

CHAPTER 22

TRANSITION METAL CHEMISTRY AND COORDINATION COMPOUNDS

- 22.11** (a) En is the abbreviation for **ethylenediamine** ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$).
(b) The oxidation number of Co is **+3**. (Why?)
(c) The coordination number of Co is **six**. (Why isn't this the same as the number of ligands?)
(d) **Ethylenediamine (en)** is a bidentate ligand. Could cyanide ion be a bidentate ligand? Ask your instructor.
- 22.12** (a) The oxidation number of Cr is **+3**.
(b) The coordination number of Cr is **6**.
(c) **Oxalate ion** ($\text{C}_2\text{O}_4^{2-}$) is a bidentate ligand.
- 22.13** (a) The net charge of the complex ion is the sum of the charges of the ligands and the central metal ion. In this case the complex ion has a -3 charge. (Potassium is always **+1**. Why?) Since the six cyanides are -1 each, the Fe must be **+3**.
(b) The complex ion has a -3 charge. Each oxalate ion has a -2 charge (Table 22.3 of the text). Therefore, the Cr must be **+3**.
(c) Since cyanide ion has a -1 charge, Ni must have a **+2** charge to make the complex ion carry a -2 net charge.
- 22.14** **Strategy:** The oxidation number of the metal atom is equal to its charge. First we look for known charges in the species. Recall that alkali metals are $+1$ and alkaline earth metals are $+2$. Also determine if the ligand is a charged or neutral species. From the known charges, we can deduce the net charge of the metal and hence its oxidation number.

Solution:

- (a) Since **sodium** is always **+1** and the oxygens are -2 , **Mo** must have an oxidation number of **+6**.
(b) **Magnesium** is **+2** and oxygen -2 ; therefore **W** is **+6**.
(c) CO ligands are neutral species, so the iron atom bears no net charge. The oxidation number of **Fe** is **0**.

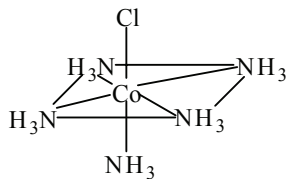
- 22.15** (a) tetraamminedichlorocobalt(III) (c) dibromobis(ethylenediamine)cobalt(III)
(b) triamminetrichlorochromium(III) (d) hexaamminecobalt(III) chloride

- 22.16** **Strategy:** We follow the procedure for naming coordination compounds outlined in Section 22.3 of the text and refer to Tables 22.4 and 22.5 of the text for names of ligands and anions containing metal atoms.

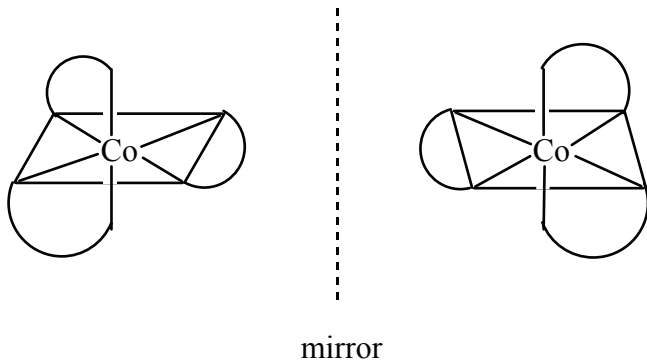
Solution:

- (a) Ethylenediamine is a neutral ligand, and each chloride has a -1 charge. Therefore, cobalt has a oxidation number of $+3$. The correct name for the ion is ***cis*-dichlorobis(ethylenediamine)cobalt(III)**. The prefix *bis* means two; we use this instead of *di* because *di* already appears in the name ethylenediamine.

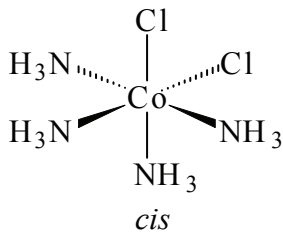
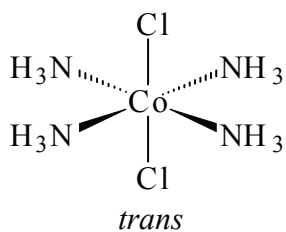
- (b) Again there are no geometric or optical isomers. To have *cis* and *trans* isomers there would have to be two chlorine ligands.



