24

Chemistry of Coordination Compounds

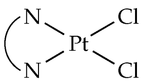
Visualizing Concepts

24.1 *Analyze*. Given the formula of a coordination compound, determine the coordination geometry, coordination number, and oxidation state of the metal.

Plan. From the formula, determine the identity of the ligands and the number of coordination sites they occupy. From the total coordination number, decide on a likely geometry. Use ligand and overall complex charges to calculate the oxidation number of the metal.

Solve.

(a) The ligands are $2Cl^-$, one coordination site each, and en, ethylenediamine, two coordination sites, for a coordination number of 4. This coordination number has two possible geometries, tetrahedral and square planar. Pt is one of the metals known to adopt square planar geometry when CN = 4.



(b) CN = 4, coordination geometry = square planar

(c) $Pt(en)Cl_2$ is a neutral compound, the en ligand is neutral, and the $2Cl^-$ ligands are each –1, so the oxidation state of Pt must be +2, Pt(II).

24.4 *Analyze*. Given 5 structures, visualize which are identical to (1) and which are geometric isomers of (1).

Plan. There are two possible ways to arrange MA_3X_3. The first has bond angles of 90° between all similar ligands; this is structure (1). The second has one 180° angle between similar ligands. Visualize which description fits each of the five structures.

Solve. (1) has all 90° angles between similar ligands.

(2) has a 180° angle between similar ligands (see the blue ligands in the equatorial plane of the octahedron)

(3) has all 90° angles between similar ligands

(4) has all 90° angles between similar ligands

(5) has a 180° angle between similar ligands (see the blue axial ligands)

Structures (3) and (4) are identical to (1); (2) and (5) are geometric isomers.

24 Coordination Compounds Solutions to Exercises

24.6 *Analyze*. Given the visible colors of two solutions, determine the colors of light absorbed by each solution.

Plan. Apparent color is transmitted or reflected light, absorbed color is basically the complement of apparent color. Use the color wheel in Figure 24.24 to obtain the complementary absorbed color for the solutions.

Solve. The left solution appears yellow-orange, so it absorbs blue-violet. The right solution appears blue-green (cyan), so it absorbs orange-red.

Introduction to Metal Complexes

24.9 (a) In Werner’s theory, *primary valence* is the charge of the metal cation at the center of the complex. *Secondary valence* is the number of atoms bound or coordinated to the central metal ion. The modern terms for these concepts are oxidation state and coordination number, respectively. (Note that “‘oxidation state” is a broader term than ionic charge, but Werner’s complexes contain metal ions where cation charge and oxidation state are equal.)

(b) Ligands are the Lewis base in metal-ligand interactions. As such, they must possess at least one unshared electron pair. NH_3 has an unshared electron pair but BH_3, with less than 8 electrons about B, has no unshared electron pair and cannot act as a ligand. In fact, BH_3 acts as a Lewis acid, an electron pair acceptor, because it is electron-deficient.

24.11 *Analyze/Plan*. Follow the logic in Sample Exercises 24.1 and 24.2. *Solve*.

(a) This compound is electrically neutral, and the NH_3 ligands carry no charge, so the charge on Ni must balance the –2 charge of the 2 Br^- ions. The charge and oxidation state of Ni is +2.

(b) Since there are 6 NH_3 molecules in the complex, the likely coordination number is 6. In some cases Br^- acts as a ligand, so the coordination number could be other than 6.

(c) Assuming that the 6 NH_3 molecules are the ligands, 2 Br^- ions are not coordinated to the Ni^{2+}, so 2 mol AgBr(s) will precipitate. (If one or both of the Br^- act as a ligand, the mol AgBr(s) would be different.)

24.13 *Analyze/Plan*. Count the number of donor atoms in each complex, taking the identity of polydentate ligands into account. Follow the logic in Sample Exercise 24.2 to obtain oxidation numbers of the metals.

(a) Coordination number = 4, oxidation number = +2

(b) 5, +4 (c) 6, +3 (d) 5, +2

(e) 6, +3 (f) 4, +2

24.15 *Analyze/Plan*. Given the formula of a coordination compound, determine the number and kinds of donor atoms. The ligands are enclosed in the square brackets. Decide which atom in the ligand has an unshared electron pair it is likely to donate. *Solve*.

(a) 4 Cl^- (b) 4 Cl^-, 1 O^{2-} (c) 4 N, 2 Cl^-

(d) 5 C. In CN^-, both C and N have an unshared electron pair. C is less electronegative and more likely to donate its unshared pair.

