Chapter 11

HE GROUP IIA(2) LEMENTS: BERYLLIUM, IAGNESIUM, CALCIUM, TRONTIUM, AND BARIUM

1-1 Introduction

Beryllium occurs in the mineral *beryl*, $Be_3Al_2(SiO_3)_6$. Compounds of Be are exceedingly toxic, especially if inhaled, whereby they cause degeneration of lung tissue similar to miners' silicosis; they must be handled with great care. This element has only minor technical importance.

The elements Mg, Ca, Sr, and Ba are widely distributed in minerals and in the sea. There are substantial deposits of limestone ($CaCO_3$), dolomite ($CaCO_3 \cdot MgCO_3$), and carnallite ($KCl \cdot MgCl_2 \cdot 6\,H_2O$). Less abundant are strontianite ($SrCO_3$) and barytes ($BaSO_4$). All isotopes of radium are radioactive. The isotope ^{226}Ra, α, 1600 years, which occurs in the ^{238}U decay series, was first isolated by Pierre and Marie Curie from the uranium ore, pitchblende. It was collected from solutions by coprecipitation with $BaSO_4$ and the nitrates subsequently fractionally crystallized. Its use in cancer therapy has been supplanted by other forms of radiation.

The positions of the Group IIA(2) elements and of the related Group IIB(12) (Zn, Cd, and Hg) elements in the periodic table and some of their properties have been given in Chapter 8.

The atomic radii are smaller than those of the Li to Cs group as a result of the increased nuclear charge (cf. Table 4-2). The number of bonding electrons in the metals is now two, so that these have higher melting and boiling points and densities. The ionization enthalpies are higher than those of Group IA(1) atoms and their enthalpies of vaporization are higher. Nevertheless, the high lattice energies and high hydration energies of M^{2+} ions compensate for these increases. The metals are hence electropositive with high chemical reactivities and standard electrode potentials. Born–Haber cycle calculations show that MX compounds would be unstable in the sense that the following reactions should have very large negative enthalpies:

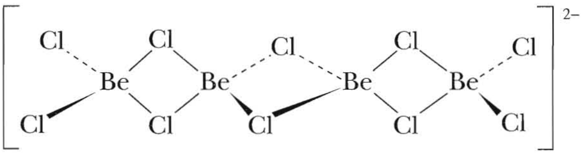
$$2\,MX = M + MX_2 \qquad (11\text{-}1.1)$$

Covalency and Stereochemistry for Beryllium

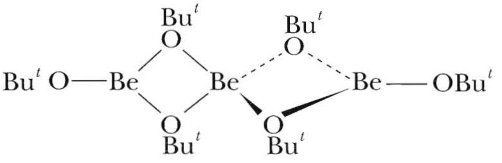
In the case of beryllium, because of its exceptionally small atomic radius and high enthalpies of ionization and sublimation, the lattice or hydration energies are insufficient to provide for complete charge separation to give a simple Be^{2+} cation in beryllium-containing compounds. (Recall the material in Chapter 4 on Born–Haber cycles for ionic compounds.) Consequently, although the oxides and fluorides of the other elements of Group IIA(2) (except perhaps Mg) are ionic, BeF_2 and BeO show evidence of covalent character. Also, covalent compounds with bonds from Be to C are quite stable. In these respects, Be resembles Zn. Note that to form two covalent bonds, promotion of Be from the $2s^2$ to the $2s^12p^1$ electron configuration is required. Thus BeX_2 molecules should be linear. Since such molecules are coordinatively unsaturated, they exist only in the gas phase. In condensed phases, at least threefold, and more commonly fourfold (maximum) coordination is achieved in the following ways.

