

## CHAPTER 16

### THE *d* BLOCK: METALS IN TRANSITION

**16.1** Elements at the left of the *d* block tend to have strongly negative standard potentials.

**16.3** (a) Sc (b) Au (c) Nb

(d) One might expect osmium to be larger than ruthenium because it is a third row transition metal and ruthenium is in row two; however, because of the lanthanide contraction, they are about the same size (Os, 135 pm; Ru, 134 pm).

**16.5** (a) Ti (b) Cu (c) Zn

(d) Because ruthenium is larger, one expects it to have a lower first ionization potential, which is observed ( $711 \text{ kJ} \cdot \text{mol}^{-1}$  vs  $759 \text{ kJ} \cdot \text{mol}^{-1}$ ).

(e) One might expect the third row transition metal to have a lower first ionization energy; however, due to the lanthanide contraction, the ionization potential for ruthenium is less ( $711 \text{ kJ} \cdot \text{mol}^{-1}$  vs  $840 \text{ kJ} \cdot \text{mol}^{-1}$ ).

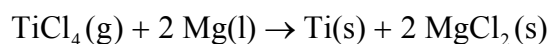
**16.7** Hg is much more dense than Cd, because the shrinkage in atomic radius that occurs between  $Z = 58$  and  $Z = 71$  (the lanthanide contraction) causes the atoms following the rare earths to be smaller than might have been expected for their atomic masses and atomic numbers. Zn and Cd have densities that are not too dissimilar, because the radius of Cd is subject only to a smaller *d*-block contraction.

**16.9** (a) Proceeding down a group in the *d* block (for example, from Cr to Mo to W), there is an increasing probability of finding the elements in higher oxidation states. That is, higher oxidation states become more stable on going down a group.

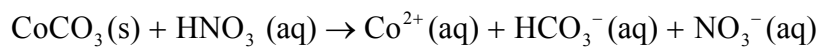
(b) The trend for the *p*-block elements is reversed. Because of the inert pair effect, the higher oxidation states tend to be less stable as one descends a group.

**16.11** In  $\text{MO}_3$ , M has an oxidation number of +6. Of these three elements, the +6 oxidation state is most stable for Cr. See Fig. 16.6.

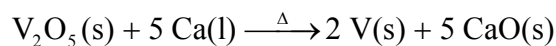
**16.13** (a)  $\text{Ti(s)}, \text{MgCl}_2(\text{s})$



(b)  $\text{Co}^{2+}(\text{aq}), \text{HCO}_3^-(\text{aq}), \text{NO}_3^-(\text{aq})$



(c)  $\text{V(s)}, \text{CaO(s)}$



**16.15** (a) titanium(IV) oxide,  $\text{TiO}_2$

(b) iron(III) oxide,  $\text{Fe}_2\text{O}_3$

(c) manganese(IV) oxide,  $\text{MnO}_2$

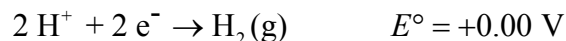
**16.17** (a)  $\text{V}^{2+} + 2 \text{e}^- \rightarrow \text{V(s)}$   $E^\circ = -1.19 \text{ V}$

$\text{V}^{3+} + \text{e}^- \rightarrow \text{V}^{2+}$   $E^\circ = -0.26 \text{ V}$

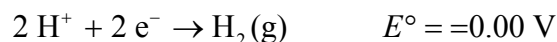
$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2(\text{g})$   $E^\circ = 0.00 \text{ V}$

Therefore,  $\text{V(s)}$  will be oxidized to  $\text{V}^{3+}$ . The products are  $\text{V}^{3+}$ ,  $\text{H}_2$ , and  $\text{Cl}^-$ .

(b)  $\text{Hg}_2^{2+} + 2 \text{e}^- \rightarrow 2 \text{Hg}$   $E^\circ = +0.79 \text{ V}$



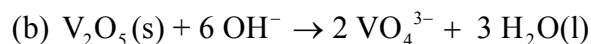
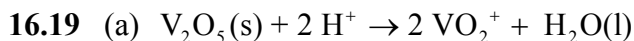
Therefore, no reaction.



Therefore, Co(s) will be oxidized to  $\text{Co}^{2+}$ . The products are  $\text{Co}^{2+}$ ,  $\text{H}_2$ , and  $\text{Cl}^{-}$ .

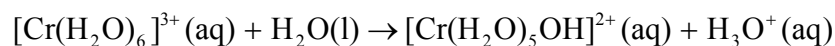
The further oxidation to  $\text{Co}^{3+}$  is not favorable by reaction of  $\text{H}^{+}$  with  $\text{Co}^{2+}$ .

