
Electron configuration of Fe^{3+}: [Ar]3d^5
Six ligands indicate an octahedral arrangement. Use Hund’s rule to fill the orbitals.
F⁻ is a weak field ligand, so the splitting energy, Δ, is not large enough to overcome the resistance to electron pairing. The electrons remain unpaired, and the complex is called high-spin.

(a) (b) (c)

23.100 a) The complex is octahedral, so the splitting is d_{xy}, d_{xz}, d_{yz} at lower energy than d_{z^2} and d_{x^2-y^2}.
Mo^{3+} has 3 d electrons.
b) The complex is octahedral, so the splitting is d_{xy}, d_{xz}, d_{yz} at lower energy than d_{z^2} and d_{x^2-y^2}.
Ni^{2+} has 8 d electrons.
c) The complex is square planar because there are four ligands and nickel has 8 d electrons. The complex is low spin because CN⁻ is a strong field ligand.

(a) (b) (c)
23.102 Figure 23.22 describes the spectrum of splitting energy, $\Delta$. NO$_2^-$ is a stronger ligand than NH$_3$, which is stronger than H$_2$O. The energy of light absorbed increases as $\Delta$ increases.

$$[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{NO}_2)_6]^{3+}$$

23.103 $[\text{Cr}(\text{CN})_6]^{3-} > [\text{Cr}(\text{en})_3]^{3+} > [\text{Cr}(\text{Cl})_6]^{3-}$

23.104 A violet complex absorbs yellow-green light. The light absorbed by a complex with a weaker ligand would be at a lower energy and higher wavelength. Light of lower energy than yellow-green light is yellow, orange, or red light. The color observed would be blue or green.

23.105 A violet complex is absorbing yellow-green light, and a green complex is absorbing red light. The green complex is absorbing lower-energy light, so it must contain a weaker ligand than H$_2$O. Thus, L could not be CN$^-$ (which is stronger than H$_2$O) but could be Cl$^-$.

23.106 In an octahedral $d^8$ complex, two electrons occupy the two $e_g$ orbitals and will be unpaired. In a square-planar $d^8$ complex, the highest-energy ($d_{x^2 - y^2}$) orbital is unoccupied and all other levels are full, making the complex diamagnetic.

23.107 The aqua ligand is weaker than the ammine ligand. The weaker ligand results in a lower splitting energy and absorbs a lower energy of visible light. The green hexaaqua complex appears green because it absorbs red light (opposite side of the color wheel). The hexammine complex appears violet because it absorbs yellow light, which is higher in energy (shorter $\lambda$) than red light.

23.108 NH$_3$ > H$_2$O > F$^-$ in ligand-field strength, so $[\text{Co(NH}_3)_6]^{3+}$ would absorb light of highest energy (lowest wavelength), followed by $[\text{Co(H}_2\text{O})_6]^{3+}$ and $[\text{Co(F}_6]^{3-}$. Yellow-orange, green, and blue complexes would absorb blue-green, red, and orange light respectively. Thus, $[\text{Co(NH}_3)_6]^{3+}$ is yellow-orange, $[\text{Co(H}_2\text{O})_6]^{3+}$ is blue and $[\text{Co(F}_6]^{3-}$ is green.

23.109 a) Their outermost electrons are in $f$ orbitals.
    b) U$^{3+}$: [Rn] 5f$^3$  
    Np$^{3+}$: [Rn] 5f$^4$  
    Pu$^{3+}$: [Rn] 5f$^5$  
    U$^{4+}$: [Rn] 5f$^1$  
    Np$^{4+}$: [Rn] 5f$^2$  
    Pu$^{4+}$: [Rn] 5f$^2$

If Np and Pu were in Groups 7B(7) and 8B(8), their maximum oxidation state would be $+7$ and $+8$, respectively (analogous to Re and Os). Since the highest fluoride of Np is only the hexafluoride, the highest oxidation state of Np apparently is $+6$ and not $+7$ as it would be in Group 7B(7).

