### Chapter 6 Applications of Coordination Compounds

The sections and subsections in this chapter are listed below.

6.1 Applications of Monodentate Complexes
6.2 Two Keys to the Stability of Transition Metal Complexes Hard and Soft Acids and Bases The Chelate Effect
6.3 Applications of Multidentate Complexes
6.4 Chelating Agents as Detergent Builders
6.5 Bioinorganic Applications of Coordination Chemistry Oxygen Transport Therapeutic Chelating Agents for Heavy Metals Platinum Antitumor Agents

Students love to know how the material they are studying can be applied to everyday life. So do I. So far in this section on coordination chemistry, the material (at least by the standards of many students) has been quite "dry." In the descriptive chemistry section (Chapters 9 through 19), as some students will know because they have already read that section first before this one, there is a great stress put on the applications of inorganic chemistry to everyday events and problems. In this section, however, this chapter is the first coverage of applied chemistry.

There are so many applications of coordination chemistry that it is difficult to decide what to include and where to begin. I have chosen to divide the topic by first discussing some of the applications of monodentate complexes and then moving on to multidentates. Starting first with some reaction chemistry that students may have encountered in earlier courses, I most always demonstrate the reactions of silver chloride and aqueous copper(II) ions with aqueous ammonia, aqueous iron(III) ions with thiocyanate, and the production of Prussian and Turnbull's blue. It's important for students to see (and, from my experience, they genuinely seem to enjoy seeing) this reaction chemistry in action. When the reaction is one they have seen before, it does not seem to detract from their enjoyment perhaps because they realize that they now have a much greater appreciation for the chemistry behind these reactions than they had when they first encountered them. Other reactions mentioned in this section include those encountered in extracting gold and silver from their ores (a process that has caused some devastating cyanide spills in eastern Europe lately), the purification of nickel, and in photographic fixers. There are, of course, many others. Do you have some favorites that you think ought to be included here? I would very much like to know about them.

As one gets deeper into these applied topics, it is apparent that there are two keys to better understanding them. One is certainly the whole idea of hard and soft acids and bases. (As mentioned earlier in the discussion of Chapter 3, I have, on occasion, covered this topic in conjunction with the synthesis of linkage isomers.) While certainly not a sophisticated, well-rationalized theory, the HSAB idea does give the student another way to judge the relative stabilities of various coordination compounds and will provide further rationalization for other applications yet to come. The chelate effect is also a central idea to understanding the relative stabilities of coordination compounds, particularly in the next section on applications of compounds involving multidentate ligands. Another rationale for covering both HSAB and the chelate effect here instead of elsewhere is to take advantage of natural student curiosity to get across a couple more important topics in coordination chemistry. Covered in the abstract, HSAB and particularly the thermodynamically-based chelate effect, are just two more theoretical ideas to learn and master. In this section, because many students are inherently interested in applications, there is an added incentive to master these two topics.

The applications of coordination compounds involving multidentate ligands are again so myriad that I have had to choose among them. I have started with the "drier" complexometric quantitative analytical applications and then moved on to topics that students say are among their favorites in the whole book. EDTA as a consumer product and food additive; phosphates, nitrilotriacetic acid (and the noncomplexing carbonate and aluminosilicates) as detergent builders; hemoglobin as the agent of oxygen transport; some of the details of carbon monoxide and cyanide poisoning; EDTA, penicillamine, and British anti-lewisite as therapeutic chelating agents; and cisplatin and its derivatives as antitumor agents are topics that, in my experience, most always thoroughly intrigue my students. As the occasion and time requirements vary each time I present these topics, I sometimes find myself talking about water hardness and softeners, the action of soaps and detergents, and the history of lead and mercury poisoning here rather than as planned elsewhere in the course syllabus and as presented in later chapters of this book. Often the amount of coverage of these topics is strongly related to the number of student questions and comments.

Throughout the discussions of the above topics, I have a variety of models available. Sometimes I build EDTA or NTA with huge framework models that seem to take over the room or at least dwarf me with their size. Other times I have a quite accurate representation of the heme section of hemoglobin to hold up and then pass around to the class. Occasionally, I will have detergent boxes, soap and other product labels to show. The more visual the presentation, I find the more the interest in these topics is enhanced.

Finally, I might mention here that I usually require students in my sophomore-level inorganic class to write a seven to ten page research paper on a topic of their choice. Some of the topics that I mention to them as possibilities are given below. I find that topics related to the applications of coordination compounds are always among the more popular.