1. Polymerization may occur through bridging groups, such as H, F, Cl, or CH_3, giving chain polymers of the type $[BeF_2]_n$, $[BeCl_2]_n$, and $[Be(CH_3)_2]_n$, as shown in Fig. 11-1. The coordination of Be in these chains is not exactly tetrahedral. For instance, the internal Cl—Be—Cl angles in $[BeCl_2]_n$ are 98.2°, which means the $Be(\mu_2\text{-}Cl)_2Be$ units are somewhat elongated in the direction of the chain axis. In contrast, the C—Be—C angles in $[Be(CH_3)_2]_n$ are 114°. These distortions from the ideal tetrahedral angle for a four-coordinate Be atom are dependent on the nature of the bridging group, and are related to the presence or absence of lone pairs on the bridging atoms.

Other important examples of bridging to Be atoms include the following. As already noted, in the gas phase at high temperature, the halides are linear molecules, X—Be—X. At low temperatures, however, the chloride exists in appreciable amounts (~20% at 560 °C) as a dimer, $[BeCl_2]_2$, in which Be is presumably three coordinate. Interestingly, in compounds of the type $(M^I)_2(Be_4Cl_{10})$ (M = K, Rb, Tl, NO, or NH_4), the anion (Structure 11-I) resembles a portion of the $[BeCl_2]_n$ chain.



11–I



11–II

2. Alkoxides, $[Be(OR)_2]_n$, usually have associated structures with both μ_2-bridging and terminal OR groups. For example, $[Be(OCH_3)_2]_n$ is a high polymer, insoluble in hydrocarbon solvents. On the other hand, the *tert*-butoxy derivative is less condensed, being only a trimer $[Be(O\text{-}t\text{-}Bu)_2]_3$ (Structure 11-II), which is soluble in hydrocarbon solvents. Only when the alkoxide is bulky are monomers obtained with two-coordinate Be, as in Structure 11-III.

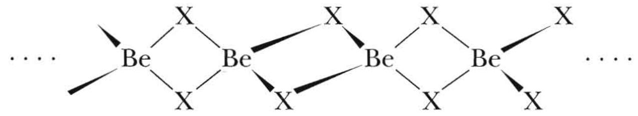
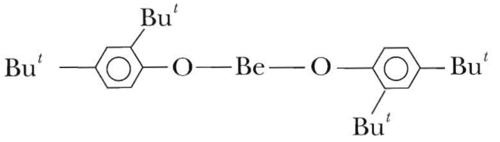


Figure 11-1 The infinite chain structure of BeX_2 compounds ($X = F$, Cl, or CH_3), whereby each Be atom achieves a coordination number of four.



11–III

Another coordinatively unsaturated Be compound containing bulky organic groups is the two-coordinate beryllium alkyl $Be(t\text{-}Bu)_2$, which reacts with *tert*-butyllithium in dry pentane at room temperature, as in Reaction 11-1.2:

$$Li\text{-}t\text{-}Bu + Be(t\text{-}Bu)_2 \longrightarrow Li[Be(t\text{-}Bu)_3] \qquad (11\text{-}1.2)$$

to give the three-coordinate lithium tri-*tert*-butylberyllate, $Li[Be(t\text{-}Bu)_3]$, in which the donor carbon atoms of the three *tert*-butyl groups are arranged in a trigonal planar coordination geometry around the Be atom. Further aspects of the organochemistry of the Group IIA(2) elements are given in Chapter 29.

3. By functioning as Lewis acids, many Be compounds obtain maximum coordination of the metal atom. The chloride $BeCl_2$ reacts with donor solvents to form four-coordinate etherates such as $BeCl_2(OEt_2)_2$. Interaction with anions gives complex ions such as BeF_4^{2-}. The aqua ion is four-coordinate, $[Be(H_2O)_4]^{2+}$. In chelate compounds, such as the acetylacetonate, $Be(acac)_2$, four approximately tetrahedral bonds are formed, with four equal C–O bonds and four equal Be–O bonds.

