

Chapter 16

The Elements: The *d* Block

16.2 Five *d*-block elements can be found in Appendix 2B with positive standard potentials. They are

Ag, $E^\circ = +0.80$ V

Cu, $E^\circ = +0.34$ V

Au, $E^\circ = +1.40$ V

Pt, $E^\circ = +1.20$ V

Hg, $E^\circ = +0.79$ V

16.4 (a) Mn (b) Zn (c) One might expect gold to be larger because it is a third row transition metal and silver is in row two, but because of the lanthanide contraction, they are essentially the same size (both have atomic radii equal to 144 pm). (d) Mo

16.6 (a) Co is very slightly higher.

(b) Fe

(c) Cr is slightly higher.

(d) Because silver is larger, one expects it to have a lower first ionization potential, which is the case ($731 \text{ kJ}\cdot\text{mol}^{-1}$).

(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 silver is less than for gold ($731 \text{ kJ}\cdot\text{mol}^{-1}$ vs. $890 \text{ kJ}\cdot\text{mol}^{-1}$).

- 16.8** Chromium has a slightly smaller atomic radius (129 pm vs. 135 pm for V) and a somewhat larger atomic mass ($52.00 \text{ g}\cdot\text{mol}^{-1}$ vs. $50.94 \text{ g}\cdot\text{mol}^{-1}$ for V). Based on these two facts alone, you would expect the density of Cr to be larger by a factor of

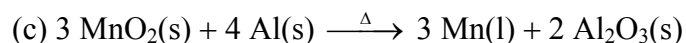
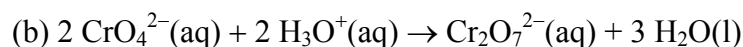
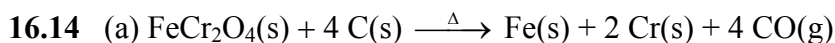
$$\left(\frac{135}{129}\right)^2 \times \left(\frac{52.00}{50.94}\right) = 1.16$$

In actuality, the ratio is

$$\left(\frac{7.19}{6.11}\right) = 1.18$$

- 16.10** A compound in which an element has a high oxidation number tends to be a good oxidizing agent. The trend toward higher oxidation state stability increases from top to bottom of the group; conversely, lower oxidation state stability increases from bottom to top. Therefore, Mn would (and does) have a more stable (low) oxidation state (+2); therefore MnO_4^- would be the best oxidizing agent.

- 16.12** In MCl_4 , M has an oxidation number of +4. Referring to Figure 16.6, we see that Zr has the most stable +4 oxidation state.



- 16.16** (a) Fe_3O_4 , which is actually a mixture of iron(II) oxide, FeO , and iron(III) oxide, Fe_2O_3
(b) iron(II) disulfide, FeS_2
(c) iron(II) titanate, FeTiO_3
(d) iron(II) chromite, FeCr_2O_4

16.18 (a) $E^\circ(\text{Ni}^{2+}/\text{Ni}) = -0.23 \text{ V}$

$$E^\circ(\text{H}^+/\text{H}_2) = 0.00 \text{ V}$$

The products are Ni^{2+} , H_2 , and Cl^- .

(b) $E^\circ(\text{Ti}^{2+}/\text{Ti}) = -1.63 \text{ V}$

$$E^\circ(\text{Ti}^{3+}/\text{Ti}^{2+}) = -0.37 \text{ V}$$

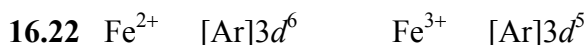
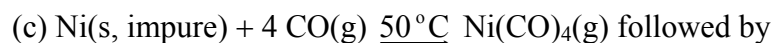
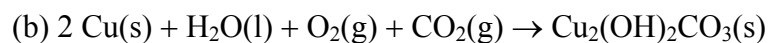
$$E^\circ(\text{Ti}^{4+}/\text{Ti}^{3+}) = 0.00 \text{ V}$$

The products are Ti^{4+} , H_2 , and Cl^- .

(c) $E^\circ(\text{Pt}^{2+}/\text{Pt}) = +1.20 \text{ V}$

$$E^\circ(\text{MnO}_4^-/\text{Mn}^{2+}) = +1.51 \text{ V}$$

The products are Pt^{2+} , Mn^{2+} , Cl^- , K^+ , and H_2O .

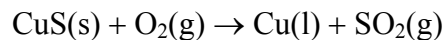


Oxidation of Fe^{2+} to Fe^{3+} readily occurs because a half-filled d -subshell is obtained, which is not the case with either Co^{2+} or Ni^{2+} . Half-filled subshells are low-energy electron arrangements; therefore, they have a strong tendency to form.

