

Chapter 3

Group 1: The Alkali Metals

3.1 The Alkali Metal Elements¹

The Group 1 metals have a particular name: the alkali metals. This is due to the formation of alkali (basic) solutions upon their reaction with water. Table 3.1 lists the derivation of the names of the alkali metals.

Element	Symbol	Name
Lithium	Li	Greek <i>lithos</i> meaning <i>stone</i>
Sodium	Na	Latin <i>natrium</i> or Arabic <i>natrun</i> meaning <i>soda</i>
Potassium	K	From the Latin <i>kalium</i> , and from Arabic <i>al-qali</i> meaning <i>plant ashes</i>
Rubidium	Rb	Latin <i>rubidus</i> meaning <i>deepest red</i>
Caesium	Cs	Latin <i>caesius</i> meaning <i>blueish grey</i>
Francium	Fr	Named after France

Table 3.1: Derivation of the names of each of the alkali metal elements.

NOTE: Caesium is the international spelling standardized by the IUPAC, but in the United States it is more commonly spelled as cesium.

3.1.1 Discovery

3.1.1.1 Lithium

Petalite ($\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$) was first discovered in 1800 by José Bonifácio de Andrada e Silva (Figure 3.1), who discovered the mineral in a Swedish mine on the island of Utö. However, it was not until 1817 that Johan August Arfwedson (Figure 3.2) working in the laboratory of Jöns Jakob Berzelius (Figure 3.3), discovered the presence of a new element while analyzing petalite ore. Named from the Greek *lithos* meaning *stone* reflected its discovery in a mineral, as opposed to sodium and potassium, which had been discovered in plant tissue; its name was later standardized as lithium. The element was not isolated until 1821, when William Brande (Figure 3.4) isolated the element by performing electrolysis on lithium oxide, a process previously employed by Sir Humphry Davy to isolate potassium and sodium.

¹This content is available online at <<http://cnx.org/content/m31909/1.2/>>.

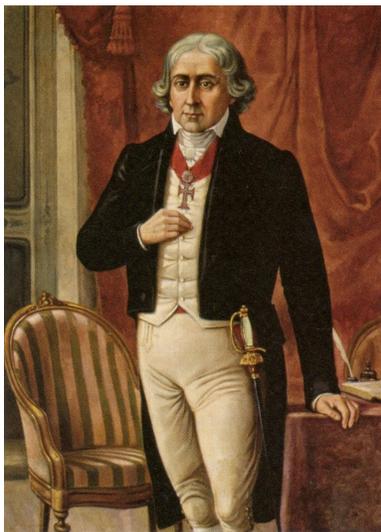


Figure 3.1: Portuguese statesman and naturalist José Bonifácio de Andrada e Silva (1763 - 1838).



Figure 3.2: Swedish chemist Johan August Arfwedson (1792 - 1841).



Figure 3.3: Swedish chemist Friherre Jöns Jacob Berzelius (1779 - 1848).

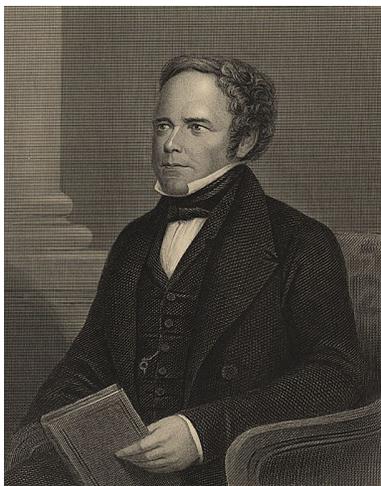


Figure 3.4: English chemist William Thomas Brande FRS (1788 - 1866).

3.1.1.2 Sodium

Elemental sodium was first isolated by Sir Humphry Davy (Figure 3.5) in 1806 by passing an electric current through molten sodium hydroxide.



Figure 3.5: British chemist and inventor Sir Humphry Davy FRS (1778 - 1829).

3.1.1.3 Potassium

The name *kalium* was taken from the word *alkali*, which came from Arabic *al qali* meaning *the calcined ashes*. The name potassium was made from the English word *potash*, meaning an alkali extracted in a pot from the ash of burnt wood or tree leaves. Potassium metal was discovered in 1807 by Sir Humphry Davy (Figure 3.5), who derived it from caustic potash (KOH), by the use of electrolysis of the molten salt.