4. Beryllium also achieves tetrahedral four coordination in compounds such as BeO and BeS, the structures of which are often those of the corresponding Zn derivatives. Thus low-temperature BeO has the ZnO–wurtzite structure, whereas BeS adopts the ZnS–zinc blende structure (Fig. 4-1). The most stable $Be(OH)_2$ polymorph has the $Zn(OH)_2$ structure. It also may be noted that Be with F gives compounds that are often isomorphous with oxygen compounds of silicon. An example is $NaBeF_3$, which is isomorphous with $CaSiO_3$. In addition, there are five different corresponding forms of Na_2BeF_4 and Ca_2SiO_4.

Magnesium

The second member of Group IIA(2) (Mg) is intermediate in behavior between Be and the remainder of the group whose chemistry is entirely ionic in nature. The Mg^{2+} ion has a high polarizing ability, and there is, consequently, a decided tendency for its compounds to have nonionic behavior, although not as much as for Be. Magnesium, therefore, readily forms bonds to carbon, as discussed in Chapter 29. Like $Be(OH)_2$, $Mg(OH)_2$ is only sparingly soluble in H_2O, whereas the hydroxides of the other members of Group IIA(2) are water soluble and highly basic.

Calcium, Strontium, Barium, and Radium

The elements Ca, Sr, Ba, and Ra form a closely related group in which the chemical and physical properties change systematically with increasing size. Examples are increases from Ca to Ra in (a) the electropositive nature of the element (cf. $E°$ values, Table 8-2); (b) hydration energies of salts; (c) insolubility of most salts, notably sulfates; and (d) thermal stabilities of carbonates and nitrates. As in Group IA(1), and as explained in Section 4-6, the larger Group IIA(2) cations can stabilize large anions such as O_2^{2-}, O_2^-, and I_3^-.

Because of similarity in charge and radius, the 2+ ions of the lanthanides (Section 26-5) resemble the Sr to Ra ions. Thus Eu, which forms an insoluble sulfate ($EuSO_4$), sometimes occurs in Group IIA(2) minerals.

11-2 Beryllium and Its Compounds

The metal, obtained by Ca or Mg reduction of $BeCl_2$, or by Mg reduction of BeF_2, is very light and has been used for windows in X-ray apparatus. The absorption of electromagnetic radiation in general depends on the electron density in matter, and Be has the lowest stopping power per unit of mass thickness of all constructional materials, hence its utility as a nonabsorbing surface, or window.

Beryllium metal is relatively unreactive compared to other members of its group, especially in its massive state, where it does not react with water at red heat, and it does not react with air below 600 °C. It can be ignited in air only when finely powdered, to give BeO and Be_3N_2. Beryllium does not react directly with hydrogen; consequently BeH_2 must be prepared by less direct methods, such as reduction of $BeCl_2$ in ether by LiH, or pyrolysis of $Be(t\text{-}Bu)_2$. Of the Group IIA(2) elements, only Be reacts with aqueous bases (NaOH or KOH) to liberate hydrogen and form the beryllate ion, $[Be(OH)_4]^{2-}$. The latter is also formed when beryllium hydroxide is dissolved is aqueous alkali. Thus beryllium metal and the hydroxide are chemically similar to aluminum and $Al(OH)_3$. The hydroxide, $Be(OH)_2$, has several polymorphs, the most stable of which is crystallized when boiled solutions of $BeCl_2$ and OH^- are cooled.

Beryllium metal is unreactive towards cold, concentrated HNO_3, due to passivation. However, Be does react with concentrated solutions of noncomplexing acids (Chapter 7) to form the tetraaqua ion, $[Be(H_2O)_4]^{2+}$, crystalline salts of which may be readily obtained. The water ligands in such salts are more strongly bound than is typical of other divalent cations. For instance, $[Be(H_2O)_4]Cl_2$ does not lose H_2O over strong dessicants such as P_2O_5. The stability of Be complexes with ligands containing nitrogen or other donors is lower than that of complexes possessing oxygen donor ligands. Thus $[Be(NH_3)_4]Cl_2$ is thermally stable, but rapidly hydrolyzed to the tetraaqua ion.