16.24 Chalcopyrite, which contains CuFeS_2 , is crushed and ground, and the sulfide is extracted in enriched form by froth flotation. “Roasting,” or heating in air, follows:



Compressed air is then forced through the resulting CuS :



16.26 (a) hexacyanoferrate(III) ion

Let x = oxidation number to be determined

$$x(\text{Fe}) + 6 \times (-1) = -3$$

$$x(\text{Fe}) = -3 - (-6) = +3$$

(b) pentaquahydroxoiron(III) ion

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

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

(c) tetraammineaquachlorocobalt(III) ion

$$x(\text{Co}) + 1 \times (-1) + 4 \times (0) + 1 \times (0) = +2$$

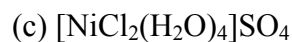
$$x(\text{Co}) = +2 - (-1) = +3$$

(d) tris(ethylenediamine)iridium(III) ion

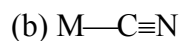
$$x(\text{Ir}) + 3 \times (0) = +3$$

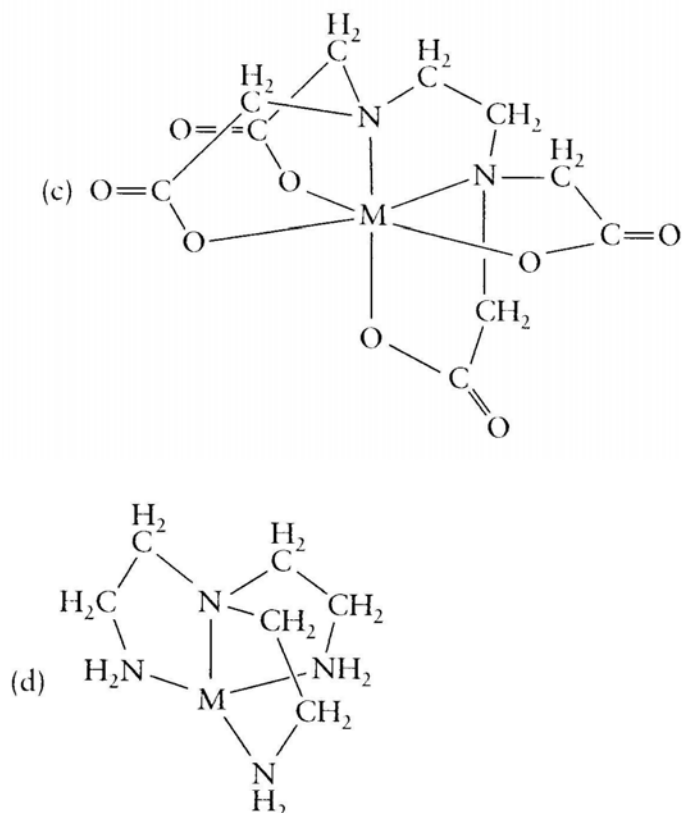
$$x(\text{Ir}) = +3$$

16.28 (a) $[\text{Cr}(\text{OH})_2(\text{NH}_3)_3(\text{H}_2\text{O})]\text{Cl}$

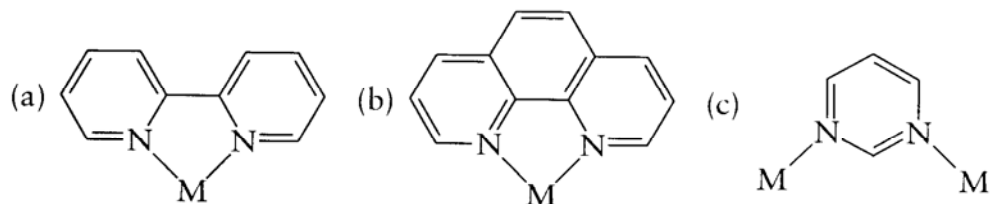


16.30 The chloride and cyanide ions can only be monodentate with respect to one metal ion. Ethylenediamine tetraacetate may bond through four oxygen atoms and two nitrogen atoms, making it a hexadentate ligand if all the arms are simultaneously bound to one metal center. The molecule $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ has four nitrogen atoms, each having a lone pair that can bind to a metal center. It can function as a tetradentate ligand.