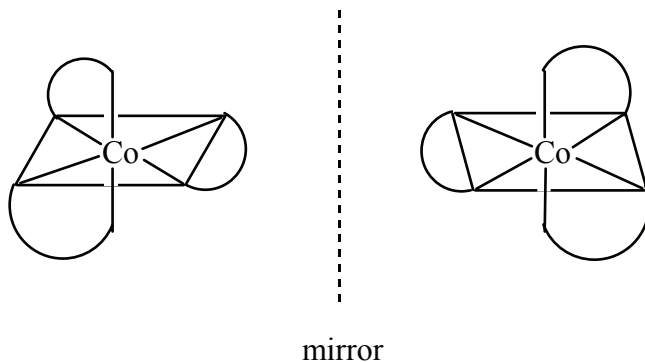
- (c) There are two optical isomers. They are like Figure 22.13 of the text with the two chlorine atoms replaced by one more bidentate ligand. The three bidentate oxalate ligands are represented by the curved lines.

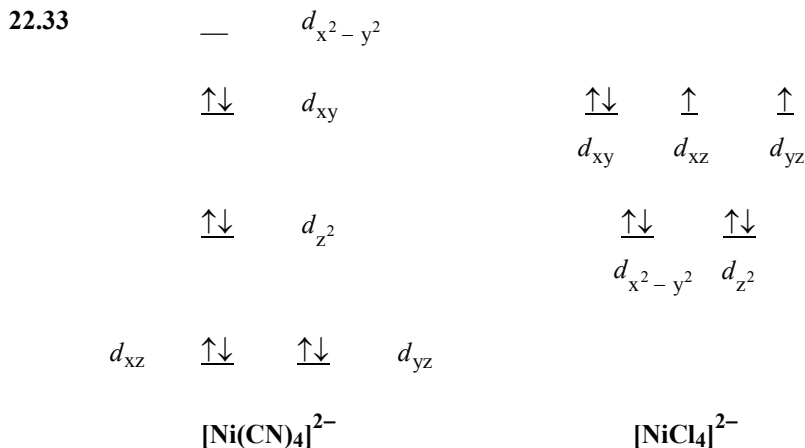


- 22.26 (a) There are *cis* and *trans* geometric isomers (See Problem 22.24). No optical isomers.



- (b) There are two optical isomers. See Figure 22.7 of the text. The three bidentate en ligands are represented by the curved lines.

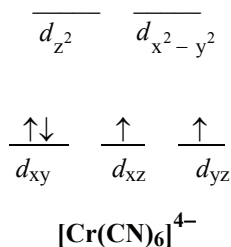




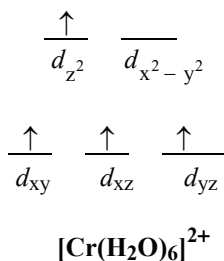
- 22.34 When a substance appears to be yellow, it is absorbing light from the blue-violet, high energy end of the visible spectrum. Often this absorption is just the tail of a strong absorption in the ultraviolet. Substances that appear green or blue to the eye are absorbing light from the lower energy red or orange part of the spectrum.

Cyanide ion is a very strong field ligand. It causes a larger crystal field splitting than water, resulting in the absorption of higher energy (shorter wavelength) radiation when a d electron is excited to a higher energy d orbital.

- 22.35 (a) Each cyanide ligand has a -1 charge, so the oxidation state of Cr is $+2$. The electron configuration of Cr^{2+} is $[\text{Ar}]3d^4$. Cyanide is a strong field ligand (see Problem 22.34). The four $3d$ electrons should occupy the three lower orbitals as shown; there should be two unpaired electrons.



- (b) Water is a weak field ligand. The four $3d$ electrons should occupy the five orbitals as shown. There should be four unpaired electrons.



- 22.36 (a) Wavelengths of 470 nm fall between blue and blue-green, corresponding to an observed color in the orange part of the spectrum.