The firm attachment of the H_2O molecules in $[Be(OH_2)_4]^{2+}$ causes a weakening of the O—H bonds. This means that the aqua ion is acidic, as shown in Reaction 11-2.1.

$$[Be(H_2O)_4]^{2+} = [Be(H_2O)_3OH]^+ + H^+ \qquad (11\text{-}2.1)$$

Thus aqueous solutions of beryllium salts are extensively hydrolyzed and are acidic. In fact, the $[Be(OH_2)_3(OH)]^+$ ion is itself unstable, and quickly trimerizes to give the $[Be_3(OH)_3(H_2O)_x]^{3+}$ ion.

The tetrafluoroberyllate ion, $[BeF_4]^{2-}$, is formed in fluoride-containing solutions. It is also obtained by dissolving BeO or $Be(OH)_2$ in concentrated aqueous fluoride solutions, or in nonaqueous melts of acid fluorides such as NH_4HF_2. The tetrafluoroberyllate anion behaves in crystals much like SO_4^{2-}; thus $PbBeF_4$ and $PbSO_4$ have similar structures and solubilities.

The white crystalline oxide BeO is obtained on ignition of Be or its compounds in air. It resembles Al_2O_3 in being highly refractory (mp 2570 °C). The high-temperature form (>800 °C) is exceedingly inert and dissolves readily only in a hot syrup of concentrated H_2SO_4 and $(NH_4)_2SO_4$. More reactive forms of BeO dissolve in hot aqueous alkali or fused $KHSO_4$.

Beryllium fluoride (BeF_2) is obtained as a glassy, hygroscopic mass by thermal decomposition of $(NH_4)_2BeF_4$. On a small scale, the chloride and the bromide are best obtained by direct interaction of the elements in a hot tube. Otherwise, $BeCl_2$ may be prepared by passing CCl_4 over BeO at 800 °C, or at 600–800 °C as in Reaction 11-2.2.

$$BeO + C + Cl_2 \longrightarrow BeCl_2 + CO \qquad (11\text{-}2.2)$$

As noted earlier, $BeCl_2$ forms long chains in the crystal, and this compound and the similar methyl derivative, $[Be(CH_3)_2]_n$, are cleaved by donor molecules or ions to give, for example in ethers, adducts of the type $BeCl_2(OR_2)_2$. (Such Lewis acid behavior is also typical of Al, Mg, and Zn halides and alkyls.) Beryllium chloride also dissolves exothermically in H_2O, and the salt $[Be(H_2O)_4]Cl_2$ can be obtained from aqueous hydrochloric acid solutions. In melts with alkali halides, chloroberyllate ions, $[BeCl_4]^{2-}$, are formed, although this ion, unlike the tetrafluoro ion, does not exist in aqueous solution.

The most unusual oxygen-containing complexes of Be have the formula $Be_4O(O_2CR)_6$ and are formed by refluxing $Be(OH)_2$ with carboxylic acids. These white crystalline compounds are soluble in nonpolar organic solvents, such as alkanes, but are insoluble in water and lower alcohols. In solution, the compounds are un-ionized and monomeric. They have the structure illustrated in Fig. 11-2. The central oxygen atom is tetrahedrally surrounded by the four Be atoms (this

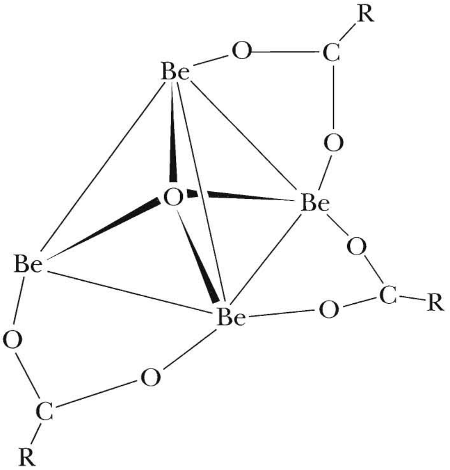


Figure 11-2 The structure of the "basic carboxylate" complexes $Be_4O(O_2CR)_6$. Only three of the six carboxylate groups are shown.

being one of the few cases, excepting solid oxides, in which oxygen is four coordinated), and each Be atom is tetrahedrally surrounded by four oxygen atoms.