23.110 There are 10 general formulas. Assuming a minimum of one of each ligand in each complex about the metal M they are:

MA$_3$BCD, MAB$_3$CD, MABC$_3$D, MABCD$_3$, MA$_2$B$_2$CD, MA$_2$BC$_2$D, MA$_2$BCD$_2$, MAB$_2$C$_2$D, MAB$_2$CD$_2$ and MAB$_2$CD$_2$.

Neglecting optical isomers, the structures for MA$_3$BCD are:

Each of these has an optical isomer.

Analogous structures arise for MAB$_3$CD, MABC$_3$D, and MABCD$_3$. Each of the formulas from the following group has 6 isomers: MA$_3$BCD, MAB$_3$CD, MABC$_3$D, and MABCD$_3$. 

23-15
Neglecting optical isomers, the structures for MA\textsubscript{2}B\textsubscript{2}CD are:

![Structure Diagram]

The first of these has an optical isomer.

Analogous structures arise for MA\textsubscript{2}B\textsubscript{2}CD, MA\textsubscript{2}BC\textsubscript{2}D, MA\textsubscript{2}BCD\textsubscript{2}, MAB\textsubscript{2}C\textsubscript{2}D, MAB\textsubscript{2}CD\textsubscript{2} and MABC\textsubscript{2}D\textsubscript{2}.

Each of the formulas from the following group has 5 isomers: MA\textsubscript{2}B\textsubscript{2}CD, MA\textsubscript{2}BC\textsubscript{2}D, MA\textsubscript{2}BCD\textsubscript{2}, MAB\textsubscript{2}C\textsubscript{2}D, MAB\textsubscript{2}CD\textsubscript{2} and MABC\textsubscript{2}D\textsubscript{2}.

23.111 The electron configuration of Hg\textsuperscript{+} is [Xe]6s\textsuperscript{1}4f\textsuperscript{14}5d\textsuperscript{10} and for Cu\textsuperscript{+} is [Ar]3d\textsuperscript{10}. In the mercury(I) ion, there is one electron in the 6s orbital that can form a covalent bond with the electron in the 6s orbital of another Hg\textsuperscript{+} ion. In the copper(I) ion, there are no electrons in the s orbital to bond with another copper(I) ion.

23.112 a) sodium tetrabromoferrate(III) b) hexaaamminenickel(II) ion c) correct
d) hexacyanovanadate(III) ion e) potassium tetrachloroferrate(III)

23.113 a) The coordination number of cobalt is 6. The two Cl\textsuperscript{-} ligands are unidentate and the two ethylenediamine ligands are bidentate, so a total of 6 ligand atoms are connected to the central metal ion.
b) The counter ion is Cl\textsuperscript{-}, so the complex ion is [Co(en)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+}. Each chloride ligand has a -1 charge and each en ligand is neutral, so cobalt has a +3 charge: +3 + 2(0) + 2(−1) = +1.
c) One mole of complex dissolves in water to yield one mole of [Co(en)\textsubscript{2}Cl\textsubscript{2}]\textsuperscript{+} ions and one mole of Cl\textsuperscript{-} ions. Therefore, each formula unit yields 2 individual ions.
d) One mole of complex dissolves to form one mole of Cl\textsuperscript{-} ions, which reacts with the Ag\textsuperscript{+} ion (from AgNO\textsubscript{3}) to form one mole of AgCl precipitate.

23.114

![Structure Diagram]

23.115 a) Any reduction with a potential which, when added to 0.38-V, gives a positive total will plate out. Of the metals in Table 23.3, the ones that will plate out are: Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and Cu\textsuperscript{2+}.
b) Equal amounts of electricity will yields equal moles of metal. (The values would not be equal if the charges were not all the same.) The metal with the lowest molar mass, Co, will yield the least mass.