Suggested Applications Paper Topics:

lead pollution and poisoning mercury pollution and poisoning cadmium pollution and poisoning transition metal poisoning - too much of a good thing arsenicals as intentional and accidental poisons Wilson's disease and other metal build-up disorders British anti-lewisite, chemical warfare and heavy metal poisoning antidote penicillamine, a gentler and kinder heavy metal poisoning antidote cisplatin and its derivatives as antitumor agents ethylenediaminetetraacetic acid - the sexidentate of many uses chelating agents in analytical chemistry transition metals in the body fusion - blowing hot and cold isotopes in medicine

threats to the ozone layer photochemical smog greenhouse effect - has it started yet? peroxides and superoxides lithium for treatment of manic depression lithium in batteries and photoelectric cells inorganic anti-knock gasoline additives, past and present potassium-argon radiochemical dating beryllium disease uses of radium, past and present fireworks, the latest generation hard water and its treatment detergent builders - past and present smokestack scrubbing systems acid rain - causes and effects glasses: ingredients, properties, and applications bleaches and their action borides, varieties and uses alums, varieties and uses alumina, varieties and uses the search for boranes as rocket fuels semiconductors  $C_{60}$ , the new truncated icosahedral buckytubes tin disease carbon 14 radiochemical dating the lead-isochron method of radiochemical dating the lead storage battery piezoelectricity - quartz and other crystals aluminosilicates - practical applications phosphate fertilizers phosphate in baking powders nitrogen fixation - natural and artificial phosphates - the detergent builders, 1945-1980 nitrites - pros and cons in balance explosives - gunpowders to plastiques matches - low tech to high tech sodium thiosulfate as photography hypo sodium-sulfide batteries photoelectric uses of selenium and tellurium sulfuric acid - the most useful chemical in the world the Xerox process acid rain - roots and remedies chlorine and other bleaches chlorination - pros, cons, and alternatives iodine and the thyroid fluoridation, past and present

the chlor-alkali process, past, present, and prognosis hypochlorites and other bleaches bromides, bromoseltzer to fire extinguishers chlorofluorocarbons (CFC's) neon lights - your name up in lights the limelight, origins and production radon as a carcinogen

# Chapter 6 Objectives

The student should be able to

- cite examples of transition metal complexes involving monodentate ligands in qualitative analysis, dyes, silver and gold ore processing, nickel purification, and black/white photography
- define, characterize, rationalize, and use the concept of hard and soft acids and bases as applied to the stability of metal-ligand interactions
- define, explain, and give examples of the chelate effect
- cite and explain applications of multidentate complexes drawn from complexometric quantitative analytical methods
- explain why EDTA is used to remove hard water deposits from hot water boilers and heaters and often added to foods and other consumer products
- explain the function of detergent builders and the advantages and disadvantages of using phosphates, nitrilotriacetic acid, and carbonates to carry out that function over the years
- explain the role of hemoglobin and its oxygen complexes in the process of respiration
- explain how carbon monoxide and cyanide poisoning work
- explain how and why EDTA, pencillamine, and British anti-lewisite function as therapeutic chelating agents for heavy metals
- briefly cite some of the history and symptoms of lead and mercury poisoning
- explain how cisplatin and its derivatives serve as antitumor agents

**Problem Solutions** 

6.1. Diamminesilver(I),  $[Ag(NH_3)_2]^+$ , contains Ag(I), a d<sup>10</sup> metal. With no vacancies in d orbitals, coordination compounds containing this cation cannot readily absorb visible light and so remain colorless. On the other hand, tetraamminecopper(II),  $[Cu(NH_3)_4]^{2+}$ , contains Cu(II), a d<sup>9</sup> metal that does have vacancies in its d orbitals and therefore readily absorbs visible light.

6.2. Both  $[Au(CN)_2]^-$  and  $[Ag(CN)_2]^-$  contain  $d^{10}$  metals and, because there are no vacancies in their d orbitals, cannot readily absorb visible light. Their compounds are most likely colorless.