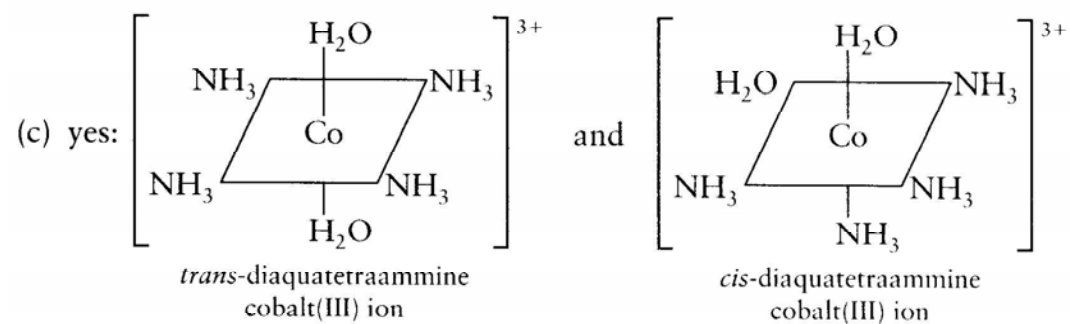
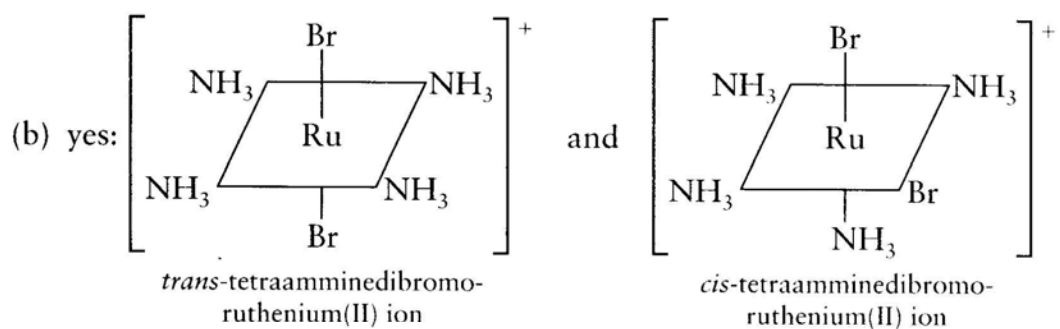
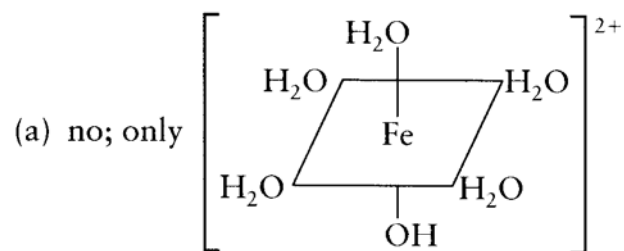
16.32 As shown below, the molecules (a) and (b) can function as chelating ligands. In (a) the two phenyl rings are free to rotate around in the single bond that connects them, making it possible for them to place the two nitrogen atoms in a proper geometrical arrangement to chelate a metal ion. The two amine groups in (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 (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.



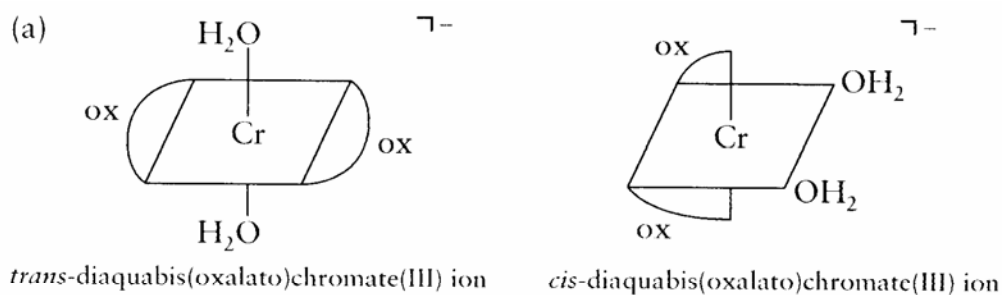
16.34 (a) 6 (en is bidentate) (b) 6 (ox is bidentate) (c) 4 (d) 5

- 16.36 (a) coordination isomerism
 (b) hydrate isomerism
 (c) linkage isomerism
 (d) coordination isomerism

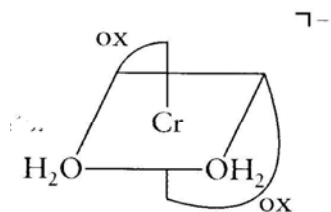
16.38



16.40

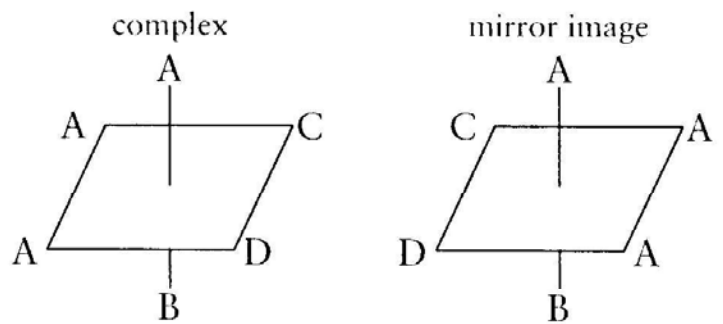


A second *cis* isomer is the mirror image of the first *cis* complex (same name).

