

## 17.4: The Formation of Complex Ions

### Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as  $\text{Cu}^{2+}$  or  $\text{Ru}^{3+}$ , have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

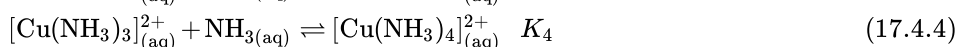
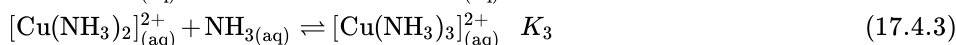
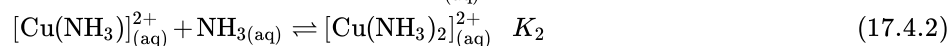
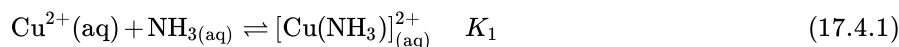
As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated  $\text{Cu}^{2+}$  ion  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ . Because it is a stronger base than  $\text{H}_2\text{O}$ , ammonia replaces the water molecules in the hydrated ion to form the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  ion. Formation of the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  complex is accompanied by a dramatic color change, as shown in Figure 17.4.1. The solution changes from the light blue of  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  to the blue-violet characteristic of the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  ion.



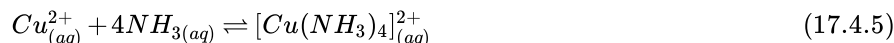
Figure 17.4.1: The Formation of Complex Ions. An aqueous solution of  $\text{CuSO}_4$  consists of hydrated  $\text{Cu}^{2+}$  ions in the form of pale blue  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  ions, usually written as  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  ion (right) because ammonia, a stronger base than  $\text{H}_2\text{O}$ , replaces water molecules from the hydrated  $\text{Cu}^{2+}$  ion. For a more complete description, see <https://www.youtube.com/watch?v=IQNcLH6OZK0>.

### The Formation Constant

The replacement of water molecules from  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  by ammonia occurs in sequential steps. Omitting the water molecules bound to  $\text{Cu}^{2+}$  for simplicity, we can write the equilibrium reactions as follows:



The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated  $\text{Cu}^{2+}$  ion contains six  $\text{H}_2\text{O}$  ligands, but the complex ion that is produced contains only four  $\text{NH}_3$  ligands, not six.



The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant ( $K_f$ )**. The equilibrium constant expression for  $K_f$  has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 2.1 \times 10^{13} = K_1 K_2 K_3 K_4 \quad (17.4.6)$$

The formation constant ( $K_f$ ) has the same general form as any other equilibrium constant expression.

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated  $\text{Cu}^{2+}(\text{aq})$  ion is represented as  $\text{Cu}^{2+}$  for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case,  $K_f$ ), the more stable the product. With  $K_f = 2.1 \times 10^{13}$ , the  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$  complex ion is very stable. The formation constants for some common complex ions are listed in Table 17.4.1.

Table 17.4.1: Formation Constants for Selected Complex Ions in Aqueous Solution\*

	Complex Ion	Equilibrium Equation	$K_f$
Ammonia Complexes	$[\text{Ag}(\text{NH}_3)_2]^+$	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+$	$1.1 \times 10^7$
	$[\text{Cu}(\text{NH}_3)_4]^{2+}$	$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$	$2.1 \times 10^{13}$
	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	$\text{Ni}^{2+} + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}$	$5.5 \times 10^8$
Cyanide Complexes	$[\text{Ag}(\text{CN})_2]^-$	$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons [\text{Ag}(\text{CN})_2]^-$	$1.1 \times 10^{18}$
	$[\text{Ni}(\text{CN})_4]^{2-}$	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Ni}(\text{CN})_4]^{2-}$	$2.2 \times 10^{31}$
	$[\text{Fe}(\text{CN})_6]^{3-}$	$\text{Fe}^{3+} + 6\text{CN}^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{3-}$	$1 \times 10^{42}$
Hydroxide Complexes	$[\text{Zn}(\text{OH})_4]^{2-}$	$\text{Zn}^{2+} + 4\text{OH}^- \rightleftharpoons [\text{Zn}(\text{OH})_4]^{2-}$	$4.6 \times 10^{17}$
	$[\text{Cr}(\text{OH})_4]^-$	$\text{Cr}^{3+} + 4\text{OH}^- \rightleftharpoons [\text{Cr}(\text{OH})_4]^-$	$8.0 \times 10^{29}$
Halide Complexes	$[\text{HgCl}_4]^{2-}$	$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons [\text{HgCl}_4]^{2-}$	$1.2 \times 10^{15}$
	$[\text{CdI}_4]^{2-}$	$\text{Cd}^{2+} + 4\text{I}^- \rightleftharpoons [\text{CdI}_4]^{2-}$	$2.6 \times 10^5$
	$[\text{AlF}_6]^{3-}$	$\text{Al}^{3+} + 6\text{F}^- \rightleftharpoons [\text{AlF}_6]^{3-}$	$6.9 \times 10^{19}$
Other Complexes	$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	$\text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-} \rightleftharpoons [\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$	$2.9 \times 10^{13}$
	$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	$\text{Fe}^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	$2.0 \times 10^{20}$