\*6.3. Cyanide acts as a halide. In fact, ions such as cyanide (CN), thiocyanate (SCN), and others (see Chapter 18 for more details) are often referred to as pseudohalides because of their similarities to these ions. Accordingly, cyanide can often be quantitatively analyzed in the same way as the halide ions. One method of doing this is to add a slight excess of a solution of silver nitrate, AgNO<sub>3</sub>, to the cyanide until silver cyanide, AgCN(s), is precipitated, isolated, and then weighed quantitatively. The Liebig method actually refers to the method in which a standardized solution of silver nitrate is used to titrate a solution of cyanide until the first appearance of a precipitate of silver dicyanoargentate(I), Ag[Ag(CN)<sub>2</sub>]. This reaction becomes the basis of a titrimetric determination of cyanide.

$$2CN^{-}(aq) + 2Ag^{+} \longrightarrow Ag[Ag(CN)_{2}](s)$$

6.4. According to Equation (6.7), the reaction (reproduced below) shifts back to the left when the temperature is raised.

$$Ni(s) + 4CO(g)$$
  $\checkmark$   $Ni(CO)_4(g)$ 

In order to force the equilibrium back to the left, heat must be present as a product. That is, the reaction must be exothermic.

6.5. Since hard acids are small, often highly-charged metal ions (Lewis acids) with high charge densities and low polarizabilities whereas hard bases are small, highly electronegative ligands (Lewis bases), the hard-hard M-L interaction is one between fairly highly charged species. It follows that the bonding between such species would tend to be predominantly ionic. On the other hand, soft acids are large, highly polarizable metals of low (even zero) oxidation states and soft bases are large, polarizable ligands of low charge, it follows that the soft-soft M-L bond between such species would not be highly ionic.

6.6. Since soft acids are large, highly polarizable metals of low (even zero) oxidation states and soft bases are large, polarizable ligands of low charge, it follows that the soft-soft M-L bond between such species would be characterized by high London dispersion forces. That is, both the ligand and metal have electron clouds in which instantaneous dipoles could readily and often occur. Such dipoles could then induce dipoles in the other electron clouds. Such a situation is characteristic of interactions with substantial London forces. On the other hand, since hard acids are small, often highly charged metal ions (Lewis acids) with large charge densities and low polarizabilities whereas hard bases are small, highly electronegative ligands (Lewis bases) of low polarizabilities, these hard-hard M-L interactions would not be characterized by high London forces.

6.7. S-thiocyanato complexes involve thiocyanate, SCN, bound through its relatively soft sulfur atom.

N-thiocyanato complexes are bound through the relatively hard nitrogen atom. Mercury(II) is a soft acid whereas cobalt(III) is hard. Given the rules of HSABs, the Hg-S and Co-N bonds are favored and not vice versa.

SCN

SCN

SCN

Br

NC

NCS

6.8. The most likely coordination sphere is a square anti-prism with bromide ligands on different squares and as far away from each other as possible. The thiocyanate would be S-bonded as this would produce soft-soft W-S interactions. There is plenty of room around the large tungsten atom for the larger S-thiocyanates (as opposed to the pencil like N-thiocyanates) to spread out.

6.9. The diacetatotetraaquairon(II) ion involves two acetate ions acting as monodentate ligands. The malonate ion has two acetate moities bound together through a common  $-CH_2$ - group. Both of the acetate moities can act as Lewis bases and make malonate a bidentate ligand. The difference between the equilibrium constants, then, is an example of the chelate effect. The malonate complex involves a chelating, multidentate ligand that is more stable than the equivalent compound involving monodentate ligands. These two situations are shown in the following two equations. (The acetates could also form a trans complex.)





Reaction (a) would have the more negative  $\Delta G^{\circ}$  and larger K because it is more entropy-driven than reaction (b). Reaction (a), as depicted above, goes from five reactant species in aqueous solution to five also in the products. Reaction (b) goes from seven to five. This result is an example of the chelate effect. The diaquabis(ethylenediamine)nickel(II) cyanide is the more thermodynamically stable of the two products.

6.11. The diacetatotetraaquairon(II) ion involves two acetate ions acting as monodentate ligands. The oxalate ion has two carboxylate (COO<sup>-</sup>) moities bound together through a carbon-carbon bond. Both of the carboxylate moities can act as Lewis bases and make oxalate a bidentate ligand. The difference between the equilibrium constants, then, is an example of the chelate effect. The oxalate complex involves a chelating, multidentate ligand that is more stable than the equivalent compound involving monodentate ligands. These two situations are shown in the following two equations.