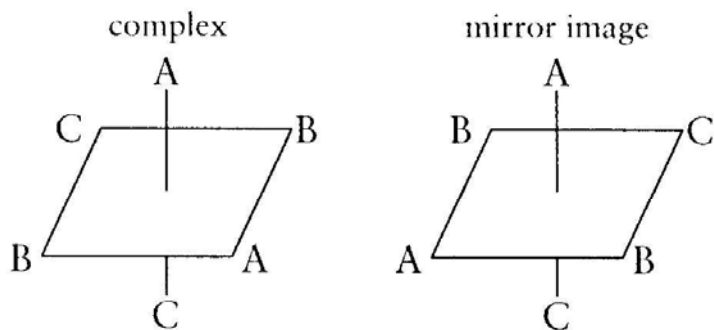


(b) The *cis* isomers are optically active.

16.42 Complex (a) is chiral; the enantiomeric pair is illustrated.



Complex (b) is not chiral.

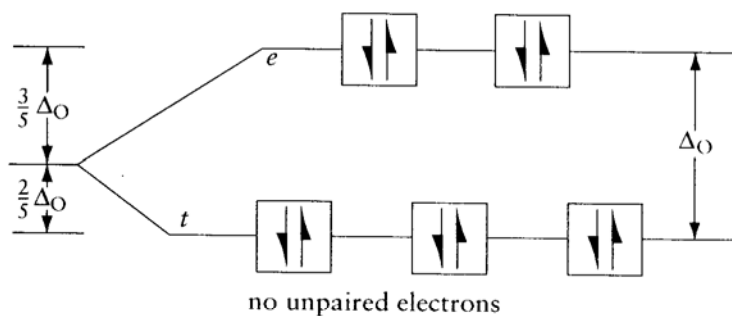


A 90° counterclockwise rotation of the mirror image about the vertical A-C axis will make the complex and mirror image match. The two complexes, (a) and (b) are not even isomers, so they cannot be enantiomers.

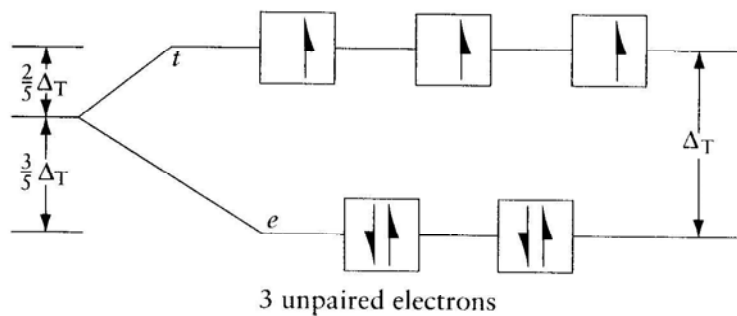
16.44 (a) 3; (b) 6; (c) 6; (d) 9; (e) 4; (f) 6

16.46 (a) 2; (b) 3; (c) 8; (d) 8; (e) 3; (f) 8

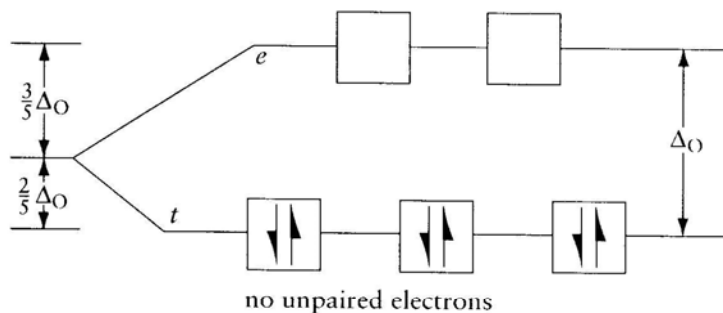
16.48 (a) octahedral: weak-field ligand, 10 e⁻



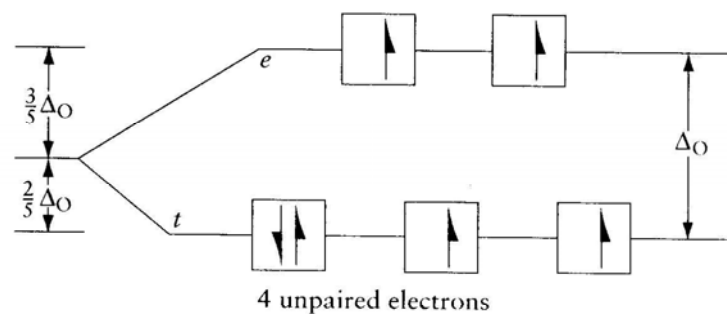
(b) tetrahedral: weak-field ligand, 7 e⁻



(c) octahedral: strong-field ligand, $6 e^-$



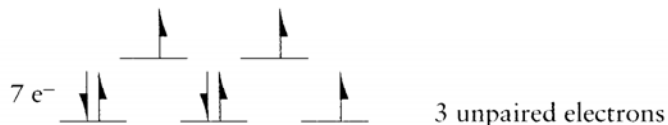
(d) octahedral: weak-field ligand, $6 e^-$



16.50 (a) $[\text{FeF}_6]^{3-}$



(b) $[\text{Co}(\text{ox})_3]^{4-}$



16.52 Because the splitting between the energies of the atomic orbitals increases when a weak-field ligand is replaced with a strong-field ligand, light absorption will occur at shorter wavelengths and the color of the complex will change, for example, from green to orange-yellow. Furthermore, the number of unpaired electrons may decrease (due to pairing of the electrons caused by the strong-field ligands) and the compound may become less paramagnetic (less total spin).