However,  $\text{Co}^{2+}$  is oxidized in air to  $\text{Co}^{3+}$ .

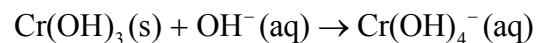
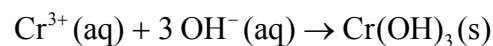


**16.21** Even though all three Group 1B/11 metal atoms have the valence shell electron configuration  $(n-1)d^{10}ns^1$ , Cu is more reactive than Ag or Au. Metals ordinarily lose one or more electrons to form cations when they react with some other species. As the value of  $n$  increases,  $d$  and  $f$  electrons become less effective at shielding the outermost, highest energy electron(s) from the attractive charge of the nucleus. This higher effective nuclear charge makes it more difficult to oxidize the metal atom or ion. So, for example,  $\text{Cu}^{2+}$  exists in many common compounds (and can be formed by  $\text{Cu}^{+}$  disproportionation in water) while  $\text{Ag}^{2+}$  does not. Furthermore, the valence electron orbital energies for most common Lewis bases match the orbitals of Cu and its cations more closely and would interact with them more favorably to form products.

**16.23** (a)  $\text{Cr}^{3+}$  ions in water form the complex  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}(\text{aq})$ , which behaves as a Brønsted acid:



(b) The gelatinous precipitate is the hydroxide  $\text{Cr}(\text{OH})_3$ . The precipitate dissolves as the  $\text{Cr}(\text{OH})_4^-$  complex ion is formed:



**16.25** (a) hexacyanoferrate(II) ion

Let  $x$  = the oxidation number to be determined

$$x(\text{Fe}) + 6 \times (-1) = -4$$

$$x(\text{Fe}) = -4 - (-6) = +2$$

(b) hexaamminecobalt(III)ion

$$x(\text{Co}) + 6 \times (0) = +3$$

$$x(\text{Co}) = +3$$

(c) aquapentacyanocobaltate(III) ion

$$x(\text{Co}) + 5 \times (-1) + 1 \times (0) = -2$$

$$x(\text{Co}) = -2 - (-5) = +3$$

(d) pentaamminesulfatocobalt(III) ion

$$x(\text{Co}) + 1 \times (-2) + 5 \times (0) = +1$$

$$x(\text{Co}) = +1 - (-2) = +3$$

**16.27** (a)  $\text{K}_3[\text{Cr}(\text{CN})_6]$

(b)  $[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Cl}$

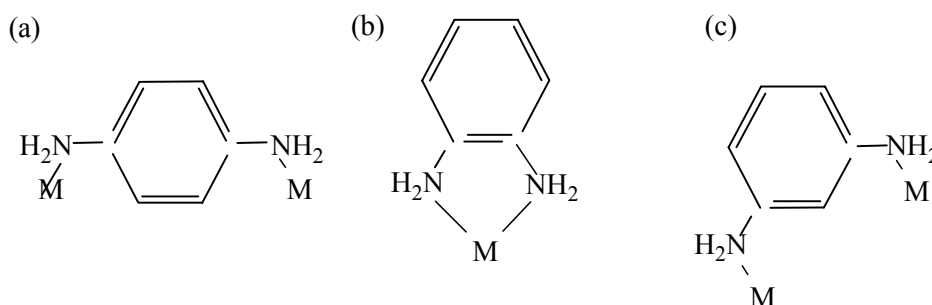
(c)  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]\text{Br}_3$

(d)  $\text{Na}[\text{Fe}(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)_2]$

**16.29** The molecule  $\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2$  has three nitrogen atoms, each with a

lone pair of electrons that may be used for bonding to a metal center. The molecule can thus function as a tridentate ligand. The  $\text{CO}_3^{2-}$  ion can bind to a metal ion through either one or two oxygen atoms. It may, therefore, serve as a mono- or bidentate ligand.  $\text{H}_2\text{O}$  is always a monodentate ligand. The oxalate ion can bind through two oxygen atoms and is usually a bidentate ligand.