3.1.1.4 Rubidium

Rubidium was discovered using spectroscopy in 1861 by Robert Bunsen (Figure 3.6) and Gustav Kirchhoff (Figure 3.7) in the mineral lepidolite. The first rubidium metal was produced by Bunsen from the reaction of rubidium chloride (RbCl) with potassium.



Figure 3.6: German chemist Robert Wilhelm Eberhard Bunsen (1811 - 1899).

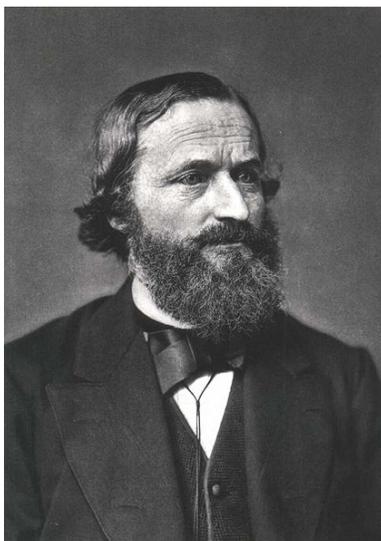


Figure 3.7: German physicist Gustav Robert Kirchhoff (1824 - 1887).

3.1.1.5 Caesium

Like Rubidium, caesium was discovered spectroscopically by Bunsen (Figure 3.6) and Kirchhoff (Figure 3.7) in 1860 in mineral water from Dürkheim, Germany. The residues of 44,000 liters of mineral water yielded several grams of a caesium salt. Its identification was based upon the bright blue lines in its spectrum and it was the first element discovered by spectral analysis. The first caesium metal was subsequently produced in 1882 by electrolysis of caesium chloride.

3.1.1.6 Francium

Originally known as eka-caesium, francium was discovered in 1939 by Marguerite Perey (Figure 3.8) of the Curie Institute in Paris, France when she purified a sample of actinium-227, which had been reported to have a decay energy of 220 keV. However, Perey noticed decay particles with an energy level below 80 keV. Perey thought this decay activity was caused by a previously unidentified element, which exhibited chemical properties of an alkali metal. This led Perey to believe that it was element 87, caused by the alpha decay of actinium-227. Perey named the new isotope actinium-K (now referred to as francium-223) and in 1946, she proposed the name catium for her newly discovered element, however, she subsequently suggested francium, after France.



Figure 3.8: French physicist Marguerite Catherine Perey (1909 - 1975), a student of Marie Curie, and the first woman to be elected to the French Académie des Sciences.

3.1.2 Abundance

The abundance of the alkali metals is given in Table 3.2. Sodium's high abundance is due mainly to large underground deposits of rock salt (NaCl). However, sodium is also more abundant in seawater (10,800 ppm) as compared to potassium (380 ppm).

Element	Terrestrial abundance (ppm)
Li	20 (Earth's crust), 40 (soil), 0.17 (sea water)
Na	23,000 (Earth's crust), 10,500 (sea water)
K	21,000 (Earth's crust), 14 (soil), 380 (sea water)
Rb	90 (Earth's crust), 30 - 250 (soil), 0.1 (sea water)
Cs	3 (Earth's crust), 0.0001 (soil), 0.0003 (sea water)
Fr	Essentially nil

Table 3.2: Abundance of alkali metal elements.

3.1.3 Isotopes

The naturally abundant isotopes of the alkali metals are listed in Table 3.3. All of the isotopes of francium are radioactive. Lithium-7 and sodium-23 are both useful NMR nucleus having $I = 1/2$.

Isotope	Natural abundance (%)
Lithium-6	7.5
Lithium-7	92.5
Sodium-23	100
Potassium-39	93
Potassium-40	0.0118
Potassium-41	6.9
Caesium-133	100

Table 3.3: Abundance of the major isotopes of the alkali metals.