Note that Be and its compounds are exceedingly poisonous. Inhalation of Be or Be compounds can cause serious respiratory disease, and soluble compounds may produce dermatitis on contact with the skin. Great precautions should be taken in handling either elemental Be or its compounds.

11-3 The Remaining Elements of Group IIA(2) and Their Properties

Magnesium

Magnesium is produced in several ways. Two important sources are dolomite rock and seawater, which contains 0.13% Mg. Dolomite is first calcined to give a CaO/MgO mixture from which the calcium can be removed by ion exchange using seawater. The equilibrium is favorable because the solubility of $Mg(OH)_2$ is lower than that of $Ca(OH)_2$

$$Ca(OH)_2 \cdot Mg(OH)_2 + Mg^{2+} \longrightarrow 2\,Mg(OH)_2 + Ca^{2+} \qquad (11\text{-}3.1)$$

The most important processes for obtaining the metal are (a) the electrolysis of fused halide mixtures (e.g., $MgCl_2 + CaCl_2 + NaCl$) from which the least electropositive metal (Mg) is deposited, and (b) the reduction of MgO or of calcined dolomite ($MgO \cdot CaO$). The latter is heated with ferrosilicon:

$$CaO \cdot MgO + FeSi = Mg + \text{silicates of Ca and Fe} \qquad (11\text{-}3.2)$$

and the Mg is distilled out. Magnesium oxide can be heated with coke at 2000 °C and the metal deposited by rapid quenching of the high-temperature equilibrium that lies well to the right.

$$MgO + C \rightleftharpoons Mg + CO \qquad (11\text{-}3.3)$$

Magnesium is grayish white and has a protective surface oxide film. Thus despite the favorable potential, it is not attacked by water unless it is amalgamated. Magnesium, however, is readily soluble in dilute acids. It is used in light constructional alloys and for the preparation of Grignard reagents (Section 29-5) by interaction with alkyl or aryl halides in ether solution. It is essential to life because it occurs in chlorophyll (cf. Section 31-4).

Calcium

Calcium, strontium, and barium are made only on a relatively small scale by reduction of the halides with Na. These elements are soft and silvery, resembling Na in their reactivities, although they are somewhat less reactive. Calcium is used for the reduction to the metal of actinide and lanthanide halides and for the preparation of CaH_2, which is a useful reducing agent.

11-4 Binary Compounds

Oxides

The oxides (MO) are white, high-melting crystalline solids, with NaCl-type lattices. They are obtained by calcining the carbonates. Calcium oxide, for instance, is made on a vast scale for the cement industry, as in Reaction 11-4.1.

$$CaCO_3 \longrightarrow CaO + CO_2(g) \qquad \Delta H^\circ = 178.1 \text{ kJ mol}^{-1} \tag{11-4.1}$$

Magnesium oxide is relatively inert, especially after ignition at high temperatures, but the other oxides react with H_2O, evolving heat, to form the hydroxides. They absorb CO_2 from the air. Magnesium hydroxide is insoluble in water ($\sim 1 \times 10^{-4}$ g L^{-1} at 20 °C) and can be precipitated from Mg^{2+} solutions; it is a much weaker base than the Ca to Ra hydroxides, although it has no acidic properties and unlike $Be(OH)_2$ is insoluble in an excess of hydroxide. The Ca to Ra hydroxides are all soluble in water, increasingly so with increasing atomic number [$Ca(OH)_2$, ~ 2 g L^{-1}; $Ba(OH)_2$, ~ 60 g L^{-1} at ~ 20 °C], and all are strong bases.

