

## 5 Chemistry of Main-Group Metals

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Metals show metallic luster, are good conductors of electricity and heat, and are very malleable and ductile. Such properties are characteristic of bulk metals, although the definition of metal atoms or ions is not simple. Metallic elements form basic oxides or hydroxides in the +1 or +2 oxidation states, and become cations in aqueous acid solutions. All transition elements are metals, but main group elements are classified into metallic and nonmetallic elements. Germanium and polonium may also be included as metals. Boron, silicon, germanium, arsenic, antimony, selenium, and tellurium exhibit some metallic characteristics and they are sometimes called metalloids.

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### 5.1 Group 1 metals

Group 1 metals are called **alkali metals**. Alkali metals are abundant in minerals and sea water. Especially the content of sodium, Na, in the Earth's crust is fourth after Al, Fe, and Ca. Although the existence of sodium or potassium ions was recognized for many years, a number of attempts to isolate the metals from aqueous solutions of their salts failed because of their high reactivity with water. Potassium (1807) and subsequently sodium were isolated by the electrolysis of molten salt of KOH or NaOH by H. Davy in the 19th century. Lithium Li was discovered as a new element (1817), and Davy soon isolated it by molten salt electrolysis of  $\text{Li}_2\text{O}$ . Rubidium, Rb and Cesium, Cs, were discovered as new elements by spectroscopy in 1861. Francium, Fr, was discovered using a radiochemical technique in 1939. Its natural abundance is very low.

**Table 5.1** Properties of group 1 metals

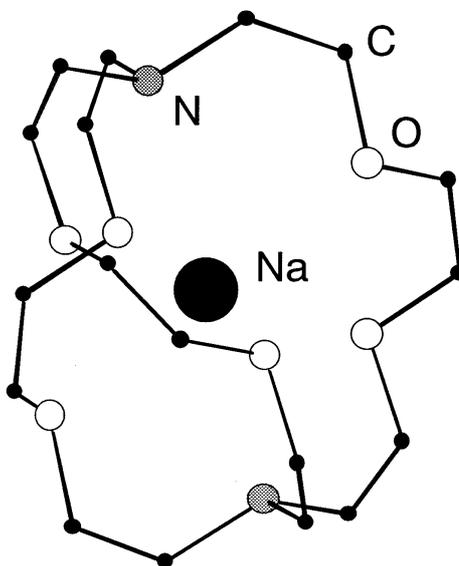
	mp (°C)	bp (°C)	d(20 °C) (g cm <sup>-3</sup> )	E <sup>0</sup> (V) M <sup>+</sup> +e <sup>-</sup>	I (kJ mol <sup>-1</sup> )
Li	181	1342	0.534	-3.04	520
Na	98	883	0.968	-2.71	496
K	63	759	0.856	-2.93	419
Rb	39	688	1.532	-2.98	403
Cs	28	671	1.90	-3.03	376

As shown in Table 5.1, melting-points, boiling points, and densities of alkali metals are low, and they are soft metals. Since the outer shell contains only one *s*-electron, the

ionization energy is very low, and mono cations of alkali metals form easily. Qualitative analysis of alkali metals is possible by means of flame reactions using characteristic luminescence lines. Especially the orange D-line of sodium is used in the sodium lamp. Alkali metals are oxidized by water evolving hydrogen gas due to their low reduction potentials. Except lithium, the heavier alkali metals react violently with water, and sufficient caution should be exercised in their handling.

**Exercise 5.1** Describe the reactivity of alkali metals in water.

[Answer] The reactivity of lithium is the lowest, sodium reacts violently, and potassium, rubidium, and cesium react explosively.