23.116 Tetrahedral complexes are never low-spin, no matter how strong the ligand. Also, certain metal ions have less tendency to go to a low-spin configuration. The statement could be revised to read: “Strong-field ligands usually give rise to low-spin octahedral complexes.”
23.117  a) There are no isomers.

b) There is an optical isomer.

c) There is an optical isomer.

*trans* and *cis* are geometric isomers; the *cis* form exists as two optical isomers.
d) There are no optical isomers.

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{Cl} \\
\text{H}_3\text{N} & \quad \text{Co}^{3+} \\
\text{NH}_3 & \quad \text{H}_3\text{N} \\
\text{Cl} & \quad \text{NH}_3
\end{align*}
\]

23.118 \( (258 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.1052 \text{ mol hypo}}{\text{L}} \right) = 0.0271416 \text{ initial mol of hypo (unrounded)} \)

The next steps requires us to assume there has been no volume change in the solution.

\( (258 \text{ mL}) \left( \frac{10^{-3} \text{ L}}{1 \text{ mL}} \right) \left( \frac{0.0378 \text{ mol hypo}}{\text{L}} \right) = 0.0097524 \text{ remaining mol of hypo (unrounded)} \)

Hypo reacting with AgBr = \( (0.0271416 - 0.0097524) = 0.0173892 \text{ mol hypo (unrounded)} \)

Mass AgBr = \( \left( \frac{1 \text{ mol AgBr}}{187.8 \text{ g AgBr}} \right) \left( \frac{187.8 \text{ g AgBr}}{1 \text{ mol AgBr}} \right) = 1.63 \text{ g AgBr} \)

\[
\begin{align*}
\text{Fe}^{6+} & & \text{Mn}^{0} \\
\text{Co}^{4+} & & \text{V}^{1+} \\
\text{Ni}^{4+} & & \text{Cu}^{4+} \\
\text{Ag}^{5+} & & \text{Ni}^{1+}
\end{align*}
\]

23.119 a) 1) \([\text{Pt(NH}_3)_6\text{Cl}_4]^{4+}\) 2) 5 ions form; 4 mol AgCl precipitating

b) 1) \([\text{Pt(NH}_3)_4\text{Cl}_2]^{2+}\) 2) 3 ions form; 2 mol AgCl precipitating

23.120 a) U = +6; Np = +7 b) +3 for both

23.121 a) 2 \(\text{Fe}^{3+}(aq) + 6 \text{Cl}^-(aq) + 4 \text{OH}^-(aq) \rightarrow 2 \text{FeO}_4^{2-}(aq) + 6 \text{Cl}^-(aq) + 2 \text{H}_2\text{O}(l) \)

b) \(K_d[\text{Mn(CN)}_6]^2(s) \rightarrow K_d[\text{Mn(CN)}_6]^0(s) \)

c) 12 \(\text{Na}_2\text{O}_2(s) + \text{Co}_2\text{O}_4(s) \rightarrow 3 \text{Na}_2\text{CoO}_2(s) + 8 \text{O}_2(g) \)

d) \(\text{VCl}_3(s) + 4 \text{Na}(s) + 6 \text{CO}(g) \rightarrow \text{Na}_2[V(\text{CO})_6](s) + 3 \text{NaCl}(s) \)

e) \(\text{BaO}_2(s) + \text{Ni}^{2+}(aq) + 2 \text{OH}^-(aq) \rightarrow \text{BaNiO}_3(s) + \text{H}_2\text{O}(l) \)

f) 11 \(\text{CO}(g) + 12 \text{OH}^-(aq) + 2 \text{CO}^{2+}(aq) \rightarrow 2 \text{[Co(CO)}_4]^+(aq) + 3 \text{CO}_3^{2-}(aq) + 6 \text{H}_2\text{O}(l) \)

g) \(\text{Cs}_2[\text{CuF}_4]s) + \text{F}_2(g) \rightarrow \text{Cs}_2[\text{CuF}_6]s) \)