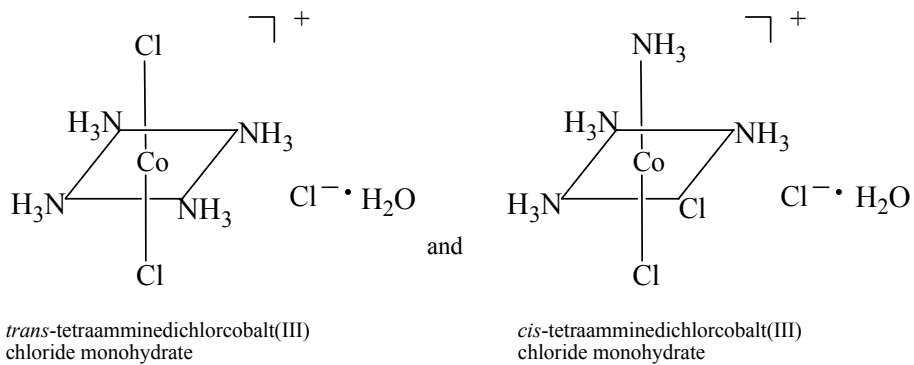
**16.31** As shown below, only the molecule (b) can function as a chelating ligand. The two amine groups in (a) and (c) are arranged so that they would not be able to coordinate simultaneously to the same metal center. It is possible for each of the amine groups in (a) and (c) to coordinate to two different metal centers, however. This is not classified as chelating. When a single ligand binds to two different metal centers, it is known as a *bridging* ligand.



**16.33** (a) 4 (b) 2 (c) 6 (en is bidentate) (d) 6 (EDTA is hexadentate)

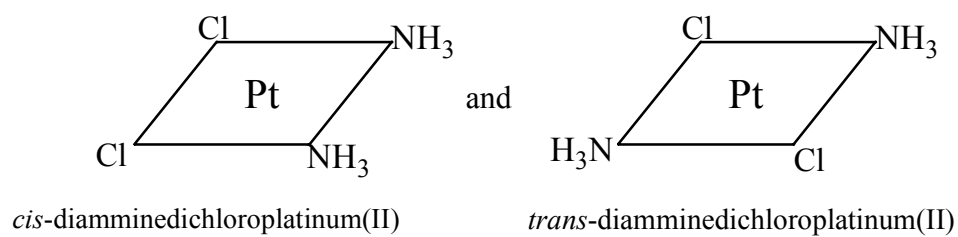
**16.35** (a) structural isomers, linkage isomers  
 (b) structural isomers, ionization isomers  
 (c) structural isomers, linkage isomers  
 (d) structural isomers, ionization isomers

**16.37** (a) yes

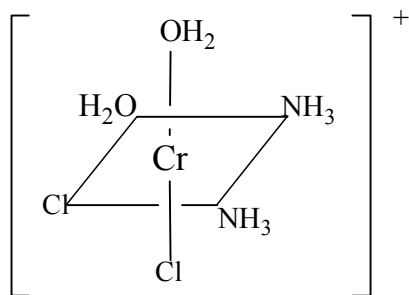


(b) no

(c) yes

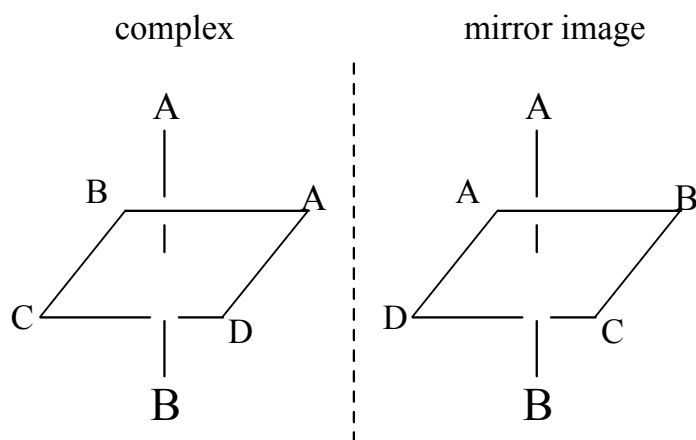


**16.39** (a)



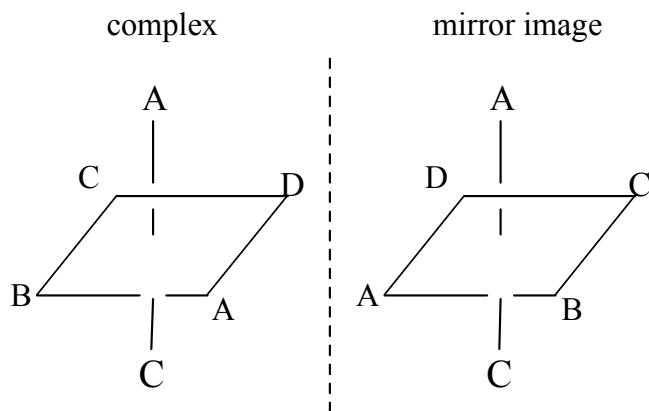
(b) Yes, the species is optically active as it has a nonsuperimposable mirror image.

**16.41** First complex:



No rotation will make the complex and its mirror image match; therefore, it is chiral.