(b) We convert wavelength to photon energy using the Planck relationship.

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{470 \times 10^{-9} \text{ m}} = 4.23 \times 10^{-19} \text{ J}$$

$$\frac{4.23 \times 10^{-19} \text{ J}}{1 \text{ photon}} \times \frac{6.022 \times 10^{23} \text{ photons}}{1 \text{ mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = \mathbf{255 \text{ kJ/mol}}$$

22.37 Recall the wavelength and energy are inversely proportional. Thus, absorption of longer wavelength radiation corresponds to a lower energy transition. Lower energy corresponds to a smaller crystal field splitting.

- (a) H₂O is a weaker field ligand than NH₃. Therefore, the crystal field splitting will be smaller for the aquo complex, and it will absorb at longer wavelengths.
- (b) Fluoride is a weaker field ligand than cyanide. The fluoro complex will absorb at longer wavelengths.
- (c) Chloride is a weaker field ligand than NH₃. The chloro complex will absorb at longer wavelengths.

22.38 *Step 1:* The equation for freezing-point depression is

$$\Delta T_f = K_f m$$

Solve this equation algebraically for molality (m), then substitute ΔT_f and K_f into the equation to calculate the molality.

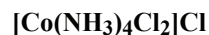
$$m = \frac{\Delta T_f}{K_f} = \frac{0.56^\circ\text{C}}{1.86^\circ\text{C}/m} = 0.30 \text{ } m$$

Step 2: Multiplying the molality by the mass of solvent (in kg) gives moles of unknown solute. Then, dividing the mass of solute (in g) by the moles of solute, gives the molar mass of the unknown solute.

$$? \text{ mol of unknown solute} = \frac{0.30 \text{ mol solute}}{1 \text{ kg water}} \times 0.0250 \text{ kg water} = 0.0075 \text{ mol solute}$$

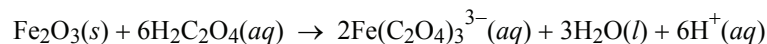
$$\text{molar mass of unknown} = \frac{0.875 \text{ g}}{0.0075 \text{ mol}} = 117 \text{ g/mol}$$

The molar mass of Co(NH₃)₄Cl₃ is 233.4 g/mol, which is twice the computed molar mass. This implies dissociation into two ions in solution; hence, there are **two moles** of ions produced per one mole of Co(NH₃)₄Cl₃. The formula must be:



which contains the complex ion [Co(NH₃)₄Cl₂]⁺ and a chloride ion, Cl⁻. Refer to Problem 22.26 (a) for a diagram of the structure of the complex ion.

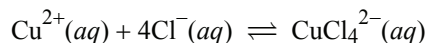
22.41 Rust stain removal involves forming a water soluble oxalate ion complex of iron like [Fe(C₂O₄)₃]³⁻. The overall reaction is:



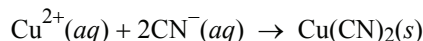
Does this reaction depend on pH?

22.42 Use a radioactive label such as $^{14}\text{CN}^-$ (in NaCN). Add NaCN to a solution of $\text{K}_3\text{Fe}(\text{CN})_6$. Isolate some of the $\text{K}_3\text{Fe}(\text{CN})_6$ and check its radioactivity. If the complex shows radioactivity, then it must mean that the CN^- ion has participated in the exchange reaction.

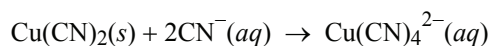
22.43 The green precipitate in CuF_2 . When KCl is added, the bright green solution is due to the formation of CuCl_4^{2-} :



22.44 The white precipitate is copper(II) cyanide.

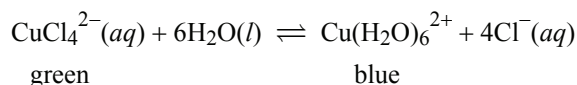


This forms a soluble complex with excess cyanide.



Copper(II) sulfide is normally a very insoluble substance. In the presence of excess cyanide ion, the concentration of the copper(II) ion is so low that CuS precipitation cannot occur. In other words, the cyanide complex of copper has a very large formation constant.