h) 6 \(\text{TaCl}_5(s) + 15 \text{Na}(s) \rightarrow 15 \text{NaCl}(s) + \text{Ta}_8\text{Cl}_13(s) \)

i) \(\text{Cs}_2[\text{AgF}_4](s) + \text{F}_2(g) \rightarrow \text{Cs}_2[\text{AgF}_6](s) \)

j) 4 \(\text{K}_4[\text{Ni(CN)}_6](s) + \text{N}_2\text{H}_4(aq) + 4 \text{OH}^-(aq) \rightarrow 2 \text{[K}_4\text{Ni(CN)}_6][s) + \text{N}_2(g) + 4 \text{H}_2\text{O}(l) + 4 \text{CN}^-(aq) \)

23.122

\[
\begin{bmatrix}
\vdots & : & O \\
\uparrow & \downarrow & \uparrow \\
O & =_{\text{Mn}} & O \\
\vdots & : & O
\end{bmatrix}
\]
23.123 Geometric (cis-trans) and linkage isomerism.

\[
\begin{align*}
\text{cis-diamminedithiocyanatoplatinum(II)} & \quad \text{trans-diamminedithiocyanatoplatinum(II)} \\
\text{cis-diamminediisothiocyanatoplatinum(II)} & \quad \text{trans-diamminediisothiocyanatoplatinum(II)} \\
\text{cis-diamminethiocyanatoisothiocyanatoplatinum(II)} & \quad \text{trans-diamminethiocyanatoisothiocyanatoplatinum(II)}
\end{align*}
\]

23.124 Anode: \( 3 \text{(Ag(s))} \rightleftharpoons \text{Ag}^{+}(aq) + e^- \) \( E^o = -(0.80 \text{ V}) \)
Cathode: \( \text{Au}^{3+}(aq) + 3 \text{ e}^- \rightleftharpoons \text{Au(s)} \) \( E^o = +1.50 \text{ V} \)
Total: \( 3 \text{ Ag(s)} + \text{Au}^{3+}(aq) \rightleftharpoons \text{Au(s)} + 3 \text{ Ag}^{+}(aq) \) \( E^o = +0.70 \text{ V} \)
The positive voltage indicates that the reaction is spontaneous.

23.125 \( [\text{Co(NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+} \) tetraammineaquachlorocobalt(III) ion
2 geometric isomers

\[
\begin{align*}
\text{trans Cl and H}_2\text{O} & \quad \text{cis Cl and NH}_3
\end{align*}
\]
[Cr(H₂O)_3Br₂Cl] triaquadibromochlorochromium(III)  
3 geometric isomers

Br’s trans

Br’s cis  
H₂O’s facial

Br’s cis  
H₂O’s meridional

(Unfortunately meridional and facial isomers are not covered in the text. Facial (fac) isomers have three adjacent corners of the octahedron occupied by similar groups. Meridional (mer) isomers have three similar groups around the outside of the complex.)

[Cr(NH₃)_2(H₂O)₂Br₂]⁺ diamminediaquadibromochromium(III) ion  
6 isomers (5 geometric)

All pairs are trans

Only NH₃’s are trans

Only H₂O’s are trans

Only Br’s are trans

All pairs are cis. These are optical isomers of each other.

23.126 In exposing the film, a photoredox reaction takes place, forming Ag and Br atoms. In developing, more Ag⁺ is reduced to Ag(s). In fixing the image, excess Ag⁺ is removed by the formation of the Ag(S₂O₃)₂⁻ ion.