Halides

The anhydrous halides can be made by dehydration (Section 20-3) of the hydrated salts. Both Mg and Ca halides readily absorb water. The ability to form hydrates, as well as the solubilities in water, decrease with increasing size, and Sr, Ba, and Ra halides are normally anhydrous. This is because the hydration energies decrease more rapidly than the lattice energies with increasing size of M^{2+}. All the halides appear to be essentially ionic.

The fluorides vary in solubility in the reverse order, that is, $Mg < Ca < Sr < Ba$, because of the small size of the F^- relative to the M^{2+} ion. The lattice energies decrease unusually rapidly because the large cations make contact with one another without at the same time making contact with the F^- ions.

Other Compounds

The metals, like the alkalis, react with many other elements. Compounds such as phosphides, silicides, or sulfides are mostly ionic and are hydrolyzed by water.

Calcium *carbide,* obtained by reduction of the oxide with carbon in an electric furnace, is an acetylide $Ca^{2+}C_2^{2-}$. It can be employed as a source of acetylene:

$$Ca^{2+}C_2^{2-} + 2\,H_2O \longrightarrow Ca(OH)_2 + HC{\equiv}CH \tag{11-4.2}$$

The binary hydrides MH_2 are ionic, apart from MgH_2, which is more covalent in nature. The compound CaH_2 reacts smoothly with water and is used as a drying agent for organic solvents and gases.

11-5 Oxo Salts, Ions, and Complexes

All the elements form *oxo salts;* those of Mg and Ca are often hydrated. The carbonates are all rather insoluble in water and the solubility products decrease with increasing size of M^{2+}; $MgCO_3$ is used in stomach powders to absorb acid. The same solubility order applies to the *sulfates;* magnesium sulfate which, as Epsom salt ($MgSO_4{\cdot}7\,H_2O$), is used as a mild laxative in "health" salts, is readily soluble in water. Calcium sulfate has a hemihydrate $2\,CaSO_4{\cdot}H_2O$ (plaster of Paris) which readily absorbs more water to form the very sparingly soluble $CaSO_4{\cdot}2\,H_2O$ (gypsum), while Sr, Ba, and Ra sulfates are insoluble and anhydrous. Barium sulfate is accordingly used for "barium meals" as it is opaque to X-rays and provides a suitable shadow in the stomach. The *nitrates* of Sr, Ba, and Ra are also anhydrous and the last two can be precipitated from cold aqueous solution by the addition of fuming nitric acid. *Magnesium perchlorate* is used as a drying agent, but contact with organic materials must be avoided because of the hazard of explosions.

For water, acetone, and methanol solutions, NMR studies have shown that the coordination number of Mg^{2+} is six, although in ammonia it appears to be five. The $[Mg(H_2O)_6]^{2+}$ ion is not acidic and in contrast to $[Be(H_2O)_4]^{2+}$ can be dehydrated fairly readily. It occurs in a number of crystalline salts.

Only Mg^{2+} and Ca^{2+} show any appreciable tendency to form *complexes* and in solution, with a few exceptions, these are of oxygen ligands. The compounds $MgBr_2$, MgI_2, and $CaCl_2$ are soluble in alcohols and polar organic solvents. Adducts such as $MgBr_2(OEt_2)_2$ and $MgBr_2(THF)_4$ can be obtained.

Oxygen chelate complexes, among the most important being those with ethylenediaminetetraacetate (EDTA) type ligands, readily form in alkaline aqueous solution. For example,

$$Ca^{2+} + EDTA^{4-} = [Ca(EDTA)]^{2-} \qquad (11\text{-}5.1)$$

The cyclic polyethers and related nitrogen compounds form strong complexes whose salts can be isolated. The complexing of calcium by $EDTA^{4-}$ and by polyphosphates is of importance not only for removal of Ca^{2+} from water, but also for the volumetric estimation of Ca^{2+}.

Both Mg^{2+} and Ca^{2+} have important biological roles (Chapter 31). The tetrapyrrole systems in chlorophyll form an exception to the rule that complexes of Mg (and the other elements) with nitrogen ligands are weak.