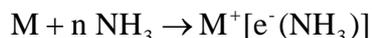


**Fig. 5.1** Structure of Na(crypt).

Alkali metals are also highly reactive to oxygen or halogens. As alkali metals are very reducing, they are used widely as reducing agents. Because of the high affinity of alkali metals to halogens, they are important in organic and inorganic syntheses which produce alkali metal halides as the result of condensation and metathesis reactions. Although it is generally difficult to dissolve metals in solvents to make atomic dispersions, alkali metals can be dispersed in liquid ammonia solutions, amalgams, and as cryptand (Fig. 5.1), naphthalene, or benzophenone ( $C_6H_5$ )<sub>2</sub>CO complexes.

Ammonia boils at  $-33.35\text{ }^\circ\text{C}$  but liquid ammonia can be easily handled. Alkali metals dissolve readily in liquid ammonia and dilute solutions are blue but concentrated ones show a bronze color. The metal is recovered when ammonia is evaporated from

metal solutions. Alkali metal solutions show the same color irrespective of the kind of alkali metals as the color is due to the solvated electrons. Namely, the dissolution is accompanied by the separation of the alkali metal atoms into metal cations and electrons solvated by ammonia, according to the following equation.



The liquid ammonia solution of an alkali metal is conductive and paramagnetic. The highly reducing solution is used for special reduction reactions or syntheses of alkali metal complexes and polyhalides.

## 5.2 Group 2 metals

Group 2 metals from beryllium Be, to radium, Ra, are also called **alkaline earth metals** (Table 5.2). Beryllium is a component of beryl or emerald. Emerald is a mineral that contains about 2% of chromium, Cr, in beryl,  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ . Beryllium metal is silver white and is used in special alloys and for the window of X-ray tubes, or a moderator of nuclear reactors, *etc.* Compounds of  $\text{Be}^{2+}$  resemble the compounds of  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ . Since beryllium is a deadly poison, it should be handled with due care.

**Table 5.2** Properties of group 2 metals

	mp (°C)	bp (°C)	$d(20\text{ °C})$ (g cm <sup>-3</sup> )	$E^0(\text{V})$ $\text{M}^{2+}+2\text{e}^-$	$I$ (kJ mol <sup>-1</sup> )	
					first	second
Be	1287	2471	1.85	-1.85	899	1757
Mg	650	1090	1.74	-2.37	737	1450
Ca	842	1484	1.55	-2.87	590	1145
Sr	777	1382	2.63	-2.90	549	1064
Ba	727	1897	3.62	-2.91	503	965
Ra	700		5.5	-2.82	509	975

Magnesium, Mg, is mainly produced as carbonates, sulfates, and silicates, and its abundance is between those of sodium and calcium, Ca. It is produced by molten salt electrolysis of magnesium chloride,  $\text{MgCl}_2$ , or the reaction of dolomite,  $\text{CaMg}(\text{CO}_3)_2$ , with ferrosilicon alloy FeSi. Magnesium metal is silver white and the surface is oxidized in air. At high temperatures, magnesium reacts with nitrogen gas to become nitride,  $\text{Mg}_3\text{N}_2$ . The metal burns very brightly and is still used for flash lights. The alloy with aluminum is light and strong and used as a structural material in cars and airplanes.

$\text{Mg}^{2+}$  is the central metal ion in the porphyrin ring of chlorophyll, and plays an

important role in photosynthesis. The Grignard reagent,  $\text{RMgX}$ , which F. A. V. Grignard of France synthesized in 1900, is a typical organometallic compound of a main-group metal and is widely used for Grignard reactions. This is an important reagent rewarded by a Nobel prize (1912), and is very useful not only for organic reactions but also for the conversion of metal halides into organometallic compounds.

Calcium is contained in silicates, carbonates, sulfates, phosphates, fluorite, *etc.* Calcium is a silver white and soft metal that is manufactured by molten salt electrolysis of calcium chloride  $\text{CaCl}_2$ .