23.127 The ligand field strength of NH₃ is greater than that of H₂O. Therefore, the crystal field splitting energy (Δ) is larger, and higher energy (shorter wavelength) light is required to excite the electrons of [Cr(NH₃)₆]³⁺. When [Cr(NH₃)₆]³⁺ absorbs higher energy blue-violet light, yellow-orange light (the compliment of blue-violet light) is observed. When [Cr(H₂O)₆]³⁺ absorbs lower energy red light, blue-gray light is observed.
23.128  a) The oxidation state of Mn in $\text{MnO}_4^{2-}$ is +6, in $\text{MnO}_4^-$ is +7, and in $\text{MnO}_2$ is +4.
   b) The two half-reactions are
      
      \[
      \text{reduction: } \text{MnO}_4^{2-}(aq) \rightarrow \text{MnO}_2(s) \\
      \text{balancing gives: } \text{MnO}_4^{2-}(aq) + 4 \text{H}^+(aq) + 2 e^- \rightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l) \\
      \text{oxidation: } \text{MnO}_4^{2-}(aq) \rightarrow \text{MnO}_4^-(aq) + e^- \\
      \text{Multiply the oxidation half-reaction by 2 and add to get} \\
      3 \text{MnO}_4^{2-}(aq) + 4 \text{H}^+(aq) \rightarrow 2 \text{MnO}_4^-(aq) + \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)
      \]

23.129  a) $2\text{K}_2\text{MnO}_4(aq) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KMnO}_4(aq) + 2\text{KOH}(aq) + \text{H}_2(g)$
   b) Moles $\text{MnO}_4^-$ = \(\left(\frac{12 \text{ Cl}}{\text{s}}\right) \times (96 \text{ h}) \times \left(\frac{3600 \text{ s}}{1 \text{ h}}\right) \times \left(\frac{1 \text{ mol e}^-}{96500 \text{ C}}\right) \times \left(\frac{1 \text{ mol MnO}_4^-}{1 \text{ mol e}^-}\right) = 42.976 = 43 \text{ mol MnO}_4^-

23.130  a) The uranium is 8 coordinate.
   b) The uranium is +5 (because Na is +1 and F is -1.)
   c)
   
   ![Uranium Coordination Diagram]

23.131  a) $\text{V}$ is +5 in $\text{VO}_3^-$ and $\text{VO}_2\text{Cl}_2^-$; $\text{Al}$ is +3 in $\text{AlCl}_4^-$ and $\text{AlOCl}_3^-$
   b) No elements change oxidation state so no redox occurs in either reaction.
   The balanced equations are:
   
   \[
   \begin{align*}
   \text{V}_2\text{O}_5 + 2 \text{HCl} & \rightarrow \text{VO}_2\text{Cl}_2^- + \text{VO}_3^- + 2 \text{H}^+ \\
   \text{V}_2\text{O}_5 + 6 \text{HCl} & \rightarrow 2 \text{VOCl}_3 + 3 \text{H}_2\text{O}
   \end{align*}
   \]
   c) \(10.0 \text{ g} \times \left(\frac{1 \text{ mol } \text{V}_2\text{O}_5}{181.88 \text{ g } \text{V}_2\text{O}_5}\right) \times \left(\frac{1 \text{ mol } \text{VO}_2\text{Cl}_2^-}{1 \text{ mol } \text{V}_2\text{O}_5}\right) \times \left(\frac{153.84 \text{ g } \text{VO}_2\text{Cl}_2^-}{1 \text{ mol } \text{VO}_2\text{Cl}_2^-}\right) = 8.458324 = 8.46 \text{ g } \text{VO}_2\text{Cl}_2^-
   
   \(10.0 \text{ g} \times \left(\frac{1 \text{ mol } \text{V}_2\text{O}_5}{181.88 \text{ g } \text{V}_2\text{O}_5}\right) \times \left(\frac{2 \text{ mol } \text{VOCl}_3}{1 \text{ mol } \text{V}_2\text{O}_5}\right) \times \left(\frac{173.29 \text{ g } \text{VOCl}_3}{1 \text{ mol } \text{VOCl}_3}\right) = 19.055421 = 19.1 \text{ g } \text{VO}_2\text{Cl}_2^-
   
23.132  a) chlorophyll: Mg; heme: Fe; vitamin B$_{12}$: Co.
   b) They all have the central metal in the center of a large planar ring containing four N donor atoms.