11-6 Summary of Group Trends for the Elements of Group IIA(2)

By using the list of periodic chemical properties developed in Section 8-11, together with the information given in this chapter, we can summarize the periodic trends in the chemical properties of the elements of Group IIA(2).

1. Beryllium
   (a) Forms covalent compounds almost exclusively, even with the most electronegative elements.
   (b) Does not form ionic compounds containing simple Be^{2+} ions, but does readily achieve a maximum coordination number of four, through formation of complex ions such as BeF_4^{2-} and $Be(H_2O)_4^{2+}$, in which the Be-to-ligand bonds possess considerable covalent character.
   (c) Forms a series of organo derivatives, BeR_2 and $[BeR_3]^-$, which contain covalent Be—C bonds.
   (d) The oxide and especially the hydroxide are amphoteric, reacting either with acids or aqueous OH^-.
   (e) The halides are covalent polymers that are readily hydrolyzed or cleaved by donors.
   (f) The hydride is a covalent polymer.

2. Magnesium
   (a) Forms ionic substances that have partial covalent character.
   (b) Forms many ionic substances containing the uncomplexed Mg^{2+} ion, and forms numerous coordination compounds having a maximum coordination number of six.
   (c) Forms an important series of organo derivatives, namely, the Grignard reagents RMgX and the dialkyls MgR_2, both of which are discussed in Chapter 29.
   (d) The oxide is basic, and the hydroxide is only weakly basic compared to the lower members of the group. Also, the hydroxide, unlike $Be(OH)_2$, does not dissolve in aqueous hydroxide.
   (e) The halides are essentially ionic.
   (f) The hydride is only partially covalent.
3. Calcium, Strontium, and Barium
   (a) Form only ionic substances.
   (b) Do not form covalent bonds as in the alkyls of magnesium.
   (c) The oxides are basic, and the hydroxides are strong bases, the solubility increasing with atomic number.
   (d) The halides are crystalline ionic substances that are readily hydrated.
   (e) The hydrides are ionic and powerfully hydridic, as discussed in Chapter 9, and illustrated in Fig. 9-4.

STUDY GUIDE

Study Questions

A. Review

1. Name the important minerals of the Group IIA(2) elements.
2. Why do these metals have higher melting points than the alkali metals?
3. Why does beryllium tend to form covalent compounds?
4. Why do linear molecules X—Be—X exist only in the gas phase?
5. Which compound, when dissolved in water, would give the most acid solution, $BeCl_2$ or $CaCl_2$?
6. Draw the structures of $BeCl_2$ and $CaCl_2$ in the solid state.
7. How is magnesium made?
8. What are the properties of the hydroxides, $M(OH)_2$?
9. How do the solubilities of (a) hydroxides, (b) chlorides, and (c) sulfates vary in Group IIA(2)?
10. What and where are the Dolomites from which $MgCO_3 \cdot CaCO_3$ gets its name?
11. What is an important fact about beryllium compounds from a safety point of view?
12. Compare the physical properties of Be, Mg, Ca, and Sr.
13. Do the alkaline earth cations form many complexes? Which cations tend most to do so and what are the best complexing agents?
14. What are the main types of compounds formed by the alkaline earth elements? Are they generally soluble in water?