Quick lime,  $\text{CaO}$ , is produced by the calcination of limestone,  $\text{CaCO}_3$ , at 950-1100 °C. Production of quick lime ranks second to sulfuric acid in inorganic chemical industries. Calcium hydroxide,  $\text{Ca(OH)}_2$ , is called also slaked lime. Calcium carbonate is the principal component of limestone and limestone is very important for the production of cement. Gypsum is a dihydrate of calcium sulfate  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and is obtained in large quantities as a by-product of stack gas desulfurization, and in addition to conventional uses is also used as a building material, *etc.*

Although calcium is not important in either the chemistry of aqueous solution systems or in organometallic chemistry in organic solvents, the element plays very important roles in living organisms. Not only is calcium the structure material of bones and teeth, calcium ions also have a wide range of functions in biological systems, such as protein stabilization, transfer of hormone action, muscular contraction, nerve communication, and blood coagulation.

Strontium, Sr, is a silver white soft metal. The surface is oxidized by air at room temperature, and it becomes a mixture of oxide,  $\text{SrO}$ , and nitride,  $\text{Sr}_3\text{N}_2$ , at high temperatures. In spite of the relatively high content of strontium in the Earth's crust, the element has not been studied widely and its application is limited. There are four natural isotopes and  $^{88}\text{Sr}$  (82.58%) is the most abundant. Since the artificial isotope  $^{90}\text{Sr}$  is obtained cheaply by nuclear reaction, it is used as a source of  $\beta$  particles, and as a radioactive tracer. However, this isotope, as well as  $^{137}\text{Cs}$ , has a long half-life (28.8 y) and both are present in the radioactive fallout that accompanies nuclear explosive tests. Both are considered to be very dangerous.

The chemistry of barium, Ba, is unexceptional but  $\text{BaSO}_4$  is used as a contrast medium for X-ray diagnosis of the stomach because it is insoluble in hydrochloric acid. The  $\text{Ba}^{2+}$  ion is highly toxic and water-soluble compounds containing the ion should be handled cautiously.

Although radium, Ra, exists in uranium ores, the content is as low as  $10^{-6}$  times that of uranium, U. Mr. and Mrs. Curie isolated a trace quantity of uranium chloride from tons of pitchblende in 1898. Elemental uranium was also isolated by Mrs. Curie via an

amalgam. Although radium has historical importance in radiochemistry, it is no longer used as a radiation source.

**Exercise 5.2** Show examples of main group organometallic compounds which are often used in synthetic chemistry.

[Answer] Butyl lithium, LiBu, Grignard reagent, RMgBr, triethylaluminum, AlEt<sub>3</sub>, and diethyl zinc ZnEt<sub>2</sub>.

### 5.3 Group 12 metals

Sulfide ores of zinc, Zn, cadmium, Cd, and mercury, Hg, of Group 12 metals (Table 5.3) serve as raw materials in metallurgy. These metals are located immediately after the transition metals in the periodic table but they do not behave like transition metals because their *d* orbitals are filled, and zinc and cadmium exhibit properties intermediate between hard and soft reactivities of magnesium. Mercury is soft and a liquid and it tends to bond to phosphorus or sulfur ligands. Mercury forms monovalent and divalent compounds but monovalent mercury is actually Hg<sub>2</sub><sup>2+</sup>. This is a cationic species which has a Hg-Hg bond, and mercury further catenates to give, for example, Hg<sub>4</sub>(AsF<sub>6</sub>)<sub>2</sub>.

**Table 5.3** Properties of group 12 metals

	mp	bp	<i>d</i> (25 °C)	<i>E</i> <sup>0</sup> (V)	<i>I</i> (kJ mol <sup>-1</sup> )		
	(°C)	(°C)	(g cm <sup>-3</sup> )	M <sup>2+</sup> +2e <sup>-</sup>	first	second	third
Zn	420	907	7.14	-0.76	906	1733	3831
Cd	321	767	8.65	-0.40	877	1631	3644
Hg	-38.8	357	13.5	0.85	1007	1809	3300

Cadmium and mercury are poisonous, especially organic cadmium and organic mercury compounds are deadly poisons and should be handled carefully.