23.133  a) \([\text{Co(NH}_3]_6[\text{Cr(CN)}]_6\] hexaamminecobalt(III) hexacyanochromate(III)
   b) \([\text{Co(NH}_3]_5\text{CN}[\text{CrNH}_3\text{(CN)]}_5\] pentaamminecyanocobalt(III) amminepentacyanochromate(III)

23.134  a) \([\text{Pt(NH}_3]_4[\text{PtCl}_6]\] tetraammineplatinum(II) hexachloroplatinum(IV)
   b) \([\text{Pt(NH}_3]_3\text{Cl}_3[\text{PtCl}_4\] tetraamminedichloroplatinum(IV) tetrachloroplatinum(II)

23.135  a) A plane that includes both ammonia ligands and the zinc ion is a plane of symmetry. The complex does not have optical isomers because it has a plane of symmetry.
   b) The Pt$^{2+}$ ion is d$^5$, so the complex is square planar. Any square planar complex has a plane of symmetry, so the complex does not have optical isomers.
   c) The trans octahedral complex has the two chloride ions opposite each other. A plane of symmetry can be passed through the two chlorides and platinum ion, so the trans-complex does not have optical isomers.
   d) No optical isomers for same reason as in part (c).
   e) The cis-isomer does not have a plane of symmetry, so it does have optical isomers.
23.136 Assume a 100-g sample (making the percentages of each element equal to the mass present in grams) and convert the mass of each element to moles using the element’s molar mass. Divide each mole amount by the smallest mole amount to determine whole number ratios of the elements to determine the empirical formula. Note, the intermediate values are unrounded to minimize rounding errors.

\[
\begin{align*}
\text{moles Pt} &= \frac{38.8 \text{ g Pt}}{195.1 \text{ g Pt}} = 0.198872 \text{ mol Pt} \\
\text{moles Cl} &= \frac{14.1 \text{ g Cl}}{35.45 \text{ g Cl}} = 0.397743 \text{ mol Cl} \\
\text{moles C} &= \frac{28.7 \text{ g C}}{12.01 \text{ g C}} = 2.389675 \text{ mol C} \\
\text{moles P} &= \frac{12.4 \text{ g P}}{30.97 \text{ g P}} = 0.400387 \text{ mol P} \\
\text{moles H} &= \frac{6.02 \text{ g H}}{1.008 \text{ g H}} = 5.972222 \text{ mol H}
\end{align*}
\]

Divide each of the moles just calculated by the smallest value (Pt) gives:

\[
\begin{align*}
\text{Pt} &= 1 & \text{Cl} &= 2 & \text{C} &= 12 & \text{P} &= 2 & \text{H} &= 30
\end{align*}
\]

The empirical formula for the compound is PtCl_2C_12P_2H_30. Each triethylphosphine ligand, P(C_2H_5)_3 accounts for one phosphorus atom, 6 carbon atoms, and 15 hydrogen atoms. According to the empirical formula, there are two triethylphosphine ligands: 2 P(C_2H_5)_3 “equals” C_12P_2H_30. The compound must have two P(C_2H_5)_3 ligands and two chloro ligands per Pt ion. The formula is [Pt[P(C_2H_5)_3]_2Cl_2]. The central Pt ion has 4 ligands and is square planar, existing as either a cis or trans compound.

\[
\begin{align*}
&\text{cis-dichlorobis(triethylphosphine)platinum(II)} & &\text{trans-dichlorobis(triethylphosphine)platinum(II)}
\end{align*}
\]

23.137 a) The longest distance will be for two of the long bonds trans to each other.

Longest distance = 2 (262 pm) = 524 pm

b) The shortest distance will be for two of the short bonds trans to each other.