16.54 NH_3 is a strong-field ligand; therefore, the splitting is large between the t_{2g} and e_g orbitals. Co^{3+} has six d electrons; therefore, the configuration is t_{2g}^6 . The splitting is large and therefore the transition is a high-energy transition. This leads to a short wavelength. The metal in $[\text{CoCl}_6]^{3-}$ is a Co^{3+} and therefore again has six d electrons. Cl^- is a weak-field ligand; therefore, the splitting is small and the configuration is $t_{2g}^4 e_g^2$. Because the splitting is small, the transition is a low-energy transition. This leads to a longer wavelength.

16.56 (a) $[\text{CuBr}_4]^{2-} \rightarrow [\text{Cu}(\text{H}_2\text{O})_6]^{2+}$

(b) violet \rightarrow blue is expected

Br^- is a weak-field ligand. H_2O is a stronger weak-field ligand. The color shift is from shorter to longer wavelength. The weaker-field complex absorbs the longer wavelengths and transmits the shorter (in this case, violet) color. The opposite is true for the stronger-field complex. Also, the $[\text{CuBr}_4]^{2-}$ ion is tetrahedral, and tetrahedral complexes in general have smaller values for Δ than octahedral complexes.

16.58 $\text{Cu}(\text{II})$ compounds contain one unpaired electron ($3d^9$ configuration); $\text{Cu}(\text{I})$ compounds have no unpaired electrons ($3d^{10}$). Therefore, $\text{Cu}(\text{II})$ compounds may be colored and paramagnetic, but $\text{Cu}(\text{I})$ compounds are not.

16.60 (a) $\Delta_0 = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{295 \times 10^{-3} \text{ m}} = 6.75 \times 10^{-19} \text{ J}$

(b) $\Delta_0 = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{435 \times 10^{-9} \text{ m}} = 4.75 \times 10^{-19} \text{ J}$

(c) $\Delta_0 = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J} \cdot \text{s}^{-1})(3.00 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{540 \times 10^{-9} \text{ m}} = 3.68 \times 10^{-19} \text{ J}$

The above numbers can be multiplied by 6.022×10^{23} to obtain the energies in $\text{kJ} \cdot \text{mol}^{-1}$.

(a) $6.74 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 4.06 \times 10^5 \text{ J} \cdot \text{mol}^{-1}$
 $= 406 \text{ kJ} \cdot \text{mol}^{-1}$

$$\begin{aligned} \text{(b)} \quad & 4.57 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 2.75 \times 10^5 \text{ J} \cdot \text{mol}^{-1} \\ & = 275 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad & 3.68 \times 10^{-19} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 2.22 \times 10^5 \text{ J} \cdot \text{mol}^{-1} \\ & = 222 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

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

16.62 The t_{2g} set, which is comprised of the d_{xy} , d_{xz} and d_{yz} orbitals

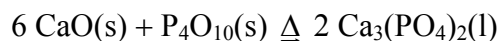
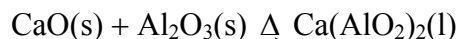
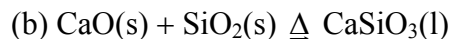
16.64 (a) NH_3 is neither a π -acid nor a π -base because it does not have any empty π -type antibonding orbitals nor does it have any extra lone pairs of electrons to donate. (b) ox has extra lone pairs in addition to the one that is used to form the σ -bond to the metal and so it can act as a π -base, donating electrons in a p -orbital to an empty d -orbital on the metal. (c) The F^- ion has extra lone pairs in addition to the one that is used to form the σ -bond to the metal and so it can act as a π -base, donating electrons in a p -orbital to an empty d -orbital on the metal. (d) CO is a π -acid ligand accepting electrons into the empty π^* -orbital created by the C—O multiple bond. $\text{F}^- < \text{ox} < \text{NH}_3 < \text{CO}$. Note that the spectrochemical series orders the ligands as π -bases $<$ σ -bond only ligands $<$ π -acceptors.

16.66 Bonding. In a complex that forms only σ -bonds, the t_{2g} set of orbitals is non-bonding. If the ligands can function as π -acceptors, the t_{2g} set becomes bonding by interaction with the π^* -orbitals on the ligands.

16.68 Antibonding. In a complex that forms only σ -bonds, the t_{2g} set of orbitals is non-bonding. If the ligands can function as π -donors, the t_{2g} set becomes antibonding by interacting with the filled p -orbitals on the ligands.