B. Additional Exercises

1. Beryllium readily forms a compound of stoichiometry $Be_4O(CO_2CH_3)_6$. Write a likely structure for this compound.
2. Write a balanced chemical equation for the synthesis of hydrogen peroxide using barium oxide.
3. Why do you think that the usual coordination numbers for Be^{2+} and Mg^{2+} are four and six, respectively?
4. The hydroxide of beryllium (actually a hydrous metal oxide) is a white, gelatinous substance that is amphoteric. Write balanced chemical equations for its reaction with H^+ and with OH^-.
5. Why does the increase in the number of valence electrons for the alkaline earth metals over that for the alkali metals give the alkaline earths higher melting points, higher boiling points, and higher densities?
6. Write balanced equations for one method of preparation of each of the metals of this group.
7. Describe the bonding in the chainlike $[Be(CH_3)_2]_n$.
8. Describe the bonding in $BeCl_2(g)$ and $[BeCl_2]_n(s)$.
9. Sketch a likely structure for $(BeCl_2)_2$, based on information provided in this chapter.
10. What type of compound does one expect on dissolution of $BeCl_2$ in donor solvents? Give two examples, with equations.
11. Write equations for each of the following reactions:
    (a) Reduction of $BeCl_2$ with magnesium.
    (b) Ignition of finely powered Be in air.
    (c) Dissolution of Be in aqueous KOH.
    (d) Dissolution of $Be(OH)_2$ in aqueous KOH.
    (e) Hydrolysis of $Be(NH_3)_4Cl_2$.
    (f) Ligand substitution in the tetraaquaberyllate ion by excess aqueous fluoride ion.
    (g) A nonaqueous synthesis of the tetrafluoroberyllate ion.
    (h) Thermal decomposition of $(NH_4)_2BeF_4$.
    (i) Hydrolysis of $BeCl_2$.
    (j) Reaction of beryllium hydroxide in refluxing acetic acid.
12. Unlike the aqua ion of beryllium, $Mg^{2+}(aq)$ has coordination number six. Also, the aqua ion of Mg^{2+} undergoes more rapid water exchange (Chapter 6) and does not ionize a proton as shown for $[Be(H_2O)_4]^{2+}$ in Reaction 11-2.1. Explain these differences based on a comparison of the properties of Be and Mg.

C. Problems from the Literature of Inorganic Chemistry

1. Consider the paper by R. Aruga, *Inorg. Chem.*, **1980**, *19*, 2895–2896.
    (a) What are the three series or behaviors in stability constants that are listed in the introduction?
    (b) How is each series distinguished?
    (c) Into which series do the Group IIA(2) cation complexes of iminodiacetate fit? of thiosulfate? of sulfate? of malate?
    (d) For which behavior (series) is entropy an important factor in determining the stability of the complexes?
2. Answer the following questions concerning lithium tri-*tert*-butylberyllate after reading the article by J. R. Wermer, D. F. Gaines, and H. A. Harris, *Organometallics*, **1988**, *7*, 2421–2422.

(a) What are the important structural facts for the title compound as far as the Be atom is concerned? Concerning the Li atom?

(b) What facts about the structure and physical properties of the title compound indicate a covalent nature for the bonding of Li in this compound?

SUPPLEMENTARY READING

Bell, N. A., “Beryllium Halides and Complexes,” *Adv. Inorg. Chem. Radiochem.*, **1972,** *14,* 225.

Boynton, R. S., *Chemistry and Technology of Lime and Limestone,* 2nd ed., Wiley, New York, 1980.

Dietrich, B., “Coordination-Chemistry of Alkali and Alkaline-Earth Cations with Macrocyclic Ligands,” *J. Chem. Educ.*, **1985,** *63,* 954.

Everest, D. A., *The Chemistry of Beryllium,* Elsevier, Amsterdam, 1964.

Hughes, M. N. and Birch, N. J., “IA and IIA Cations in Biology,” *Chem. Br.*, **1982,** 196–198.

Poonia, N. S. and Bajag, A. V., “Complexes of the Group II Elements,” *Coord. Chem. Rev.*, **1988,** *87,* 55.

Skilleter, D. N., “Properties, Uses and Toxicity of Beryllium,” *Chem. Br.*, **1990,** 26.

Sobota, P., “$MgCl_2$ Reactions and Complexes,” *Polyhedron,* **1992,** *11,* 715.

Spiro, T. G., Ed., *Calcium in Biology,* Wiley-Interscience, New York, 1983.

Wacker, W. E. C., *Magnesium and Man,* Harvard University Press, Cambridge, MA, 1980.