Second complex:



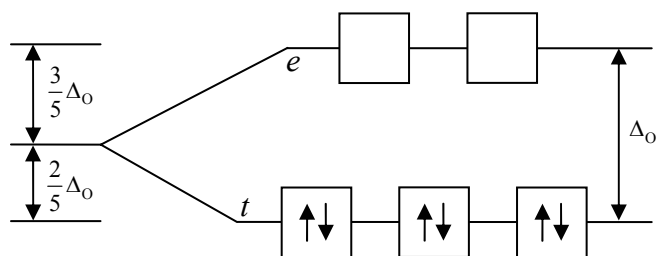
A double rotation shows that the complex and its mirror image are superimposable; therefore, it is not chiral.

The two complexes are not enantiomers; they are not even isomers.

**16.43** (a) 1; (b) 6; (c) 5; (d) 3; (e) 6; (f) 6

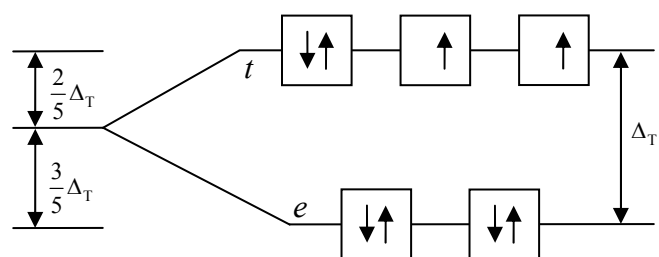
**16.45** (a) 2; (b) 5; (c) 8; (d) 10; (e) 0 (or 8); (f) 10

**16.47** (a) octahedral; strong-field ligand,  $6 e^-$



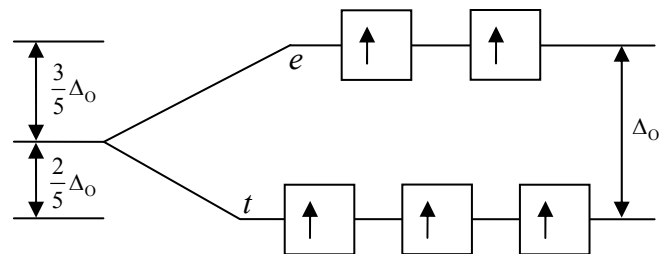
diamagnetic, no unpaired electrons

(b) tetrahedral: weak-field ligand,  $8 e^-$



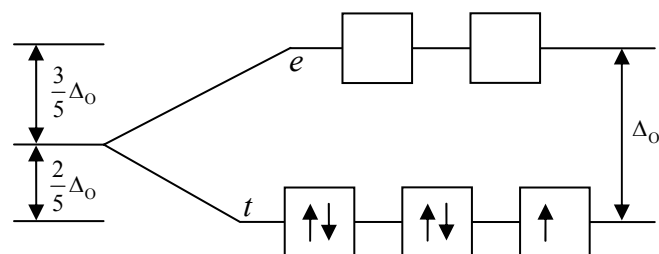
2 unpaired electrons

(c) octahedral: weak-field ligand,  $5 e^-$



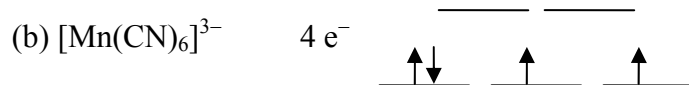
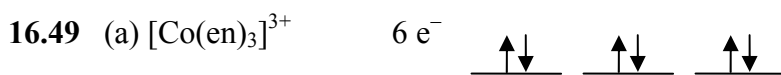
5 unpaired electrons

(d) octahedral: strong-field ligand,  $5 e^-$



one unpaired electron





**16.51** Weak-field ligands do not interact strongly with the  $d$ -electrons in the metal ion, so they produce only a small crystal field splitting of the  $d$ -electron energy states. The opposite is true of strong-field ligands. With weak-field ligands, unpaired electrons remain unpaired if there are unfilled orbitals; hence, a weak-field ligand is likely to lead to a high-spin complex. Strong-field ligands cause electrons to pair up with electrons in lower energy orbitals. A strong-field ligand is likely to lead to a low-spin complex. Ligands arranged in the spectrochemical series help to distinguish strong-field and weak-field ligands. Measurement of magnetic susceptibility (paramagnetism) can be used to determine the number of unpaired electrons, which, in turn, establishes whether the associated ligand is weak-field or strong-field in nature.