\*Reported values are overall formation constants.

Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

### Example 17.4.1

If 12.5 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of  $\text{Cu}^{2+}(\text{aq})$ ?

**Given:** mass of  $\text{Cu}^{2+}$  salt and volume and concentration of ammonia solution

**Asked for:** equilibrium concentration of  $\text{Cu}^{2+}(\text{aq})$

**Strategy:**

- Calculate the initial concentration of  $\text{Cu}^{2+}$  due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 17.4.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.
- Substitute the final concentrations into the expression for the formation constant (Equation 17.4.6) to calculate the equilibrium concentration of  $\text{Cu}^{2+}(\text{aq})$ .

**Solution**

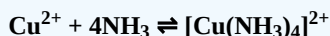
Adding an ionic compound that contains  $\text{Cu}^{2+}$  to an aqueous ammonia solution will result in the formation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}(\text{aq})$ , as shown in Equation 17.4.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous

ammonia is negligible.

A The initial concentration of  $\text{Cu}^{2+}$  from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5 \cancel{\text{ g}} \text{ Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} \left( \frac{1 \text{ mol}}{295.65 \cancel{\text{ g}}} \right) \left( \frac{1}{500 \cancel{\text{ mL}}} \right) \left( \frac{1000 \cancel{\text{ mL}}}{1 \text{ L}} \right) = 0.0846 \text{ M} \quad (17.4.7)$$

Because the stoichiometry of the reaction is four  $\text{NH}_3$  to one  $\text{Cu}^{2+}$ , the amount of  $\text{NH}_3$  required to react completely with the  $\text{Cu}^{2+}$  is  $4(0.0846) = 0.338 \text{ M}$ . The concentration of ammonia after complete reaction is  $1.00 \text{ M} - 0.338 \text{ M} = 0.66 \text{ M}$ . These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large ( $2.1 \times 10^{13}$ ), the equilibrium will lie far to the right. Thus we will assume that the formation of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  in the first step is complete and allow some of it to dissociate into  $\text{Cu}^{2+}$  and  $\text{NH}_3$  until equilibrium has been reached. If we define  $x$  as the amount of  $\text{Cu}^{2+}$  produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  is  $-x$ , and the change in the concentration of ammonia is  $+4x$ , as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.



	$[\text{Cu}^{2+}]$	$[\text{NH}_3]$	$[[\text{Cu}(\text{NH}_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	$x$	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (Equation 17.4.6) and assuming that  $x \ll 0.0846$ , which allows us to remove  $x$  from the sum and difference,

$$K_f = \frac{[[\text{Cu}(\text{NH}_3)_4]^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \quad (17.4.8)$$

$$x = 2.1 \times 10^{-14} \quad (17.4.9)$$

The value of  $x$  indicates that our assumption was justified. The equilibrium concentration of  $\text{Cu}^{2+}(\text{aq})$  in a  $1.00 \text{ M}$  ammonia solution is therefore  $2.1 \times 10^{-14} \text{ M}$ .