### 5.4 Group 13 metals

Aluminum, Al, among Group 13 metals (Table 5.4) exists as aluminosilicates in the Earth's crust and is more abundant than iron. The most important mineral for metallurgy is bauxite, AlO<sub>x</sub>(OH)<sub>3-2x</sub> (0 < x < 1). Although the Al metal was as valuable as noble metals in the 19th century, the price fell dramatically after it came to be manufactured in large quantities by electrolysis of alumina, Al<sub>2</sub>O<sub>3</sub>, melted in cryolite, Na<sub>3</sub>AlF<sub>6</sub>. However, because its production requires consumption of a large amount of electrical power, the metallurgy of aluminum is economically feasible only in countries where the price of

electrical power is low. Therefore, Japan has withdrawn from aluminum smelting, but Japan's consumption of the metal is second only to the United States. The properties of aluminum are well known as it is widely used and encountered in every day life, for example in one-yen coins, aluminum foil, cooking pans, aluminum window sashes, *etc.* Aluminum metal usually exceeds 99% purity, and the metal itself and its alloys, like duralumin, are widely used.

**Table 5.4** Properties of group 13 metals

	mp (°C)	bp (°C)	$d(20\text{ }^\circ\text{C})$ (g cm <sup>-3</sup> )	$E^0(\text{V})$ $\text{M}^{3+}+3\text{e}^-$	$I(\text{kJ mol}^{-1})$		
					first	second	third
Al	660	2519	2.70	-1.66	577	1816	2744
Ga	29.8	2204	5.90	-0.55	579	1979	2962
In	157	2072	7.31	-0.34	558	1820	2704
Tl	304	1473	11.9	+0.74	589	1971	2877

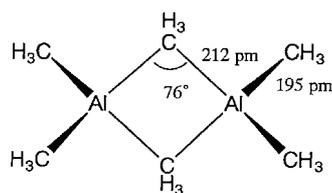
Aluminum metal dissolves in mineral acids, except concentrated nitric acid, and in aqueous solutions of alkali metal hydroxides evolving hydrogen. Aluminum forms compounds with most nonmetallic elements and shows a rich chemistry, but unlike boron, no cluster hydrides are known. As oxide and halides have already been described (4.3 (c), 4.5 (d)), organo-aluminum compounds will be mentioned here.

### Organoaluminum compounds

Organoaluminum compounds are used in large quantities for olefin polymerization, and they are industrially manufactured from aluminum metal, hydrogen, and an olefin as follows.



They are dimers except those with bulky hydrocarbyl groups. For example, trimethylaluminum,  $\text{Al}_2(\text{CH}_3)_6$ , is a dimer in which methyl groups bridge aluminum atoms by electron deficient bonds (Fig. 5.2). Organoaluminum compounds are very reactive and burn spontaneously in air. They react violently with water and form saturated hydrocarbons, with aluminium changing to aluminium hydroxide as follows.



**Fig. 5.2** Structure of trimethylaluminum.



Therefore, they should be handled in the laboratory under a perfectly inert atmosphere. The Ziegler-Natta catalyst, comprising an organoaluminium compound and a transition metal compound was an epoch-making olefin polymerization catalyst developed in the 1950s, for which the Nobel prize (1963) was awarded.

A transition-metal alkyl compound is formed when an organoaluminum compound reacts with a transition-metal compound. The transition-metal alkyl compound so formed can be isolated when stabilization ligands are coordinated to the metal center.

Gallium, Ga, has the largest temperature difference of the melting point and boiling point among all the metals. Since it melts slightly above a room temperature, the temperature range of the liquid state is very wide and it is used as a high temperature thermometer. In recent years, the metal is used for the manufacture of the compound semiconductors gallium arsenide, GaAs, and gallium phosphide, GaP.

Indium In is a soft metal also with a low melting-point. It is the raw material for compound semiconductors InP, InAs, *etc.* Indium has two stable states, In (I) or In (III), and In (II) compounds are considered to be **mixed-valence compounds** of monovalent and trivalent In.