22.45 The overall reaction is:



Addition of excess water (dilution) shifts the equilibrium to the right (Le Châtelier's principle).

22.46 The formation constant expression is:

$$K_f = \frac{[\text{Fe}(\text{H}_2\text{O})_5\text{NCS}^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}][\text{SCN}^-]}$$

Notice that the original volumes of the $\text{Fe}(\text{III})$ and SCN^- solutions were both 1.0 mL and that the final volume is 10.0 mL. This represents a tenfold dilution, and the concentrations of $\text{Fe}(\text{III})$ and SCN^- become 0.020 M and 1.0×10^{-4} M, respectively. We make a table.

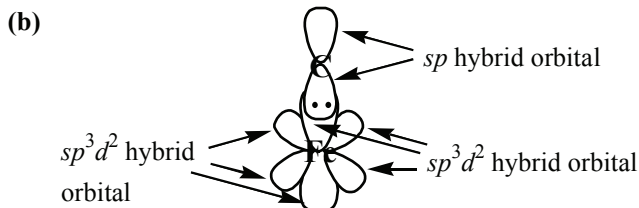
	$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	+	SCN^-	\rightleftharpoons	$\text{Fe}(\text{H}_2\text{O})_5\text{NCS}^{2+}$	+	H_2O
Initial (M):	0.020		1.0×10^{-4}		0		
Change (M):	-7.3×10^{-5}		-7.3×10^{-5}		$+7.3 \times 10^{-5}$		
Equilibrium (M):	0.020		2.7×10^{-5}		7.3×10^{-5}		

$$K_f = \frac{7.3 \times 10^{-5}}{(0.020)(2.7 \times 10^{-5})} = 1.4 \times 10^2$$

22.47 The third ionization energy increases rapidly from left to right. Thus metals tend to form M^{2+} ions rather than M^{3+} ions.

22.48 Mn^{3+} is $3d^4$ and Cr^{3+} is $3d^5$. Therefore, Mn^{3+} has a greater tendency to accept an electron and is a stronger oxidizing agent. The $3d^5$ electron configuration of Cr^{3+} is a stable configuration.

22.49 (a) Since carbon is less electronegative than oxygen, it is more likely that carbon will share electrons with Fe forming a metal-to-ligand sigma bond. The sp orbital on carbon containing the lone pair overlaps with the empty sp^3d^2 orbital on Fe.



22.50 Ti is +3 and Fe is +3.

22.51 The three cobalt compounds would dissociate as follow:



In other words, the concentration of free ions in the three 1.00 M solutions would be 4.00 M , 3.00 M , and 2.00 M , respectively. If you made up 1.00 M solutions of FeCl_3 , MgCl_2 , and NaCl , these would serve as reference solutions in which the ion concentrations were 4.00 M , 3.00 M , and 2.00 M , respectively. A 1.00 M solution of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ would have an electrolytic conductivity close to that of the MgCl_2 solution, etc.

22.52 A 100.00 g sample of hemoglobin contains 0.34 g of iron. In moles this is:

$$0.34 \text{ g Fe} \times \frac{1 \text{ mol}}{55.85 \text{ g}} = 6.1 \times 10^{-3} \text{ mol Fe}$$

The amount of hemoglobin that contains one mole of iron must be:

$$\frac{100.00 \text{ g hemoglobin}}{6.1 \times 10^{-3} \text{ mol Fe}} = 1.6 \times 10^4 \text{ g hemoglobin/mol Fe}$$

We compare this to the actual molar mass of hemoglobin:

$$\frac{6.5 \times 10^4 \text{ g hemoglobin}}{1 \text{ mol hemoglobin}} \times \frac{1 \text{ mol Fe}}{1.6 \times 10^4 \text{ g hemoglobin}} = 4 \text{ mol Fe/1 mol hemoglobin}$$

The discrepancy between our minimum value and the actual value can be explained by realizing that one hemoglobin molecule contains **four** iron atoms.