\*6.12. (a)  $[Ni(H_2O)_6]Cl_2 + 2(CH_3CH_2)_2NCH_2CH_2NH_2 - ethanol \rightarrow$  $[Ni(H_2O)_2\{(CH_3CH_2)_2NCH_2CH_2NH_2\}_2]Cl_2 + 4H_2O$ 

(b) The product the second reaction is diaquabis(diethylamine)bis(ethylamine)nickel(II) chloride.

The latter reaction, that is, the one in part (b), would have the less negative  $\Delta G^{\circ}$  and smaller K because it proceeds from five reactant species to five also in the product. The equation for the reaction in part (a) involving the N,N-diethylethyldiamine bidentate ligands goes from three species to five. The reaction of part (a) is more entropy-driven than that in part (b).

6.13. Acetone is a monodentate ligand whereas acetylacetonate, [CH<sub>3</sub>COCHCOCH<sub>3</sub>], made up of two acetone [or acetyl, CH<sub>3</sub>CO] moities connected together by a common -CH- group, is bidentate. The

difference between the stability of acetone and acetylacetonate, then, is due to the chelate effect. The acac complexes involve chelating, bidentate ligands that form more stable compounds than the equivalent compounds involving two monodentate ligands.

\*6.14. The equilibrium constants indicate that the oxalate complex is more stable than the malonate. As shown below, the oxalate forms a five-membered ring (including the metal) whereas the malonate forms a six-membered ring. These results indicate that the five-membered ring is the more stable.



6.15. Using Equations (6.9) and (6.10) as shown below, we can calculate the equilibrium constant for the substitution of three ethylenediamine ligands for six ammines in the Ni(II) coordination sphere.

$$\frac{[\text{Ni}(\text{NH}_3)_6]^{2^+}(\text{aq}) \longrightarrow \text{Ni}^{2^+}(\text{aq}) + 6\text{NH}_3(\text{aq})}{[\text{Ni}^{2^+}(\text{aq}) + 3\text{en}(\text{aq}) \longrightarrow [\text{Ni}(\text{en})_3]^{2^+}(\text{aq}) + 6\text{NH}_3(\text{aq})} \qquad \begin{array}{l} K = 1/\beta = 1/(4.0 \text{ x } 10^8) \\ \beta = 2.0 \text{ x } 10^{18} \\ K = 2.0 \text{ x } 10^{18} \\ K = 2.0 \text{ x } 10^{18} \\ 4.0 \text{ x } 10^8 \end{array}$$

6.16. From the data given in Problem 6.11, we know the following information given below.

$$[Co(H_2O)_6]^{2^+}(aq) + 2CH_3COO^{-}(aq) \longrightarrow [Co(CH_3COO)_2(H_2O)_4](aq) + 2H_2O \qquad K = 80 [Co(H_2O)_6]^{2^+}(aq) + C_2O_4^{2^-} \longrightarrow [Co(H_2O)_4(C_2O_4)] + 2H_2O \qquad K = 5.0 \times 10^4$$

Reversing the first equation and adding it to the second would yield the reaction in question.

$$[Co(CH_3COO)_2(H_2O)_4] + C_2O_4^{2-} \longrightarrow [Co(H_2O)_4(C_2O_4)] + 2CH_3COO^- K = \frac{5.0 \times 10^4}{80} = 6.2 \times 10^2$$

6.17. The dmgH ligand has a molecular formula of  $C_4H_7O_2N_2$  and a molecular weight of 115.11 g/mol. Since one mole of Ni yields one mole of Ni(dmgH)<sub>2</sub>, we can calculate the mass of nickel in the ore as follows:

% Ni = <u>0.1588g Ni</u> x 100 = 45.94% 0.3456g ore 6.18. 8-Quinolinol or 8-hydroxyquinoline, oximeH, has a molecular formula of  $C_9H_7ON$  and a molecular weight of 145.16 g/mol. Since one mole of Al yields one mole of Al(oxime)<sub>3</sub>, we can calculate the mass of aluminum and aluminum ore needed to produce 0.50g of the precipitate, Al(oxime)<sub>3</sub>.