Thallium Tl also has two stable states, Tl (I) and Tl (III), and Tl (II) is a mixed valence compound of monovalent and trivalent Tl. Since the element is very poisonous, the metal and its compounds should be handled carefully. As it is a weak reductant compared to Na(C<sub>5</sub>H<sub>5</sub>), thallium cyclopentadienide, Tl(C<sub>5</sub>H<sub>5</sub>), is sometimes used for the preparation of cyclopentadienyl compounds, and is a useful reagent in organometallic chemistry.

**Exercise 5.3** Give the example of the metals for which stable ions differing in oxidation numbers exist.

[Answer] In(I), In(III), Tl(I), Tl(III), Sn(II), Sn(IV).

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### The reaction of organoaluminum compounds

Organoaluminum compounds were synthesized for the first time in 1859, but they were not regarded as important as Grignard reagents or organolithium compounds as synthetic reagents for some time. This is in part due to the low reactivity of the ether adducts,  $R_3Al:OEt_2$ , which were present because of the frequent use of ether as a solvent. The studies of K. Ziegler changed this situation. K. Ziegler also discovered oligomerization of ethylene by organoaluminum compounds and the formation of higher organoaluminum compounds by the insertion of ethylene in aluminum-carbon bonds. Since alcohols were formed by hydrolysis of organoaluminum compounds, these discoveries were important for organic synthesis.

The discovery of the action of trace amount of nickel in the reaction vessel to give only butene from ethylene led to investigation of the effect of transition metals upon this reaction. Many transition metal salts were examined and Ziegler discovered that titanium compounds gave the highest degree of polymerization of ethylene. This was the birth of the so-called Ziegler catalysts. It should be remembered that this great discovery of the 1950s occurred when the petrochemical industry was beginning to develop and revolutionized the chemical industry of higher polymers.

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### 5.5 Group 14 metals

Of the ten isotopes of tin, Sn,  $^{118}\text{Sn}$  (24.22%) and  $^{120}\text{Sn}$  (33.59%) are the most abundant. Metallic tin is present as  $\alpha$  tin (gray tin), which is stable below 13.2 °C and  $\beta$  tin which is stable at higher temperatures. At low temperatures, the phase transition is quick. Divalent and tetravalent compounds are common, and divalent compounds are reducing agents.

$^{208}\text{Pb}$  (52.4%) is the most abundant among the four stable isotopes of lead, Pb. Lead is the end product of natural radioactive decay and has 82 protons. The atomic number 82 is important as it is especially stable. Thus, Pb exhibits high abundance for a heavy element. The divalent and tetravalent oxidation states are most common and usually lead is present as  $\text{Pb}^{2+}$  except in organometallic compounds.  $\text{PbO}_2$  is a tetravalent compound and readily becomes divalent, hence it is a very strong oxidizing agent. Although tetraethyl lead was previously used as an anti-knock agent in gasoline, only unleaded gasoline is now permitted for use in Japan.

It has been known since the 1930s that when Ge, Sn, or Pb are reduced by sodium in liquid ammonia, multi nuclear anions such as  $\text{Ge}_9^{4-}$ ,  $\text{Sn}_5^{2-}$ , and  $\text{Pb}_9^{4-}$ , are formed. These

are called Zintl phases. These multi-atom anions were crystallized as  $[\text{Na}(\text{crypt})]_4 [\text{Sn}_9]$  *etc.* recently using a cryptand, and cluster structures have been elucidated.

### **Problem**

**5.1** Write a balanced equation for the formation of butyllithium.

**5.2** Potassium permanganate is insoluble in benzene but it dissolves in this solvent in the presence of a crown ether which is a cyclic polyether. Why is the solubility of potassium permanganate increased in the presence of a crown ether?

**5.3** Why is trimethylaluminum called an electron deficient compound?