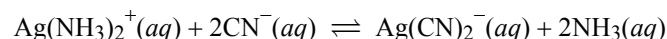
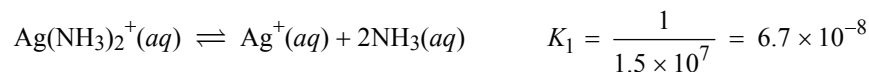
22.53 (a) Zinc(II) has a completely filled $3d$ subshell giving the ion greater stability.

(b) Normally the colors of transition metal ions result from transitions within incompletely filled d subshells. The $3d$ subshell of zinc(II) ion is filled.

22.54 (a) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$, (b) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$, (c) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

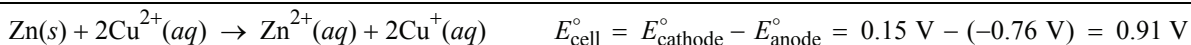
The compounds can be identified by a conductance experiment. Compare the conductances of equal molar solutions of the three compounds with equal molar solutions of NaCl, MgCl_2 , and FeCl_3 . The solution that has similar conductance to the NaCl solution contains (c); the solution with the conductance similar to MgCl_2 contains (b); and the solution with conductance similar to FeCl_3 contains (a).

22.55 Reversing the first equation:



$$K = K_1 K_2 = (6.7 \times 10^{-8})(1.0 \times 10^{21}) = 6.7 \times 10^{13}$$

$$\Delta G^\circ = -RT \ln K = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln(6.7 \times 10^{13}) = -7.89 \times 10^4 \text{ J/mol}$$



We carry additional significant figures throughout the remainder of this calculation to minimize rounding errors.

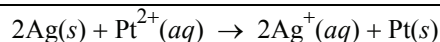
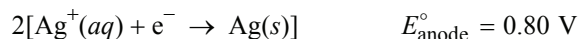
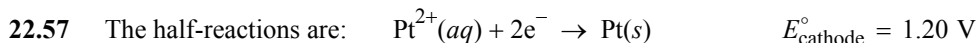
$$\Delta G^\circ = -nFE^\circ = -(2)(96500 \text{ J/V}\cdot\text{mol})(0.91 \text{ V}) = -1.756 \times 10^5 \text{ J/mol} = -1.8 \times 10^2 \text{ kJ/mol}$$

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

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-1.756 \times 10^5 \text{ J/mol})}{(8.314 \text{ J/K}\cdot\text{mol})(298 \text{ K})}$$

$$\ln K = 70.88$$

$$K = e^{70.88} = 6 \times 10^{30}$$



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 1.20 \text{ V} - 0.80 \text{ V} = 0.40 \text{ V}$$

Since the cell voltage is positive, products are favored at equilibrium.

At 25°C,

$$E^\circ_{\text{cell}} = \frac{0.0257 \text{ V}}{n} \ln K$$

$$0.40 \text{ V} = \frac{0.0257 \text{ V}}{2} \ln K$$

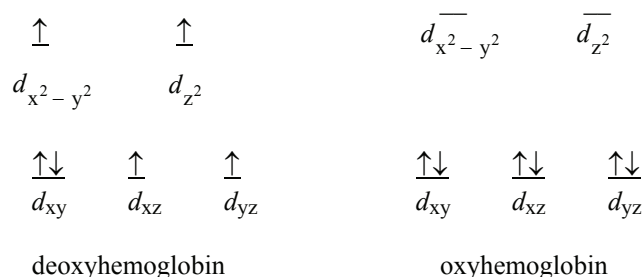
$$\ln K = 31.1$$

$$K = e^{31.1} = 3 \times 10^{13}$$

22.58 Iron is much more abundant than cobalt.

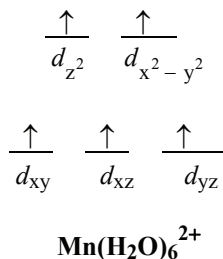
22.59 *Geometric isomers* are compounds with the same type and number of atoms and the same chemical bonds but different spatial arrangements; such isomers cannot be interconverted without breaking a chemical bond. *Optical isomers* are compounds that are nonsuperimposable mirror images.