**16.53** Because  $\text{F}^-$  is a weak-field ligand and en a strong-field ligand, the splitting between levels is less in (a) than in (b). Therefore, (a) will absorb light of longer wavelength than will (b) and consequently will display a shorter wavelength color. Blue light is shorter in wavelength than yellow light, so (a)  $[\text{CoF}_6]^{3-}$  is blue and (b)  $[\text{Co}(\text{en})_3]^{3+}$  is yellow.

$$16.55 \quad E_{\text{photon}} = \left( \frac{209 \text{ kJ}}{\text{mol}} \right) \left( \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ photons}} \right) = 3.47 \times 10^{-22} \text{ kJ} \cdot \text{photon}^{-1}$$

$$\nu = \frac{E}{h} = \frac{3.47 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J} \cdot \text{s}} = 5.24 \times 10^{14} \text{ s}^{-1}$$

$$\lambda = \frac{c}{\nu} = \left( \frac{3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{5.24 \times 10^{14} \text{ s}^{-1}} \right) \left( \frac{10^9 \text{ nm}}{1 \text{ m}} \right) = 573 \text{ nm}$$

This wavelength is in the yellow region of the visible spectrum. Since the complex absorbs yellow light, it transmits the complement, or purple (a.k.a. violet).

**16.57** In  $\text{Zn}^{2+}$ , the  $3d$ -orbitals are filled ( $d^{10}$ ). Therefore, there can be no electronic transitions between the  $t$  and  $e$  levels; hence, no visible light is absorbed and the aqueous ion is colorless. The  $d^{10}$  configuration has no unpaired electrons, so Zn compounds would be diamagnetic, not paramagnetic.

$$\mathbf{16.59} \quad (\text{a}) \quad \Delta_o = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{740 \times 10^{-9} \text{ m}} = 2.69 \times 10^{-19} \text{ J}$$

$$(\text{b}) \quad \Delta_o = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{460 \times 10^{-9} \text{ m}} = 4.32 \times 10^{-19} \text{ J}$$

$$(\text{c}) \quad \Delta_o = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{575 \times 10^{-9} \text{ m}} = 3.46 \times 10^{-19} \text{ J}$$

These numbers can be multiplied by  $6.02 \times 10^{23}$  to obtain  $\text{kJ} \cdot \text{mol}^{-1}$ .

$$(\text{a}) \quad 2.69 \times 10^{-19} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 162 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(\text{b}) \quad 4.32 \times 10^{-19} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 260 \text{ kJ} \cdot \text{mol}^{-1}$$

$$(\text{c}) \quad 3.46 \times 10^{-19} \text{ J} \times 6.02 \times 10^{23} \text{ mol}^{-1} = 208 \text{ kJ} \cdot \text{mol}^{-1}$$

$\text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3$  (spectrochemical series)

**16.61** The  $e_g$  set, which comprises the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals.

**16.63** (a) The  $\text{CN}^-$  ion is a  $\pi$ -acid ligand accepting electrons into the empty  $\pi^*$  orbital created by the C—N multiple bond. (b) The  $\text{Cl}^-$  ion has extra lone pairs in addition to the one that is used to form the  $\sigma$ -bond to the metal, and so it can act as a  $\pi$ -base, donating electrons in a  $p$ -orbital to an empty  $d$ -orbital on the metal. (c)  $\text{H}_2\text{O}$ , like  $\text{Cl}^-$ , also has an

“extra” lone pair of electrons that can be donated to a metal center, making it a weak  $\pi$ -base; (d) en is neither a  $\pi$ -acid nor a  $\pi$ -base, because it does not have any empty  $\pi$ -type antibonding orbitals nor does it have any extra lone pairs of electrons to donate.  $\text{Cl}^- < \text{H}_2\text{O} < \text{en} < \text{CN}^-$ . Note that the spectrochemical series orders the ligands as  $\pi$ -bases  $<$   $\sigma$ -bond only ligands  $<$   $\pi$ -acceptors.

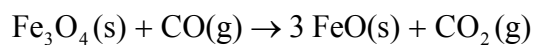
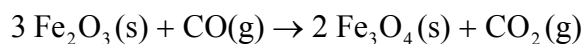
**16.65** Nonbonding or slightly antibonding. In a complex that forms only  $\sigma$ -bonds, the  $t_{2g}$  set of orbitals is nonbonding. If the ligands can function as weak  $\pi$ -donors (those close to the middle of the spectrochemical series, such as  $\text{H}_2\text{O}$ ), the  $t_{2g}$  set becomes slightly antibonding by interacting with the filled  $p$ -orbitals on the ligands.

**16.67** Antibonding. The  $e_g$  set of orbitals on an octahedral metal ion are always antibonding because of interactions with ligand orbitals that form the  $\sigma$ -bonds. This is true regardless of whether the ligands are  $\pi$ -acceptors,  $\pi$ -donors, or neither.