16.70 Ethylenediamine is a σ -bond-forming ligand that cannot function as either a π -acceptor or a π -donor. CO, on the other hand, can function as a π -acceptor ligand. When it does so, it lowers the energy of the t_{2g} set of orbitals, making Δ larger.

16.72 (a) Limestone is converted to CaO, which helps remove acidic (nonmetal oxide) anhydride and amphoteric impurities from the ore.



16.74 Chromium

16.76 Up to 40% zinc in copper.

16.78 +3

16.80 A diamagnetic substance has no unpaired electrons and is weakly pushed out of a magnetic field. Paramagnetism refers to the presence of unpaired electrons in a substance. A paramagnetic compound is pulled toward a magnetic field. Ferromagnetism is an extensive property that occurs when the unpaired electrons on a number of metal ions within a sample align with each other. Paramagnetism is a property of any substance with unpaired electrons, whereas ferromagnetism is a property of certain substances that can become permanently magnetized. Their spins become aligned, and this alignment can be retained even in the absence of a magnetic field. In a paramagnetic substance, the alignment is lost when the magnetic field is removed. Antiferromagnetism is the opposite of ferromagnetism—it occurs when the unpaired electrons on a number of metal ions within a sample pair between the metal ions, so that the overall magnetism cancels.

16.82 $n(\text{H}_2\text{O}) = 2.387 \text{ g H}_2\text{O} \times \frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} = 0.1324 \text{ mol}$

$$n(\text{Cl}_2) = 1.57 \text{ g Cl}_2 \times \frac{1 \text{ mol Cl}_2}{70.90 \text{ g Cl}_2} = 0.0221 \text{ mol Cl}_2$$

$$n(\text{H}_2\text{O}) = \frac{0.1324 \text{ mol}}{0.0221 \text{ mol}} = 5.99$$

Six water molecules are present in the complex.

16.84 Concentration (mol/L) $\text{Ni}^{2+}(\text{aq}) + 6 \text{NH}_3(\text{aq}) \rightarrow [\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq})$

Start	0.10	0.75	0.0
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Assume complete rxn.

New initial	0.0	0.15	0.10
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Change	+x	+6x	-x
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Equilibrium	x	0.15+6x	0.10-x
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$$K = 1.0 \times 10^9 = \frac{[\text{Ni}(\text{NH}_3)_6]^{2+}}{[\text{Ni}^{2+}][\text{NH}_3]^6} = \frac{(0.10 - x)}{(x)(0.15 + 6x)^6} \approx \frac{(0.10)}{(x)(0.15)^6}$$

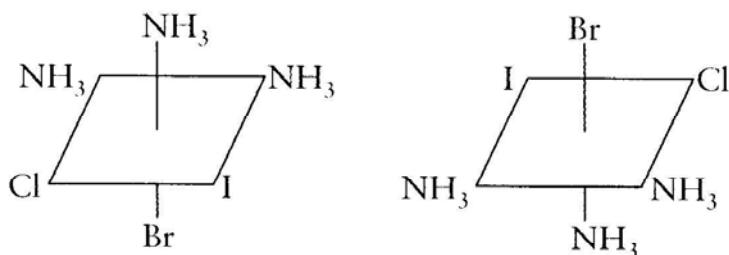
$$x = 8.8 \times 10^{-6} \text{ M}$$

$$[\text{Ni}^{2+}] = 8.8 \times 10^{-6} \text{ M}$$

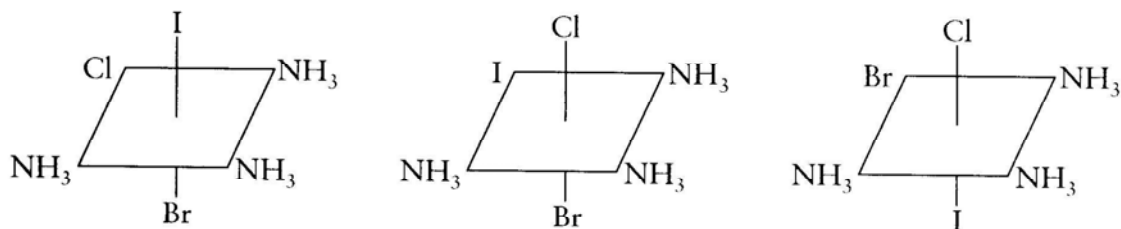
$$[\text{NH}_3] = 0.15 \text{ M}$$

$$[\text{Ni}(\text{NH}_3)_6]^{2+} = 0.10 \text{ M}$$

16.86

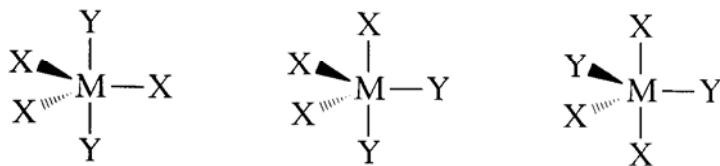


The above isomers are chiral and enantiomers of each other.