 $0.50g \operatorname{Al}(\operatorname{oxime})_{3} \quad \underline{1 \mod \operatorname{Al}(\operatorname{oxime})_{3}}_{459.42g \operatorname{Al}(\operatorname{oxime})_{3}} x \quad \underline{1 \mod \operatorname{Al}}_{1 \mod \operatorname{Al}(\operatorname{oxime})_{3}} x \quad \underline{26.98 \text{ g Al}}_{1 \mod \operatorname{Al}} = 0.029g \operatorname{Al}_{1 \mod \operatorname{Al}}$   $24\% \operatorname{Al} = \underline{0.029g \operatorname{Al}} x \ 100, \text{ therefore } x = 0.12g \text{ ore}$ 

6.19. One mole of EDTA complexes one mole of  $Ca^{2+}$ , therefore we can calculate the grams and percentage of calcium in the sample as follows.

% Ca = 0.04483g Ca x 100 = 22.41% 0.2000 g sample

x g ore

6.20. First we can calculate the molarity of the lead in solution as follows:

 $\underbrace{\frac{0.03487 \text{L x } 0.02000 \text{ mol EDTA x } 1 \text{ mol Pb}^{2+}}{\text{L } 1 \text{ mol EDTA}} = 0.03487 \text{M Pb}^{2+}}_{0.02000 \text{L solution}}$ 

The total molarity of the lead and cadmium combined is obtained in a similar manner.

$$\underbrace{\begin{array}{cccc} 0.04594L & x & 0.02000 \text{ mol EDTA} & x & 1 \text{ mol Pb}^{2+} \text{ and Cd}^{2+} \\ \underline{ & L & 1 \text{ mol EDTA} \\ 0.02000L \text{ solution} \end{array}} = 0.04594 \text{M Pb}^{2+} \text{ and Cd}^{2+}$$

The molarity of the  $Cd^{2+}$  can be obtained by difference.

M Cd<sup>2+</sup> = ( 0.04594M Pb<sup>2+</sup> and Cd<sup>2+</sup>) - ( 0.03487M Pb<sup>2+</sup>) = 0.01107M Cd<sup>2+</sup>

\*6.21. One mole of trien complexes one mole of  $Cu^{2+}$ , therefore we can calculate the grams of copper in the 10.00mL aliquot (or portion) of the original solution.

 $0.02275L \ge 0.01000 \text{ mol trien} \ge x \underline{-1 \text{ mol } \text{Cu}} = 0.01446 \text{ g Cu}$ L 1 mol trien 1 mole Cu

If there are  $0.01446g \text{ Cu}^{2+}$  in the 10.00mL aliquot, there must be 0.1446g in the full 100mL volumetric flask. Therefore we can calculate the percentage of copper in the sample as follows:

% Cu = 0.1446g Cu \_ x 100 = 72.10% 0.2005g sample 6.22. Three moles of 1,10-phenanthroline (phen) complexes one mole of  $Fe^{3+}$ , therefore we can calculate the grams of iron in the sample as follows.

6.25. Dear Econ Major:

Phosphates have been an important component of synthetic detergents because they let the soap-like part of a detergent do its job unhindered by hard water. In other words, phosphates render the hard water ions (calcium, magnesium, and iron) incapable of interfering with the action of the soap-like molecules in detergents. Phosphates have also been important because they are inexpensive and readily available to the detergent manufacturer. (See footnote at the end of this chapter.)

6.26. The pentasodium salt of diethylenetriaminepentaacetic acid is a derivative of diethylenetriamine in the same way that the tetrasodium salt of ethylenediaminetetraacetate is a derivative of ethylenediamine. In other words, to make diethylenetriaminepentaacetate, the five hydrogen atoms in the N-H bonds in diethylenetriamine are replaced with acetate moities (-CH<sub>2</sub>COO<sup>-</sup>) as shown below.



This is potentially an octadentate ligand. Most likely its full denticity would not be used although very large heavy metals might be able to achieve a coordination number of 8.

#### \*6.27. Dear Biology Major:

You may recall from your mind-bending introductory chemistry class that things are colored because they absorb some wavelengths of visible light and either allow other wavelengths through or reflect them to our eyes so that we perceive something to be colored. Sometimes this process is expressed by a color wheel like the one shown on the next page. This wheel says that if an object, for example, absorbs blue-green wavelengths it will therefore reflect or transmit red light to our eyes. Red light has a wavelength in the range of 750-610 nm. What causes light to be absorbed? Usually this is attributed to various energy levels in an atom or molecule. In the hemoglobin of the blood there are a number of iron ions surrounded by a so-called heme group. This heme group causes a split among the d orbitals of the iron resulting in the absorption of blue-green light so that our blood appears red. When the blood is oxygenated, an oxygen molecule  $(O_2)$  also exerts a slight influence on the split among the d orbitals of the iron. Now the "oxyhemoglobin" absorbs at a slightly different range of wavelengths so that the blood now appears a brighter shade of red. (See footnote at the end of this chapter.)