(e) 6 O. $C_2O_4^{2-}$ is a bidentate ligand; each ion is bound through 2 O atoms for a total of 6 O donor atoms.

(f) 4 N. en is a bidentate ligand bound through 2 N atoms.

Polydendate Ligands; Nomenclature

24.17 (a) A monodendate ligand binds to a metal in through one atom; a bidendate ligand binds through two atoms.

(b) If a bidentate ligand occupies two coordination sites, three bidentate ligands fill the coordination sphere of a six-coordinate complex.

(c) A tridentate ligand has at least three atoms with unshared electron pairs in the correct orientation to simultanously bind one or more metal ions.

24.19 *Analyze/Plan*. Given the formula of a coordination compound, determine the number of coordination sites occupied by the polydentate ligand. The coordination number of the complexes is either 4 or 6. Note the number of monodentate ligands and determine the number of coordination sites occupied by the polydentate ligands. *Solve*.

(a) *ortho*-phenanthroline, *o*-phen, is bidentate

(b) oxalate, $C_2O_4^{2-}$, is bidentate

(c) ethylenediaminetetraacetate, EDTA, is pentadentate

(d) ethylenediamine, en, is bidentate

24.21 (a) The term *chelate effect* means there is a special stability associated with formation of a metal complex containing a polydentate (chelate) ligand relative to a complex containing only monodentate ligands.

(b) When a single chelating ligand replaces two or more monodendate ligands, the number of free molecules in the system increases and the entropy of the system increases. Chemical reactions with $+\Delta S$ tend to be spontaneous, have negative ΔG, and large positive values of K.

(c) Polydentate ligands can be used to bind metal ions and prevent them from undergoing unwanted chemical reactions without removing them from solution. The polydentate ligand thus hides or *sequesters* the metal ion.

24.23 *Analyze/Plan*. Given the name of a coordination compound, write the chemical formula. Refer to Table 24.2 to find ligand formulas. Place the metal complex (metal ion + ligands) inside square brackets and the counter ion (if there is one) outside the brackets. *Solve*.

(a) $[Cr(NH_3)_6](NO_3)_3$ (b) $[Co(NH_3)_4CO_3]_2SO_4$ (c) $[Pt(en)_2Cl_2]Br_2$

(d) $K[V(H_2O)_2Br_4]$ (e) $[Zn(en)_2][HgI_4]$

24.25 *Analyze/Plan.* Follow the logic in Sample Exercise 24.4, paying attention to naming rules in Section 24.3. *Solve.*

(a) tetraamminedichlororhodium(III) chloride

(b) potassium hexachlorotitanate(IV)

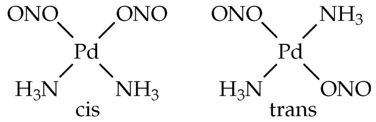
(c) tetrachlorooxomolybdenum(VI)

(d) tetraaqua(oxalato)platinum(IV) bromide

Isomerism

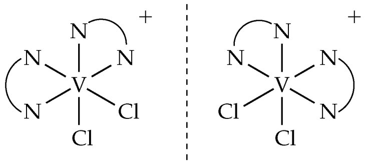
24.27 *Analyze/Plan.* Consider the definitions of the various types of isomerism, and which of the complexes could exhibit isomerism of the specified type. *Solve.*

(a)



(b) $[Pd(NH_3)_2(ONO)_2]$, $[Pd(NH_3)_2(NO_2)_2]$

(c)

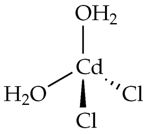


(d) $[Co(NH_3)_4Br_2]Cl$, $[Co(NH_3)_4BrCl]Br$

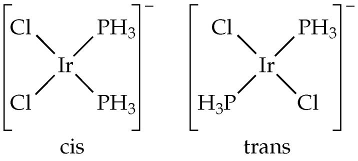
24.29 Yes. A tetrahedral complex of the form MA_2B_2 would have neither structural nor stereoisomers. For a tetrahedral complex, no differences in connectivity are possible for a single central atom, so the terms cis and trans do not apply. No optical isomers with tetrahedral geometry are possible because M is not bound to four different groups. The complex must be square planar with cis and trans geometric isomers.