Shortest distance = 2 (207 pm) = 414 pm

23.138 Use the ideal gas equation, PV = nRT

\[
P = \frac{nRT}{V} = \left[\frac{20.0 \text{ mg Hg}}{1 \text{ mg}} \left(\frac{10^{-3} \text{ g}}{1 \text{ mg}}\right) \left(\frac{10^{-3} \text{ m}^3}{1 \text{ L}}\right) \left(\frac{1 \text{ mol Hg}}{200.6 \text{ g Hg}}\right) \right] \left(\frac{0.0821 \text{ L} \cdot \text{ atm}}{\text{mol} \cdot \text{K}}\right) (273 + 25)\text{K}
\]

\[
P = 2.439262 \times 10^{-6} = 2.44 \times 10^{-6} \text{ atm}
\]

23.139 Zinc ions prefer a tetrahedral environment. The other ions listed prefer other environments. If the other ions are placed in a tetrahedral environment in place of the zinc, they cannot behave as well as zinc.
23.140 a) The first reaction shows no change in the number of particles. In the second reaction, the number of reactant particles is greater than the number of product particles. A decrease in the number of particles means a decrease in entropy, while no change in number of particles indicates little change in entropy. Based on entropy change only, the first reaction is favored.

b) The ethylenediamine complex is more stable with respect to ligand exchange with water because the entropy change is unfavorable.

23.141 a) \[[\text{Cr(H}_2\text{O)}_6]^{3+}\] 562 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 2.1299878 \times 10^5 = 2.13 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Cr(CN)}_6]^{3-}\] 381 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 3.14187 \times 10^5 = 3.14 \times 10^{-19} \text{ J/mol}
\]

\[[\text{CrCl}_6]^{3-}\] 735 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 1.62864 \times 10^5 = 1.63 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Cr(NH}_3)_6]^{3+}\] 462 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 2.591024 \times 10^5 = 2.59 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Ir(NH}_3)_6]^{3+}\] 244 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 4.9059555 \times 10^5 = 4.91 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Fe(H}_2\text{O)}_6]^{2+}\] 966 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 1.239185 \times 10^5 = 1.24 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Fe(H}_2\text{O)}_6]^{3+}\] 730 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 1.6397988 \times 10^5 = 1.64 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Co(NH}_3)_6]^{3+}\] 405 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 2.9556868 \times 10^5 = 2.96 \times 10^{-19} \text{ J/mol}
\]

\[[\text{Rh(NH}_3)_6]^{3+}\] 295 nm

\[
E = \frac{hc}{\lambda} = \left(\frac{6.626 \times 10^{-34} \text{ J s}}{3.00 \times 10^8 \text{ m/s}}\right) \left(\frac{1 \text{ nm}}{10^{-9} \text{ m}}\right) \left(\frac{6.022 \times 10^{23} \text{ mol}}{6.626 \times 10^{34} \text{ J s}}\right) = 4.057807 \times 10^5 = 4.06 \times 10^{-19} \text{ J/mol}
\]
b) Comparing the energies of the chromium complexes, we find the energy increases in the order:
\[ \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{CN}^- \]
This is an abbreviated spectrochemical series.
c) The higher the oxidation number (Fe$^{3+}$ versus Fe$^{2+}$) the greater the crystal field splitting ($\Delta$).
d) When moving down a column on the periodic table, in this case from Co to Rh to Ir, the greater the energy required, and the greater the crystal field splitting ($\Delta$).

23.142 a) The immediate reaction with AgNO$_3$ to yield a red precipitate (Ag$_2$CrO$_4$) indicates that the chromate is not directly coordinated to M. The potassium will not be coordinated to M. Silver nitrate does not easily form a white precipitate thus the chloride must be coordinated to M as part of an inert complex. The ammonia is probably coordinated to M. The coordination number of M comes from two chlorides plus four ammonia to give a total of 6.
b) The ammonia and chloride ligands are covalently bonded to M, and the potassium and chromate are ionically bonded.
c) The ability of oxalate to displace chloride from only one form is the clue. Oxalate is chelating, and will only displace chlorides in a cis arrangement, not a trans arrangement. Form A is the cis complex, and form B is the trans complex.