22.60 Oxyhemoglobin absorbs higher energy light than deoxyhemoglobin. Oxyhemoglobin is diamagnetic (low spin), while deoxyhemoglobin is paramagnetic (high spin). These differences occur because oxygen (O_2) is a strong-field ligand. The crystal field splitting diagrams are:



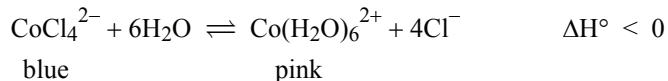
22.61 The orbital splitting diagram below shows five unpaired electrons. The Pauli exclusion principle requires that an electron jumping to a higher energy $3d$ orbital would have to change its spin. A transition that involves a change in spin state is forbidden, and thus does not occur to any appreciable extent.

The colors of transition metal complexes are due to the emission of energy in the form of visible light when an excited d electron relaxes to the ground state. In Mn^{2+} complexes, the promotion of a d electron to an excited state is spin forbidden; therefore, there is little in the way of an emission spectrum and the complexes are practically colorless.

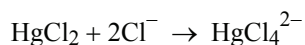


22.62 Complexes are expected to be colored when the highest occupied orbitals have between one and nine d electrons. Such complexes can therefore have $d \rightarrow d$ transitions (that are usually in the visible part of the electromagnetic radiation spectrum). The ions V^{5+} , Ca^{2+} , and Sc^{3+} have d^0 electron configurations and Cu^+ , Zn^{2+} , and Pb^{2+} have d^{10} electron configurations: these complexes are colorless. The other complexes have outer electron configurations of d^1 to d^9 and are therefore colored.

22.63 Co^{2+} exists in solution as CoCl_4^{2-} (blue) or $\text{Co}(\text{H}_2\text{O})_6^{2+}$ (pink). The equilibrium is:



Low temperature and low concentration of Cl^- ions favor the formation of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ions. Adding HCl (more Cl^- ions) favors the formation of CoCl_4^{2-} . Adding HgCl_2 leads to:



This reaction decreases $[\text{Cl}^-]$, so the pink color is restored.

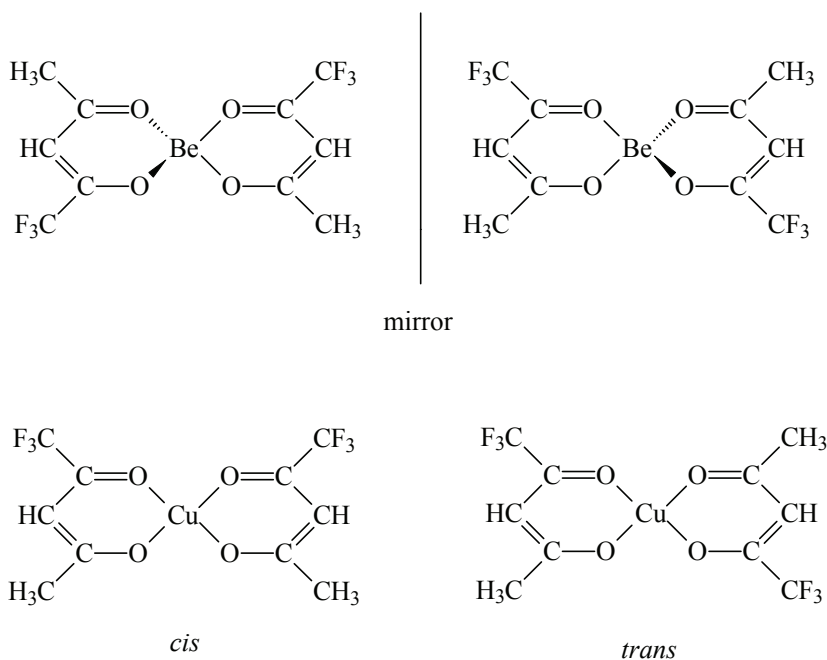
22.64 Dipole moment measurement. Only the *cis* isomer has a dipole moment.