24.31 *Analyze/Plan.* Follow the logic in Sample Exercise 24.5 and 24.6. *Solve.*

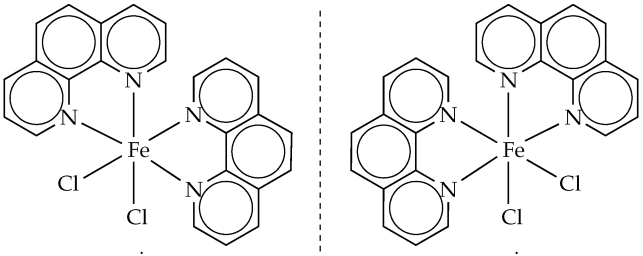
(a)



(b)

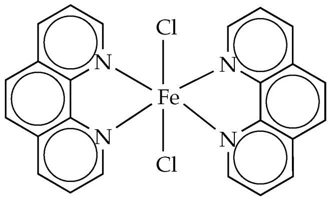


(c)



cis cis

optical isomers



trans

(The three isomeric complex ions in part (c) each have a 1+ charge.)

Color, Magnetism; Crystal-Field Theory

24.33 (a) Visible light has wavelengths between 400 and 700 nm.

(b) *Complementary* colors are opposite each other on a color wheel such as Figure 24.24.

(c) A colored metal complex absorbs visible light of its complementary color. For example, a red complex absorbs green light.

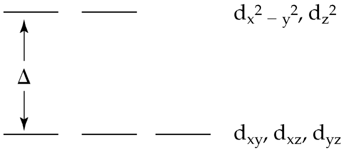
(d) E(J/photon) = hν = hc/λ. Change J/photon to kJ/mol.

$$E = \frac{6.626 \times 10^{-34}\ \text{J-s}}{610\ \text{nm}} \times \frac{3.00 \times 10^{8}\ \text{m}}{\text{s}} \times \frac{1\ \text{nm}}{1 \times 10^{-9}\ \text{m}} = 3.259 \times 10^{-19} = 3.26 \times 10^{-19}\ \text{J}$$

$$\frac{3.259 \times 10^{-19}\ \text{J}}{\text{photon}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} \times \frac{6.022 \times 10^{23}\ \text{photons}}{\text{mol}} = 196\ \text{kJ/mol}$$

24.35 Most of the electrostatic interaction between a metal ion and a ligand is the attractive interaction between a positively charged metal cation and the full negative charge of an anionic ligand or the partial negative charge of a polar covalent ligand. Whether the interaction is ion-ion or ion-dipole, the ligand is strongly attracted to the metal center and can be modeled as a point negative charge.

24.37 (a)



(b) The magnitude of Δ and the energy of the d-d transition for a d^1 complex are equal.

(c) $$\frac{6.626\times10^{-34}\ \text{J-s}}{590\ \text{nm}}\times\frac{3.00\times10^{8}\ \text{m}}{\text{s}}\times\frac{1\ \text{nm}}{1\times10^{-9}\ \text{m}}\times\frac{1\ \text{kJ}}{1000\ \text{J}}\times\frac{6.022\times10^{23}\ \text{photons}}{\text{mol}}$$

= 203 kJ/mol

24.39 *Analyze/Plan.* Consider the relationship between the color of a complex, the wavelength of absorbed light, and the position of a ligand in the spectrochemical series. *Solve.*

Cyanide is a strong field ligand. The d-d electronic transitions occur at relatively high energy, because Δ is large. A yellow color corresponds to absorption of a photon in the violet region of the visible spectrum, between 430 and 400 nm. H_2O is a weaker field ligand than CN^-. The blue or green colors of aqua complexes correspond to absorptions in the region of 620 nm. Clearly, this is a region of lower energy photons than those with characteristic wavelengths in the 430 to 400 nm region. These are very general and imprecise comparisons. Other factors are involved, including whether the complex is high spin or low spin.