### ? Exercise 17.4.1

The ferrocyanide ion  $[\text{Fe}(\text{CN})_6]^{4-}$  is very stable, with a  $K_f$  of  $1 \times 10^{35}$ . Calculate the concentration of cyanide ion in equilibrium with a  $0.65 \text{ M}$  solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

**Answer**

$$1.2 \times 10^{-5} \text{ M}$$

## The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of  $\text{AgBr}$ , or mixtures of  $\text{AgBr}$  and other silver halides.  $\text{AgBr}$  is a sparingly soluble salt, with a  $K_{sp}$  of  $5.35 \times 10^{-13}$  at  $25^\circ\text{C}$ . When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts  $\text{AgBr}$  to black  $\text{Ag}$  metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of  $\text{AgBr}$  converted, with the areas exposed to the most light being darkest. To fix the image and prevent more  $\text{AgBr}$  crystals from being converted to  $\text{Ag}$  metal during processing of the film, the unreacted  $\text{AgBr}$  on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

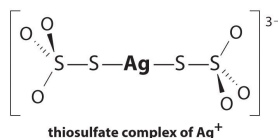
The reaction for the dissolution of silver bromide is as follows:



with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25^{\circ}\text{C} \quad (17.4.11)$$

The equilibrium lies far to the left, and the equilibrium concentrations of  $\text{Ag}^{+}$  and  $\text{Br}^{-}$  ions are very low ( $7.31 \times 10^{-7}$  M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



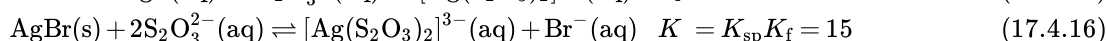
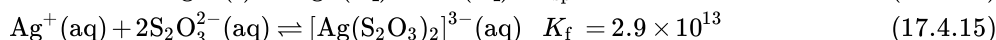
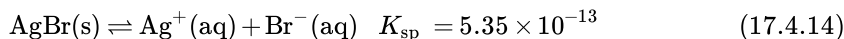
The reaction of  $\text{Ag}^{+}$  with thiosulfate is as follows:



with

$$K_f = 2.9 \times 10^{13} \quad (17.4.13)$$

The magnitude of the equilibrium constant indicates that almost all  $\text{Ag}^{+}$  ions in solution will be immediately complexed by thiosulfate to form  $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ . We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:



Comparing  $K$  with  $K_{sp}$  shows that the formation of the complex ion increases the solubility of AgBr by approximately  $3 \times 10^{13}$ . The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

*If a complex ion has a large  $K_f$ , the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

#### ✓ Example 17.4.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ( $\text{AgCl}_2^{-}$ ). Calculate the solubility of AgCl in each situation:

- in pure water
- in 1.0 M KCl solution, ignoring the formation of any complex ions
- the same solution as in part (b) except taking the formation of complex ions into account, assuming that  $\text{AgCl}_2^{-}$  is the only  $\text{Ag}^{+}$  complex that forms in significant concentrations

At  $25^{\circ}\text{C}$ ,  $K_{sp} = 1.77 \times 10^{-10}$  for AgCl and  $K_f = 1.1 \times 10^5$  for  $\text{AgCl}_2^{-}$ .

**Given:**  $K_{sp}$  of AgCl,  $K_f$  of  $\text{AgCl}_2^{-}$ , and KCl concentration

**Asked for:** solubility of AgCl in water and in KCl solution with and without the formation of complex ions

### Strategy:

- Write the solubility product expression for AgCl and calculate the concentration of  $\text{Ag}^+$  and  $\text{Cl}^-$  in water.
- Calculate the concentration of  $\text{Ag}^+$  in the KCl solution.
- Write balanced chemical equations for the dissolution of AgCl and for the formation of the  $\text{AgCl}_2^-$  complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
- Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

### Solution

- a. **A** If we let  $x$  equal the solubility of AgCl, then at equilibrium  $[\text{Ag}^+] = [\text{Cl}^-] = x$  M. Substituting this value into the solubility product expression,

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(x) = x^2 = 1.77 \times 10^{-10}$$

$$x = 1.33 \times 10^{-5}$$

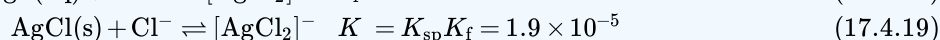
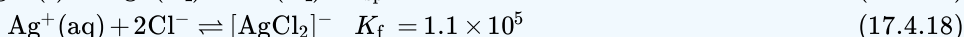
Thus the solubility of AgCl in pure water at 25°C is  $1.33 \times 10^{-5}$  M.