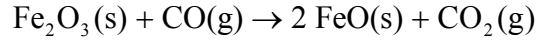
**16.69** Water has two lone pairs of electrons. Once one of these is used to form the  $\sigma$ -bond to the metal ion, the second may be used to form a  $\pi$ -bond. This causes the  $t_{2g}$  set of orbitals to move up in energy, making  $\Delta$  smaller; therefore, water is a weak-field ligand. Ammonia does not have this extra lone pair of electrons and consequently cannot function as a  $\pi$ -donor ligand.

**16.71** (a) CO

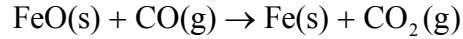
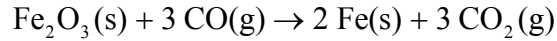
(b) In Zones D & C,



These reactions combine to give



In Zone B,



(c) carbon

**16.73** The major impurity is carbon; it is removed by oxidation of the carbon to  $\text{CO}_2$ , followed by capture of the  $\text{CO}_2$  by base to form a slag.

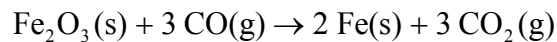
**16.75** Copper and zinc

**16.77** Alloys are usually (1) harder and more brittle, and (2) poorer conductors of electricity than the metals from which they are made.

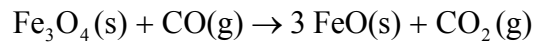
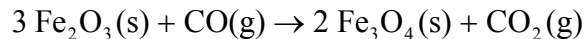
**16.79** The compound is ferromagnetic below  $T_c$  because the magnetization is higher. Above the Curie temperature, the compound is a simple paramagnet with randomly oriented spins, but below that temperature, the spins align and the magnetization increases.

**16.81** (a) More than one kind of reduction occurs.

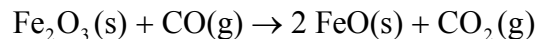
In Zone C,



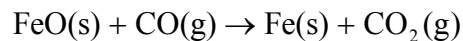
In Zone D,

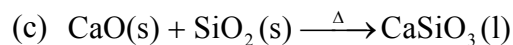
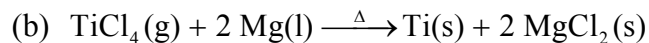


These reactions combine to give



In Zone C,

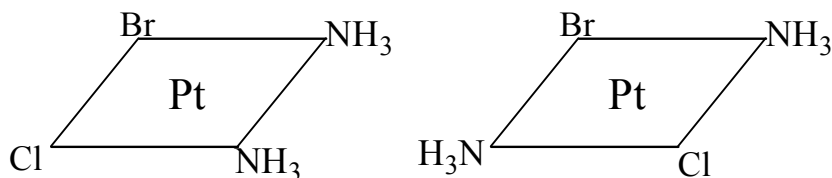




$$\Delta G^\circ = -nFE^\circ = -RT \ln K$$

$$\ln K = \frac{nFE^\circ}{RT} = \frac{(3)(96\,485 \text{ J} \cdot \text{V}^{-1} \cdot \text{mol}^{-1})(-0.60 \text{ V})}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -70.1$$

$$K_{sp} = e^{-70.1} = 3.6 \times 10^{-31}$$



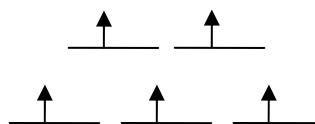
*cis*-Diamminebromochloroplatinum(II)      *trans*-Diamminebromochloroplatinum(II)

(b) If the compound were tetrahedral, there would be only one compound, not two.

16.87 (a) The first,  $[\text{Ni}(\text{SO}_4)(\text{en})_2]\text{Cl}_2$ , will give a precipitate of  $\text{AgCl}$  when  $\text{AgNO}_3$  is added; the second will not. (b) The second,  $[\text{NiCl}_2(\text{en})_2]\text{I}_2$ , will show free  $\text{I}_2$  when mildly oxidized with, for example,  $\text{Br}_2$ , but the first will not.



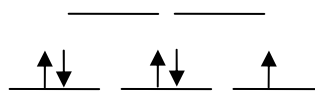
$5 e^-$ ,  $\text{Cl}^-$  is a weak-field ligand





5  $e^-$ ,  $\text{CN}^-$  is a strong-field ligand

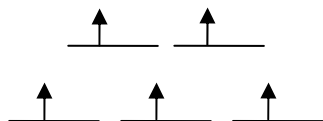
one unpaired electron



(b) one unpaired electron in  $[\text{Mn}(\text{CN})_6]^{4-}$

(c) Complexes with strong-field ligands absorb shorter wavelength light, therefore,  $[\text{Mn}(\text{CN})_6]^{4-}$  transmits longer wavelengths.