Potassium has three isotopes (Table 3.3), of which potassium-40 is radioactive and provides the basis for the determination of the age of rocks between 10^5 and 10^9 years old, i.e., those formed in proterozoic and cenozoic periods of geological time. The decay of potassium-40 occurs with a half life of 1.31×10^9 years, by two routes. That associated with a beta particle decay accounts for 89% of the decay:



While that associated with an electron capture and by positron emission decay accounts for 11% of the decay to give argon-40. Since many rocks contain potassium containing minerals the decay of potassium-40 after solidification of the rock will result in the formation of argon trapped in the rock. The argon-40 content is determined by mass spectrometry, while the potassium content is determined by flame spectrophotometry. The ratio of the two, (3.2), will allow for the determination of the elapsed time since the rock solidified.

$$\frac{[{}_{18}^{40}\text{Ar}]}{[{}_{19}^{40}\text{K}]} \quad (3.2)$$

Caesium has at least 39 known isotopes (more than any other element except francium) ranging from caesium-112 caesium-151; however, caesium-133 is the only naturally occurring stable isotope. The other isotopes have half-lives from a few days to fractions of a second. The radiogenic isotope caesium-137 is produced from the detonation of nuclear weapons and is produced in nuclear power plants, and was released to the atmosphere most notably from the 1986 Chernobyl accident.

3.1.4 Physical properties

Many of the physical properties of the alkali metals (Table 3.4) are typical of metals, e.g., thermal and electrical conductivity. However, due to the relatively weak inter-atomic forces (weak M-M bonding) they are soft and readily cut with a knife.

Element	Mp (°C)	Bp (°C)	Density (g/cm ³)	Electrical resistivity (Ω·cm)
Li	453	1615	0.534	12.17 @ 86 °C
Na	370	1156	0.968	5.23 @ 29 °C
K	336	1032	0.89	7.01 @ 22.8 °C
Rb	312	961	1.532	12.53 @ 53 °C
Cs	301	944	1.93	37.38 @ 28.1 °C

Table 3.4: Selected physical properties of the alkali metal elements.

3.1.5 Reactivity

All the alkali metals are highly reactive and are as a consequence of the stability of the M⁺ ion are strong reducing agents (Table 3.5). The metals react readily with hydrogen and oxygen.



Reduction	Reduction potential (V)
Li ⁺ + e ⁻ → Li	-3.045
Na ⁺ + e ⁻ → Na	-2.7109
K ⁺ + e ⁻ → K	-2.924
Rb ⁺ + e ⁻ → Rb	-2.925
Cs ⁺ + e ⁻ → Cs	-2.923

Table 3.5: Electrochemical reduction potential for alkali metals.

All of the alkali metals react with water to liberate hydrogen.



WARNING: The reactions of alkali metals with water are exothermic and the heat generated is sufficient to ignite the hydrogen. In addition the solutions formed are highly alkaline. Caution should be taken when handling alkali metals and storage should always be under mineral oil.

A similar, but less violent, reaction is also observed with ammonia when catalyzed by transition metal ions.



In the absence of a catalyst, the Group 1 metals dissolve in liquid ammonia to form solutions with characteristic properties.

- Highly reducing.
- Blue color.
- ESR signal due to solvated electrons.

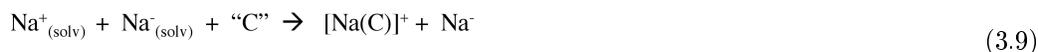
As an example, the dissolution of sodium in liquid ammonia results in the formation of solvated Na^+ cations and electrons.



The solvated electrons are stable in liquid ammonia and form a complex: $[\text{e}^-(\text{NH}_3)_6]$. It is this solvated electron that gives the strong reducing properties of the solution as well as the characteristic signal in the ESR spectrum associated with a single unpaired electron. The blue color of the solution is often ascribed to these solvated electrons; however, their absorption is in the far infra-red region of the spectrum. A second species, $\text{Na}^-_{(\text{solv})}$, is actually responsible for the blue color of the solution.



The formation of the sodium anion is confirmed by complexation of the cation with a cryptan ligand (“C”) such as a crown ether.



The resulting complex is found to be isostructural to the iodide analog in the solid state.



3.1.6 Vapor phase

All the alkali metals form M_2 dimers in the vapor phase in an analogous manner to hydrogen. As with dihydrogen the bonding is associated with the molecular orbital combination of the two valence s-orbitals (Figure 3.9).