Wavelength Range (nm)

750-610red610-590orange590-570yellow570-500green500-450blue450-370violet

6.28. Carboxyhemoglobin has a carbon monoxide molecule coordinated to the iron(II) of the heme in hemoglobin. One way to depict the coordination chemistry part of the molecule is shown at right.

Color





## 6.29. Dear Doctor:

You may recall a group of molecules called the hemes. Hemes are made up of four nitrogen atoms (incorporated into a impressive array of organic heterocyclic rings) that are bound to a central iron cation. For example, hemes are an essential part of hemoglobin that is, as you know, responsible for transporting oxygen molecules ( $O_2$ ) from the lungs to the cells. Hemes are also a vital part of the cytochromes (c, a, a<sub>3</sub>, etc.) that play a large role in cellular respiration, the process whereby  $O_2$  is converted to water. The problem with cyanide,  $CN^2$ , is that it binds or coordinates to the central iron cation of cytochromes and essentially shuts down cellular respiration. For this reason, of course, it is important to minimize patient exposure to cyanide. (See footnote at the end of this chapter.)

\*6.30. A low-spin d<sup>6</sup> Fe<sup>2+</sup> has a  $t_{2g}^{6}$  configuration in which all the electrons of the metal occupy orbitals that point in between the ligands of a square planar coordination sphere. When the Fe<sup>2+</sup> changes to a high-spin state with a  $t_{2g}^{4}e_{g}^{2}$  electronic configuration, two metal d electrons now occupy orbitals that point directly at the ligands. The resulting extra repulsions between the metal and the ligands in the high-spin case cause the metal to be *effectively* larger (the ligands are pushed away somewhat) and make the metal ion less able to fit into the square planar site.

6.31. This is potentially an octadentate ligand. It would literally surround a Mn ion. Some of its Lewis base sites would most likely go unused.



6.32. Lead (Pb<sup>2+</sup>) is a soft metal cation. It prefers to interact with soft anions such as sulfide (S<sup>2-</sup>) rather than a relatively hard anion like oxide (O<sup>2-</sup>).

6.33. Mercury is a soft metal and will prefer to interact with soft groups like the sulfur-containing mercaptans.

6.34. Of EDTA, penicillamine, and BAL, the latter two are optically active. Both have a carbon atom with four different groups attached to it. Such a "center of chirality" produces a lack of an internal mirror plane and optical activity.

6.35. Both histidine and cysteine are tridentates that could readily coordinate with cobalt and remove it. This sequestering effect would be the basis of its use for cobalt detoxification.

6.36. Cysteine, with its soft mercaptan (-SH) group would be the better antidote for the soft heavy metals.

6.37. Of serine and cysteine, the latter with its soft mercapto (-SH) group, would be the better antidote against the soft heavy metals.

6.38. Cysteine is probably the better antidote against heavy metals because it forms 5-membered rings with metals whereas methionine forms 6-membered rings. 5-membered rings are generally more stable.

\*6.39. Dear English Major:

You may recall from your AP chem course that cis means "on the same side of" while trans means "over" or "across." (These terms are both from the Latin.) Cisplatin then has two groups (chlorine atoms as it turns out) on the same side of a platinum atom. When cisplatin interacts with fastgrowing tumor tissue, many researchers believe that the two chlorides are replaced with adjacent sections ("nitrogen-bases" if you recall this much from that long ago AP experience) of DNA. In this form (attached to a platinum atom) the DNA is incapable of reproducing faithfully and the growth of the tumor cells is retarded or even reversed. When the trans analog of cisplatin is used, it cannot interact with adjacent sections of DNA and cannot significantly interfere with the replication of the tumor cells. The tumor continues to grow unchecked. (See following footnote.)

### Footnote:

(Dear readers: I know you can do better than I did in writing letters to various academic majors and professionals. I would love to see the various short paragraphs that you all come up with. You'll be famous; I might put your paragraph in the next version of this Solution Manual! (If there is a next version.) Submit your entries to the author at Department of Chemistry, Allegheny College, Meadville, PA 16335.