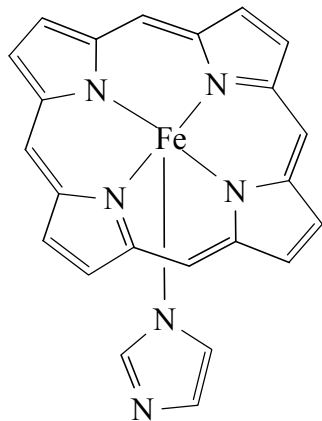
**16.91** High spin  $\text{Mn}^{2+}$  ions have a  $d^5$  configuration with 5 unpaired electrons, as shown below.



In order for light to be absorbed in the visible region of the spectrum, an electron from the  $t_{2g}$  set has to be moved into the  $e_g$  set of orbitals.

Because each orbital is already singly occupied by an electron and all five electrons have parallel spins, the electron making the transition must change spin in order to spin pair in the upper orbital. This sort of transition is called “spin-forbidden” because it has a very low quantum mechanical probability of occurring, and so the complexes usually are only faintly colored.

**16.93**



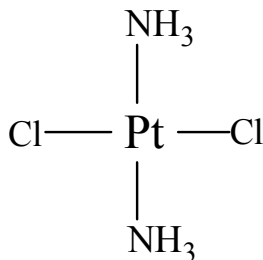
- 16.95** The correct structure for  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  consists of four ions,  $\text{Co}(\text{NH}_3)_6^{3+}$ , and 3  $\text{Cl}^-$  in aqueous solution. The chloride ions can be easily precipitated as  $\text{AgCl}$ . This would not be possible if they were bonded to the other  $(\text{NH}_3)$  ligands. If the structure were  $\text{Co}(\text{NH}_3-\text{NH}_3-\text{Cl})_3$ , VSEPR theory would predict that the  $\text{Co}^{3+}$  ion would have a trigonal planar ligand arrangement. The splitting of the  $d$ -orbital energies would not be the same as the octahedral arrangement and would lead to different spectroscopic and magnetic properties inconsistent with the experimental evidence. In addition, neither optical nor geometrical isomers would be observed.
- 16.97** The spectrochemical series given in Figure 16.32 shows the relative ligand field strengths of the halide ions to lie in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$ . Since their electronegativities follow the same trend, there is a positive correlation between ligand field strength and electronegativity for the halide ions. The value of  $\Delta$  correlates with the ability of the ligand's extra lone pairs of electrons to interact with the  $t_{2g}$  set of the octahedral metal ion. This means that the less electronegative the ligand is, the easier it is for the ligand to donate electrons to the metal ion, the more the energy of the  $t_{2g}$  in the complex is raised, and the smaller  $\Delta$  becomes (see Figure 16.40(a)).
- 16.99** In order to determine these relationships, we need to consider the types of interactions that the ligands on the ends of the spectrochemical series will have with the metal ions. Those that are weak-field (form high spin complexes,  $\pi$ -bases) have extra lone pairs of electrons that can be donated to a metal ion in a  $\pi$  fashion. The strong-field ligands (form low spin complexes,  $\pi$ -acids) accept electrons from the metals. The complexes that will be more stable will be produced in general by the

match between ligand and metal. Thus, the early transition metals in high oxidation states will have few or no electrons in the *d*-orbitals. These metal ions will become stabilized by ligands that can donate more electrons to the metal—the *d*-orbitals that are empty can readily accept electrons. The more stable complexes will be formed with the weak-field ligands. The opposite is true for metals with many electrons, which are the ones at the right side of the periodic table, in low oxidation states. These metals generally have most of the *d*-orbitals filled, so they would, in fact, be destabilized by  $\pi$  donation. They form instead more stable complexes with the  $\pi$ -acceptor ligands (strong-field,  $\pi$ -acids) that can remove some of the electron density from the metal ions.

- 16.101** (a)  $\text{ZrO}_2$  : there are 4 zirconium atoms in the unit cell. ( $1/8 \times 8$  corner atoms +  $1/2 \times 6$  face-centered atoms) and 8 oxygen atoms (All O atoms lie completely inside the unit cell.); (b) face-centered cubic; (c) eight; (d) coordination number = 4, tetrahedral; (e) An obvious difference is that zirconia is composed of two different types of atoms, whereas diamond is made up solely of carbon; however, both structures are based upon a face-centered cubic unit cell. In zirconia, all of the tetrahedral holes created in the cubic close-packed arrangement of zirconium atoms are occupied by oxide ligands. In the case of diamond, only half of the tetrahedral holes are filled. The consequence is that the zirconium atoms are connected to twice as many oxygen atoms as carbon is connected to other carbon atoms.