22.65 Fe^{2+} is $3d^6$; Fe^{3+} is $3d^5$.

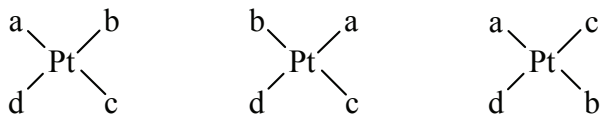
Therefore, Fe^{3+} (like Mn^{2+} , see Problem 22.61) is nearly colorless, so it must be light yellow in color.

22.66 EDTA sequesters metal ions (like Ca^{2+} and Mg^{2+}) which are essential for growth and function, thereby depriving the bacteria to grow and multiply.

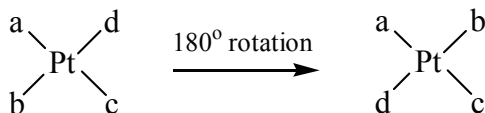
22.67 The Be complex exhibits optical isomerism. The Cu complex exhibits geometric isomerism.



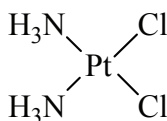
22.68 The square planar complex shown in the problem has 3 geometric isomers. They are:



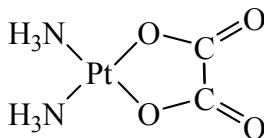
Note that in the first structure a is *trans* to c, in the second a is *trans* to d, and in the third a is *trans* to b. Make sure you realize that if we switch the positions of b and d in structure 1, we do not obtain another geometric isomer. A 180° rotation about the a–Pt–c axis gives structure 1.



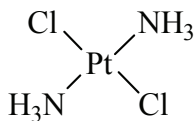
22.69 Isomer I must be the *cis* isomer.



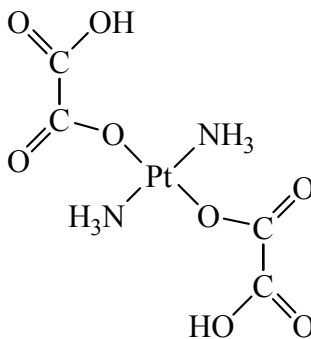
The chlorines must be *cis* to each other for one oxalate ion to complex with Pt.



Isomer II must be the *trans* isomer.



With the chlorines on opposite sides of the molecule, each Cl is replaced with a hydrogen oxalate ion.



22.70 The reaction is: $\text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$

$$K_f = 1.0 \times 10^{21} = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2}$$

First, we calculate the initial concentrations of Ag^+ and CN^- . Then, because K_f is so large, we assume that the reaction goes to completion. This assumption will allow us to solve for the concentration of Ag^+ at equilibrium. The initial concentrations of Ag^+ and CN^- are:

$$[\text{CN}^-] = \frac{\frac{5.0 \text{ mol}}{1 \text{ L}} \times 9.0 \text{ L}}{99.0 \text{ L}} = 0.455 \text{ M}$$

$$[\text{Ag}^+] = \frac{\frac{0.20 \text{ mol}}{1 \text{ L}} \times 90.0 \text{ L}}{99.0 \text{ L}} = 0.182 \text{ M}$$

We set up a table to determine the concentrations after complete reaction.

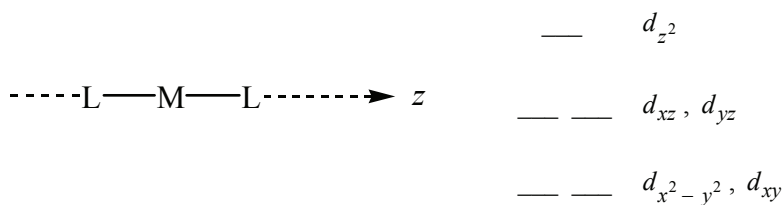
	$\text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$		
Initial (M):	0.182	0.455	0
Change (M):	-0.182	-(2)(0.182)	+0.182
Final (M):	0	0.0910	0.182