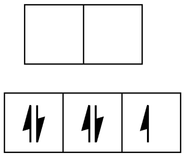
24.41 *Analyze/Plan.* Determine the charge on the metal ion, subtract it from the row number (3-12) of the transition metal, and the remainder is the number of d-electrons. *Solve.*

(a) Ti^{3+}, d^1 (b) Co^{3+}, d^6 (c) Ru^{3+}, d^5

(d) Mo^{5+}, d^1 (e) Re^{3+}, d^4

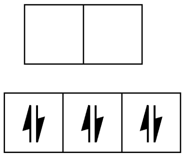
24.43 *Analyze/Plan.* Follow the logic in Sample Exercise 24.9. *Solve.*

(a) Mn: $[Ar]4s^2 3d^5$
Mn^{2+}: $[Ar]3d^5$



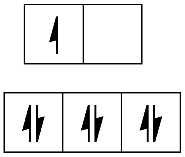
1 unpaired electron

(b) Ru: $[Kr]5s^1 4d^7$
Ru^{2+}: $[Kr]4d^6$



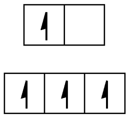
0 unpaired electrons

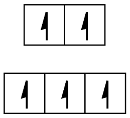
(c) Rh: $[Kr]5s^1 4d^8$
Rh^{2+}: $[Kr]4d^7$

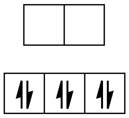


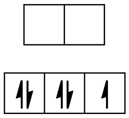
1 unpaired electron

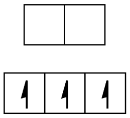
24.45 *Analyze/Plan*. All complexes in this exercise are six-coordinate octahedral. Use the definitions of high-spin and low-spin along with the orbital diagram from Sample Exercise 24.9 to place electrons for the various complexes. *Solve*.

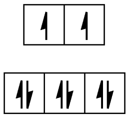
(a)

d^4, high spin

(b)

d^5, high spin

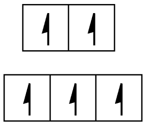
(c)

d^6, low spin

(d)

d^5, low spin

(e)

d^3

(f)

d^8

24.47 *Analyze/Plan*. Follow the ideas but reverse the logic in Sample Exercise 24.9. *Solve*.


high spin

Additional Exercises

24.49 $[Pt(NH_3)_6]Cl_4$; $[Pt(NH_3)_4Cl_2]Cl_2$; $[Pt(NH_3)_3Cl_3]Cl$; $[Pt(NH_3)_2Cl_4]$; $K[Pt(NH_3)Cl_5]$

24.52 (a) [24.51(a)] *cis*-tetraamminediaquacobalt(II) nitrate

[24.51(b)] sodium aquapentachlororuthenate(III)

[24.51(c)] ammonium *trans*-diaquabisoxalatocobaltate(III)

[24.51(d)] *cis*-dichlorobisethylenediammineruthenium(II)

(b) Only the complex in 24.51(d) is optically active. The mirror images of (a)-(c) can be superimposed on the original structure. The chelating ligands in (d) prevent its mirror images (enantiomers) from being superimposable.

24.54 (a) In a square planar complex such as $[Pt(en)Cl_2]$, if one pair of ligands is trans, the remaining two coordination sites are also trans to each other. Ethylenediamine is a relatively short bidentate ligand that cannot occupy trans coordination sites, so the trans isomer is unknown.

(b) A polydentate ligand such as EDTA necessarily occupies trans positions in an octahedral complex. The minimum steric requirement for a bidentate ligand is a medium-length chain between the two coordinating atoms that will occupy the trans positions. In terms of reaction rate theory, it is unlikely that a flexible bidentate ligand will be in exactly the right orientation to coordinate trans. The polydentate ligand has a much better chance of occupying trans positions, because it locks the metal ion in place with multiple coordination sites (and shields the metal ion from competing ligands present in the solution).

24.57 (a) $AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$

(b) $[Cr(en)_2Cl_2]Cl(aq) + 2H_2O(l) \rightarrow [Cr(en_2)(H_2O)_2]^{3+}(aq) + 3Cl^-(aq)$

green brown-orange

$3Ag^+(aq) + 3Cl^-(aq) \rightarrow 3AgCl(s)$

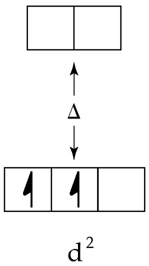
$[Cr(en)_2(H_2O)_2]^{3+}$ and $3NO_3^-$ are spectator ions in the second reaction.

(c) $Zn(NO_3)_2(aq) + 2NaOH(aq) \rightarrow Zn(OH)_2(s) + 2NaNO_3(aq)$

$Zn(OH)_2(s) + 2NaOH(aq) \rightarrow [Zn(OH)_4]^{2-}(aq) + 2Na^+(aq)$

(d) $Co^{2+}(aq) + 4Cl^-(aq) \rightarrow [CoCl_4]^{2-}(aq)$

24.60 (a)



(b) These complexes are colored because the crystal-field splitting energy, Δ, is in the visible portion of the electromagnetic spectrum. Visible light with $\lambda = hc/\Delta$ is absorbed, promoting one of the d-electrons into a higher energy d-orbital. The remaining wavelengths of visible light are reflected or transmitted; the combination of these wavelengths is the color we see.