These isomers are not chiral.

16.88 Isomerism is possible. The following are the different isomers:



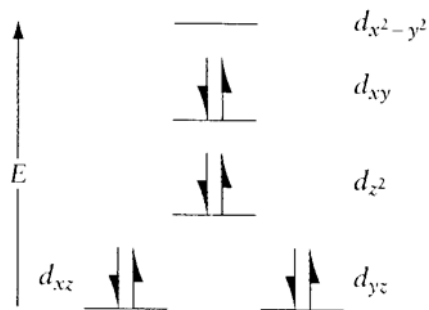
16.90 (a) strong field (b) weak field

16.92 Although the hydride ion H^- is similar to halide ions because it has a -1 charge, it is different because it has no extra lone pairs of electrons. H^- would therefore be a stronger-field ligand than the halide ions, which have lone pairs that will tend to make Δ smaller.

16.94 All of these species might be able to bind to the iron by donating a lone pair to the empty d_{z^2} orbital. However, CO can bind more strongly than O_2 because it has the ability to act as a π -acceptor through an empty π^* orbital (see Figure 14.36, π -backbonding). Nitrite anion may be able to act as a π -acceptor, too, so it will probably bind fairly tightly to the iron center. Chloride and boron trifluoride would be expected to bind more weakly, if at all, since they only have lone pairs to donate and have no empty π^* orbitals. The relative energy of the σ -donating orbital on each ligand compared to that of the σ -accepting orbital on iron would also be important in determining the stability of the bond. If these energies do not match closely enough, a bond will not form.

16.96 See Figure 16.28. Remove (mentally) the ligands along the $\pm z$ axes. From the shape of the atomic orbitals and their orientation with respect to the x , y , and z axes, it is clear that the $d_{x^2-y^2}$ -orbital will have the greatest overlap, therefore repulsion, from the ligands in the xy plane. The d_{xy} -orbital will have the next strongest repulsion from these ligands, d_{z^2} next, and finally, the weakest

repulsion will be with d_{xz} and d_{yz} . Therefore, the energy-level diagram will be (schematically):



The building-up principle is illustrated in the diagram with a d^8 ion (Pd^{2+}). The separation in energy between the $d_{x^2-y^2}$ and d_{xy} orbitals determines whether or not there will be unpaired electrons.

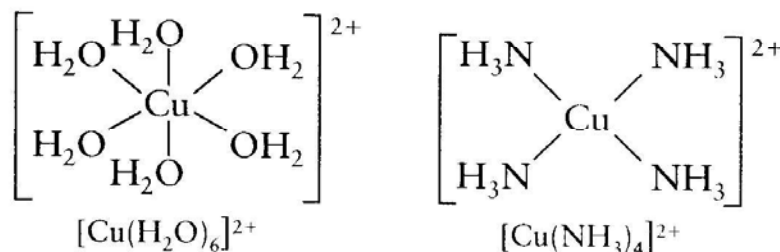
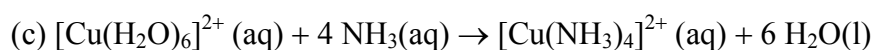
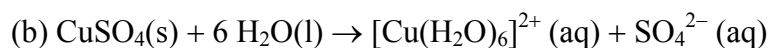
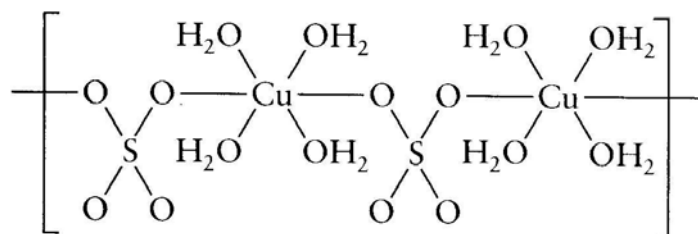
16.98 If the sample were 100% pure, its optical rotation would be 48.0 degrees $(\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^{-1}$. Because the rotation is only 46.5 degrees $(\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^{-1}$, we know that the percentage of the sample of A that is giving rise to the rotation is $(46.5 \div 48.0) \times 100 = 96.9\%$. But because the impurity is A^* , this is not all of the A in the sample.

Consider the case where $[A] = [A^*]$, which gives rise to no rotation of light because the degree of rotation of A^* will exactly cancel the rotation of A. If we have a mixture of 10% A^* and 90% A, then the rotation of 10% of A^* will cancel an equal amount of rotation by A. Thus, the observed rotation will be 80% of the value of pure A or $0.80 \times 48.0 \text{ degrees} \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^{-1} = 38.4 \text{ degrees} \cdot (\text{mol} \cdot \text{L}^{-1})^{-1} \cdot \text{cm}^{-1}$. For the specific case in hand, the 3.1% rotation that is lost must be due to a 1:1 mixture of A and A^* . So the total amount of A in the sample will be $96.9\% + 1/2(3.1\%) = 98.5\%$.