$$K_f = \frac{[\text{Ag}(\text{CN})_2^-]}{[\text{Ag}^+][\text{CN}^-]^2}$$

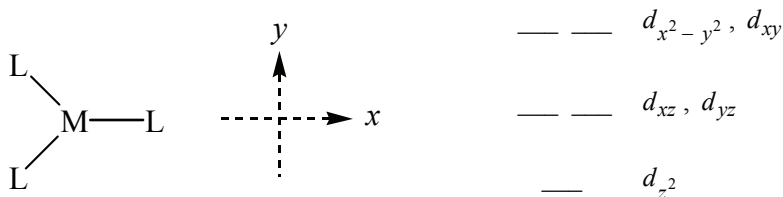
$$1.0 \times 10^{21} = \frac{0.182 \text{ M}}{[\text{Ag}^+](0.0910 \text{ M})^2}$$

$$[\text{Ag}^+] = 2.2 \times 10^{-20} \text{ M}$$

- 22.71 (a)** If the bonds are along the z -axis, the d_{z^2} orbital will have the highest energy. The $d_{x^2-y^2}$ and d_{xy} orbitals will have the lowest energy.



- (b)** If the trigonal plane is in the xy -plane, then the $d_{x^2-y^2}$ and d_{xy} orbitals will have the highest energy, and d_{z^2} will have the lowest energy.

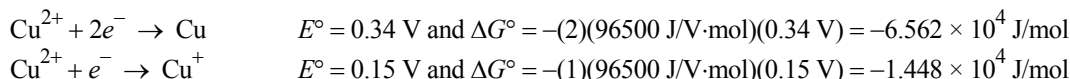


- (c) If the axial positions are along the z -axis, the d_{z^2} orbital will have the highest energy. The trigonal plane will be in the xy -plane, and thus the $d_{x^2-y^2}$ and d_{xy} orbitals will be next highest in energy.

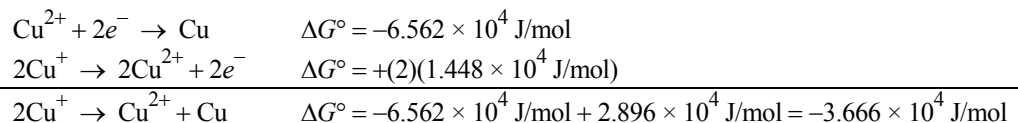


- 22.72 (a) The equilibrium constant can be calculated from ΔG° . We can calculate ΔG° from the cell potential.

From Table 19.1 of the text,



These two equations need to be arranged to give the disproportionation reaction in the problem. We keep the first equation as written and reverse the second equation and multiply by two.



We use Equation (18.14) of the text to calculate the equilibrium constant.

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

$$K = e^{-\Delta G^\circ/RT}$$

$$K = e^{-(-3.666 \times 10^4 \text{ J/mol}) / (8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}$$

$$K = 2.7 \times 10^6$$

- (b) Free Cu^+ ions are unstable in solution [as shown in part (a)]. Therefore, the only stable compounds containing Cu^+ ions are insoluble.

- 22.73 (a) The second equation should have a larger ΔS° because more molecules appear on the products side compared to the reactants side.
- (b) Consider the equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The ΔH° term for both reactions should be approximately the same because the C–N bond strength is approximately the same in both complexes. Therefore, ΔG° will be predominantly dependent on the $-T\Delta S^\circ$ term.

Next, consider Equation (18.14) of the text.

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

A more negative ΔG° will result in a larger value of K . Therefore, the second equation will have a larger K because it has a larger ΔS° , and hence a more negative ΔG° . This exercise shows the effect of bi- and polydentate ligands on the position of equilibrium.

- 22.74 (a) Cu^{3+} would not be stable in solution because it can be easily reduced to the more stable Cu^{2+} . From Figure 22.3 of the text, we see that the 3rd ionization energy is quite high, about 3500 kJ/mol. Therefore, Cu^{3+} has a great tendency to accept an electron.
- (b) **Potassium hexafluorocuprate(III)**. Cu^{3+} is $3d^8$. CuF_6^{3-} has an octahedral geometry. According to Figure 22.17 of the text, CuF_6^{3-} should be paramagnetic, containing two unpaired electrons. (Because it is $3d^8$, it does not matter whether the ligand is a strong or weak-field ligand. See Figure 22.22 of the text.)
- (c) We refer to Figure 22.24 of the text. The splitting pattern is such that all the square-planar complexes of Cu^{3+} should be diamagnetic.