- b. **B** If  $x$  equals the solubility of AgCl in the KCl solution, then at equilibrium  $[\text{Ag}^+] = x$  M and  $[\text{Cl}^-] = (1.0 + x)$  M. Substituting these values into the solubility product expression and assuming that  $x \ll 1.0$ ,

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = (x)(1.0 + x) \approx x(1.0) = 1.77 \times 10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

- c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to  $K_{\text{sp}}$  and  $K_{\text{f}}$  gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of  $K_{\text{sp}}$  and  $K_{\text{f}}$ :



- D** If we let  $x$  equal the solubility of AgCl in the KCl solution, then at equilibrium  $[\text{AgCl}_2^-] = x$  and  $[\text{Cl}^-] = 1.0 - x$ . Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that  $x \ll 1.0$ ,

$$K = \frac{[\text{AgCl}_2^-]}{[\text{Cl}^-]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a  $1.9 \times 10^{-5}$  M solution of the  $\text{AgCl}_2^-$  complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is  $10^5$  times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

### ? Exercise 17.4.2

Calculate the solubility of mercury(II) iodide ( $\text{HgI}_2$ ) in each situation:

- pure water
- a 3.0 M solution of NaI, assuming  $[\text{HgI}_4]^{2-}$  is the only Hg-containing species present in significant amounts

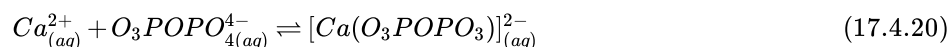
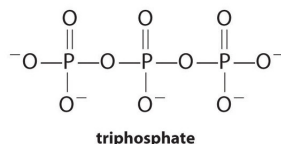
$$K_{\text{sp}} = 2.9 \times 10^{-29} \text{ for } \text{HgI}_2 \text{ and } K_{\text{f}} = 6.8 \times 10^{29} \text{ for } [\text{HgI}_4]^{2-}.$$

### Answer

- $1.9 \times 10^{-10}$  M
- 1.4 M

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which are present in high concentrations in “hard” water. The precipitation of these salts produces a bathtub ring and gives a

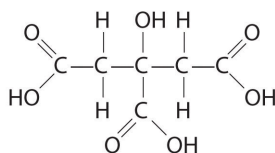
gray tinge to clothing. Adding a complexing agent such as pyrophosphate ( $\text{O}_3\text{POPO}_3^{4-}$ , or  $\text{P}_2\text{O}_7^{4-}$ ) or triphosphate ( $\text{P}_3\text{O}_{10}^{5-}$ ) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



with

$$K_f = 4 \times 10^4 \quad (17.4.21)$$

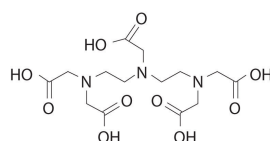
However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. “Phosphate-free” detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,  
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of  $\text{Na}^+$ , but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the  $^1\text{H}$  nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as “MRI contrast agents.” Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and allows doctors to “see” each of these separately (Figure 17.4.2). One of the most important metal ions for this application is  $\text{Gd}^{3+}$ , which with seven unpaired electrons is highly paramagnetic. Because  $\text{Gd}^{3+}(\text{aq})$  is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as  $\text{DTPA}^{5-}$  (diethylenetriamine pentaacetic acid), whose fully protonated form is shown here.



DTPA (diethylenetriaminepentaacetic acid)

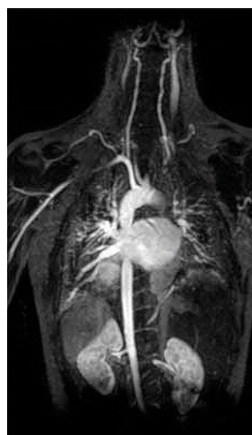
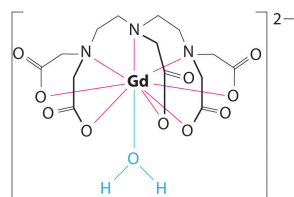


Figure 17.4.2 An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

## Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large  $K_f$ . A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant ( $K_f$ ). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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