(c) $[V(H_2O)_6]^{3+}$ will absorb light with higher energy. H_2O is in the middle of the spectrochemical series, and causes a larger Δ than F^-, a weak-field ligand. Since Δ and λ are inversely related, larger Δ corresponds to higher energy and shorter λ.

24.62 According to the spectrochemical series, the order of increasing Δ for the ligands is $Cl^- < H_2O < NH_3$. (The tetrahedral Cl^- complex will have an even smaller Δ than an octahedral one.) The smaller the value of Δ, the longer the wavelength of visible light absorbed. The color of light absorbed is the complement of the observed color. A blue complex absorbs orange light (580–650 nm), a pink complex absorbs green light (490-560 nm) and a yellow complex absorbs violet light (400–430 nm). Since $[CoCl_4]^{2-}$ absorbs the longest wavelength, it appears blue. $[Co(H_2O)_6]^{2+}$ absorbs green and appears pink, and $[Co(NH_3)_6]^{3+}$ absorbs violet and appears yellow.

24.64 (a) The term *isoelectronic* means that the three ions have the same number of valence electrons and the same electron configuration.

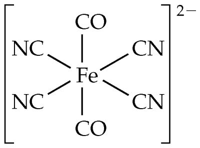
(b) In each ion, the metal is in its maximum oxidation state and has a d^0 electron configuration. That is, the metal ions have no *d*-electrons, so there should be no *d-d* transitions.

(c) A *ligand-metal charge transfer* transition occurs when an electron in a filled ligand orbital is excited to an empty d-orbital of the metal.

(d) Absorption of 565 nm yellow light by MnO_4^- causes the compound to appear violet, the complementary color. CrO_4^{2-} appears yellow, so it is absorbing violet light of approximately 420 nm. The wavelength of the LMCT transition for chromate, 420 nm, is shorter than the wavelength of LCMT transition in permanganate, 565 nm. This means that there is a larger energy difference between filled ligand and empty metal orbitals in chromate than in permanganate.

(e) Yes. A white compound indicates that no visible light is absorbed. Going left on the periodic chart from Mn to Cr, the absorbed wavelength got shorter and the energy difference between ligand and metal orbitals increased. The 420 nm absorption by CrO_4^- is at the short wavelength edge of the visible spectrum. It is not surprising that the ion containing V, further left on the chart, absorbs at a still shorter wavelength in the ultraviolet region and that VO_4^{3-} appears white.

24.66 (a)



(b) sodium dicarbonyltetracyanoferrate(II)

(c) +2, 6 d-electrons

(d) We expect the complex to be low spin. Cyanide (and carbonyl) are high on the spectrochemical series, which means the complex will have a large Δ splitting characteristic of low spin complexes.

Integrative Exercises

24.71 In a complex ion, the transition metal is an electron pair acceptor, a Lewis acid; the ligand is an electron pair donor, a Lewis base. In carbonic anhydrase, the Zn^{2+} ion withdraws electron density from the O atom of water. The electronegative oxygen atom compensates by withdrawing electron-density from the O—H bond. The O—H bond is polarized and H becomes more ionizable, more acidic than in the bulk solvent. This is similar to the effect of an electronegative central atom in an oxyacid such as H_2SO_4.

24.73 Determine the empirical formula of the complex, assuming the remaining mass is due to oxygen, and a 100 g sample.

$$10.0\text{ g Mn} \times \frac{1\text{ mol Mn}}{54.94\text{ g Mn}} = 0.1820\text{ mol Mn};\ 0.182/0.182 = 1$$

$$28.6\text{ g K} \times \frac{1\text{ mol K}}{39.10\text{ g K}} = 0.7315\text{ mol K};\ 0.732/0.182 = 4$$

$$8.8\text{ g C} \times \frac{1\text{ mol C}}{12.0\text{ g C}} = 0.7327\text{ mol C};\ 0.733/0.182 = 4$$

$$29.2\text{ g Br} \times \frac{1\text{ mol Br}}{79.904\text{ g Br}} = 0.3654\text{ mol Br};\ 0.365/0.182 = 2$$

$$23.4\text{ g O} \times \frac{1\text{ mol O}}{16.00\text{ g O}} = 1.463\text{ mol O};\ 1.46/0.182 = 8$$

There are 2 C and 4 O per oxalate ion, for a total of two oxalate ligands in the complex. To match the conductivity of $K_4[Fe(CN)_6]$, the oxalate and bromide ions must be in the coordination sphere of the complex anion. Thus, the compound is $K_4[Mn(ox)_2Br_2]$.