- 16.103** (a)  $\text{PtCl}_2(\text{NH}_3)_2$ , *cis*-diamminedichloroplatinum(II); (b) The only other isomer is the *trans* form. Neither the *cis* nor the *trans* form is optically active.





(c) square planar

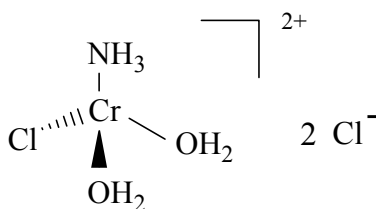
**16.105** number of moles of complex =  $\frac{2.11 \text{ g}}{211.42 \text{ g} \cdot \text{mol}^{-1}}$

=  $9.98 \times 10^{-3} \text{ mol complex}$

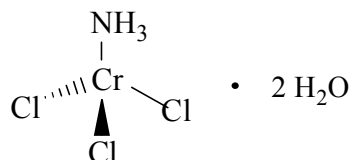
number of moles of  $\text{Cl}^-$  =  $2.87 \text{ g AgCl} \left( \frac{1 \text{ mole AgCl}}{143.32 \text{ g} \cdot \text{mol}^{-1}} \right) \left( \frac{1 \text{ mole Cl}^-}{1 \text{ mole AgCl}} \right)$

=  $2.00 \times 10^{-2} \text{ mole Cl}^-$

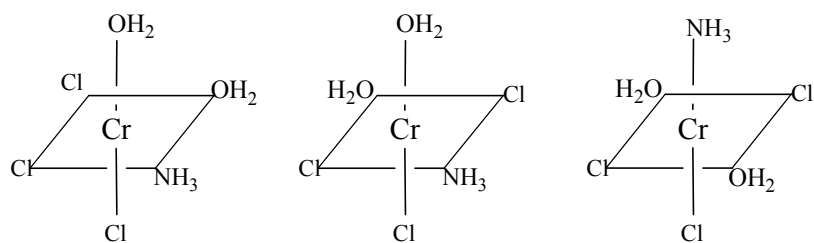
Therefore the compound contains 2 moles of  $\text{Cl}^-$  counterion for every mole of complex (assuming that the incorrect formula gives the correct molar mass). Then the correct formula of the compound would be  $[\text{CrNH}_3\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}_2$ . Since the  $\text{Cr}^{3+}$  is  $d^3$  and coordinated by four ligands, the complex cation is likely to be tetrahedral. There are no linkage isomers possible and no enantiomers for this complex ion.



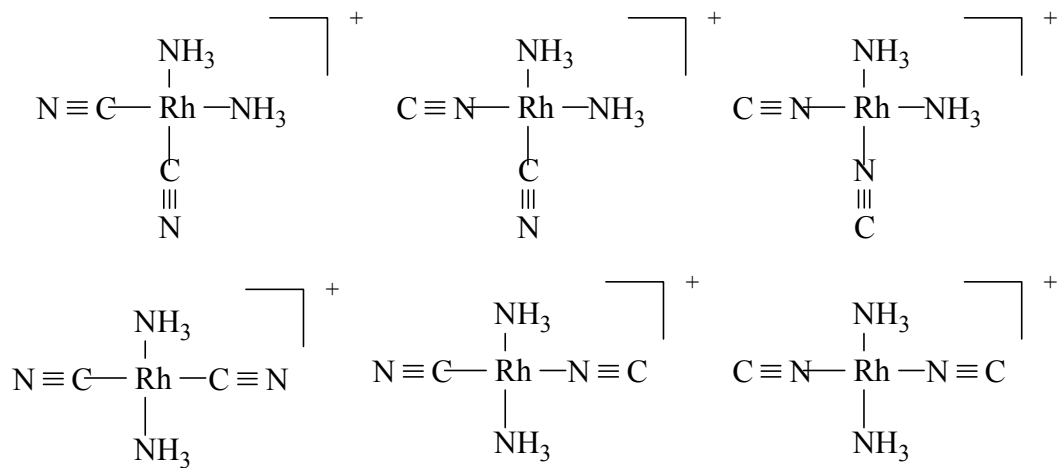
However, the compound as a whole has several isomers, including one that corresponds to the incorrect formula,  $[\text{CrNH}_3\text{Cl}_3] \cdot 2 \text{ H}_2\text{O}$ .



The other reasonable isomers include octahedral species that result if the chloride ions as well as both water molecules are all attached directly to the metal ion.



16.107



Since the rhodium ion has a 3+ charge, its electron configuration is  $d^6$ .