16.100 (a) $\text{CuSO}_4(\text{s}) + 5 \text{H}_2\text{O}(\text{l}) \rightarrow \text{CuSO}_4 \cdot 5 \text{H}_2\text{O}(\text{s})$

The pentahydrate has a complicated structure. It consists of the $\text{Cu}(\text{H}_2\text{O})_4^{2+}$ ion bonded to two sulfate ions. The four water molecules of the tetrahydrate ion form an approximate square planar structure around the copper atom, with the sulfate

oxygen atoms in the remaining two coordination sites. The fifth water is hydrogen-bonded to the sulfate and not directly associated with the Cu^{2+} ion.



16.102 (a) Iron is four and six coordinate, oxygen is four coordinate.

(b) Iron is approximately octahedral or tetrahedral, and oxygen is tetrahedral.

(c) Iron atoms:

$1/4 \times 12$ octahedral iron atoms on the unit cell edges	3 atoms
$1/2 \times 12$ atoms on the unit cell faces	6 atoms
7 octahedral atoms completely inside the unit cell	7 atoms
8 tetrahedral atoms completely inside the unit cell	8 atoms
Total	24 atoms

Oxygen atoms:

$1/4 \times 24$ atoms on unit cell edges	6 atoms
$1/2 \times 24$ atoms on unit cell faces	12 atoms
14 atoms completely within the unit cell	14 atoms
Total	32 atoms

The overall formula is $\text{Fe}_{24}\text{O}_{32}$ or Fe_3O_4 .

(d) The unit cell is face centered cubic.

(e) The edge length is 839 pm and there are eight formula units per unit cell. The mass in the unit cell is

$$8 \times 231.55 \text{ g}\cdot\text{mol}^{-1} \div 6.02 \times 10^{23} \text{ formula units}\cdot\text{mol}^{-1} = 3.08 \times 10^{-21} \text{ g}\cdot\text{mol}^{-1}$$

The volume of the unit cell is

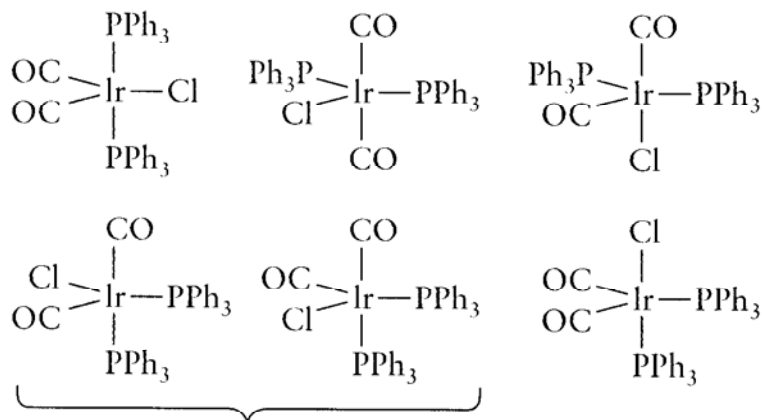
$$(839 \text{ pm} \times 10^{-10} \text{ cm}\cdot\text{pm}^{-1})^3 = 5.90 \times 10^{-22} \text{ cm}^3$$

$$\text{density} = 3.08 \times 10^{-21} \text{ g}\cdot\text{mol}^{-1} \div 5.90 \times 10^{-22} \text{ cm}^3 = 5.22 \text{ g}\cdot\text{cm}^3$$

16.104 (a) trigonal bipyramidal

(b) +1

(c) There are six possible isomers (including the one shown on the Web site).



nonsuperimposable mirror images

nonsuperimposable mirror images

16.106 $\text{Hg}_2^{2+} + 2 \text{e}^- \rightarrow 2 \text{Hg}$ (1) $E^\circ = +0.79 \text{ V}$

$2 \text{Hg}^{2+} + 2 \text{e}^- \rightarrow \text{Hg}_2^{2+}$ (2) $E^\circ = +0.92$

Reversing Eq. 2 gives

$\text{Hg}_2^{2+} \rightarrow 2 \text{Hg}^{2+} + 2 \text{e}^-$ (3)

The cathode process is given by Eq. 1; the anode process by Eq. 3. Combining them yields the overall (disproportionation) reaction:

$2 \text{Hg}_2^{2+} \rightarrow 2 \text{Hg}^{2+} + 2 \text{Hg}$

The potential of this reaction is

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$E^{\circ}_{\text{cell}} = +0.79 \text{ V} - (+0.92 \text{ V}) = -0.13 \text{ V}$$

$$\ln K = \frac{nFE}{RT} = \frac{-0.13 \text{ V}}{0.025\,693 \text{ V}} = -5.1$$

$$K = 6 \times 10^{-3}$$