24.75 First determine the empirical formula, assuming that the remaining mass of complex is Pd.

$$37.6\text{ g Br} \times \frac{1\text{ mol Br}}{79.904\text{ g Br}} = 0.4706\text{ mol Br};\ 0.4706/0.2361 = 2$$

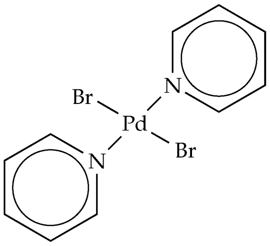
$$28.3\text{ g C} \times \frac{1\text{ mol C}}{12.01\text{ g C}} = 2.356\text{ mol C};\ 2.356/0.2361 = 10$$

$$6.60\text{ g N} \times \frac{1\text{ mol N}}{14.01\text{ g N}} = 0.4711\text{ mol N};\ 0.4711/0.2361 = 2$$

$$2.37\text{ g H} \times \frac{1\text{ mol H}}{1.008\text{ g H}} = 2.351\text{ mol H};\ 2.351/0.2361 = 10$$

$$25.13\text{ g Pd} \times \frac{1\text{ mol Pd}}{106.42\text{ g Pd}} = 0.2361\text{ mol Pd};\ 0.2361/0.2361 = 1$$

The chemical formula is $[Pd(NC_5H_5)_2Br_2]$. This should be a neutral square-planar complex of Pd(II), a nonelectrolyte. Because the dipole moment is zero, we can infer that it must be the trans isomer.



24.77 Calculate the concentration of Mg^{2+} alone, and then the concentration of Ca^{2+} by difference. $M \times L = mol$

$$\frac{0.0104\text{ mol EDTA}}{1\text{ L}} \times 0.0187\text{ L} \times \frac{1\text{ mol Mg}^{2+}}{1\text{ mol EDTA}} \times \frac{24.31\text{ g Mg}^{2+}}{1\text{ mol Mg}^{2+}} \times \frac{1000\text{ mg}}{\text{g}} \times \frac{1}{0.100\text{ L H}_2\text{O}} = 47.28 = 47.3\text{ mg Mg}^{2+}/\text{L}$$

$$0.0104\ M\text{ EDTA} \times 0.0315\text{ L} = \text{mol }(Ca^{2+} + Mg^{2+})$$

$$\underline{0.0104\ M\text{ EDTA} \times 0.0187\text{ L} = \text{mol Mg}^{2+}}$$

$$0.0104\ M\text{ EDTA} \times 0.0128\text{ L} = \text{mol Ca}^{2+}$$

$$0.0104\ M\ \text{EDTA} \times 0.0128\ L \times \frac{1\ \text{mol Ca}^{2+}}{1\ \text{mol EDTA}} \times \frac{40.08\ \text{g Ca}^{2+}}{1\ \text{mol Ca}^{2+}} \times \frac{1000\ \text{mg}}{\text{g}} \times \frac{1}{0.100\ \text{L H}_2\text{O}}$$

$$= 53.35 = 53.4\ \text{mg Ca}^{2+}/\text{L}$$

24.80 $$\frac{182 \times 10^3\ \text{J}}{1\ \text{mol}} \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{molecules}} = 3.022 \times 10^{-19} = 3.02 \times 10^{-19}\ \text{J/photo}$$

$\Delta E = h\nu = 3.02 \times 10^{-19}$ J; $\nu = \Delta E/h$

$\nu = 3.022 \times 10^{-19}\ \text{J}/6.626 \times 10^{-34}\ \text{J - s} = 4.561 \times 10^{14} = 4.56 \times 10^{14}\ \text{s}^{-1}$

$$\lambda = \frac{2.998 \times 10^8\ \text{m/s}}{4.561 \times 10^{14}\ \text{s}^{-1}} = 6.57 \times 10^{-7}\ \text{m} = 657\ \text{nm}$$

We expect that this complex will absorb in the visible, at around 660 nm. It will thus exhibit a blue-green color (Figure 24.24).