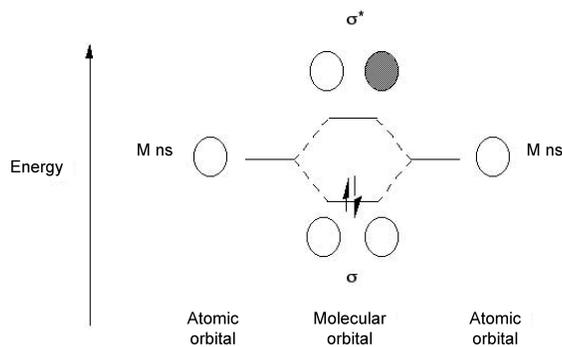


Figure 3.9: Molecular orbital diagram for the formation of M_2 .

Sodium vapor is commonly used for lighting in a gas discharge lamp, which uses sodium in an excited state to produce light (Figure 3.10). There are two varieties of such lamps: low pressure and high pressure.



Figure 3.10: A low pressure sodium streetlamp.

3.2 Compounds of the Alkali Metals²

The chemistry of the alkali metals is dominated by the stability of the +1 oxidation state and the noble gas configuration of the M^+ cation. The alkali metals all have low first ionization energies (Table 3.6) but very high second ionization energies.

²This content is available online at <http://cnx.org/content/m31917/1.3/>.

Element	1 st ionization energy (kJ/mol)
Li	526
Na	502
K	425
Rb	409
Cs	382

Table 3.6: First ionization potentials for the alkali metals.

As a consequence of the stability of M^+ , the Group 1 metals have the least variation in chemistry of the any Group in the periodic table. The only exceptions are the subtle trends that exist for lithium due to its small size (Table 3.7). All of the metals are more electropositive than hydrogen (Table 3.8).

Element	Atomic radius (Å)	Ionic radius (Å)	Covalent radius (Å)	Van der Waals radius (Å)
Li	1.52	0.68	1.52	1.82
Na	1.86	0.97	1.53	2.27
K	2.31	1.33	1.90	2.75
Rb	2.44	1.47	2.47	-
Cs	2.62	1.67	2.65	-
Fr	-	1.80	2.70	-

Table 3.7: Radii of alkali metals. N.B. Some values are unknown.

Element	Electronegativity
H	2.20
Li	0.98
Na	0.93
K	0.82
Rb	0.82
Cs	0.79
Fr	0.70

Table 3.8: Pauling electronegativities of Group 1 elements.

3.2.1 Solid state

In the solid state the compounds of the alkali metals generally form ionic lattices, e.g., Na^+Cl^- . These structures are essentially electrostatic in nature and the lattice energy is usually defined as the enthalpy of formation of the ionic compound from gaseous ions and as such is invariably exothermic.



In all cases the lattice energy is high and is found to be proportional to the ratio of the charges on the ions and the sum of the ionic radii (r).

$$U \propto \frac{z^+z^-}{\Sigma(r)} \quad (3.12)$$

The ionic radii for alkali metal cations are given in Table 3.7; those for common anions are given in Table 3.9.

Anion	Ionic radius (Å)
F ⁻	1.33
Cl ⁻	1.81
Br ⁻	1.96
I ⁻	2.20
H ⁻	1.54
O ²⁻	1.32

Table 3.9: Ionic radii of common anions.

The ratio of the ionic radii (r^+/r^-) neatly defines the structural type observed for alkali metal salts (Table 3.10). The unit cells for ZnS (zinc blende), NaCl (rock salt), and CsCl are shown in Figure 3.11, Figure 3.12, and Figure 3.13, respectively.

r^+/r^-	Structural type	Metal coordination number
0.225 – 0.414	ZnS (zinc blende)	4
0.414 – 0.732	NaCl (rock salt)	6
0.732 -	CsCl	8

Table 3.10: Defining MX structural types for alkali metal salts.

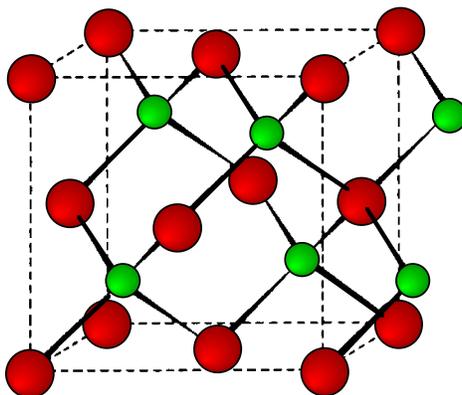


Figure 3.11: Unit cell structure of a zinc blende (ZnS) lattice.

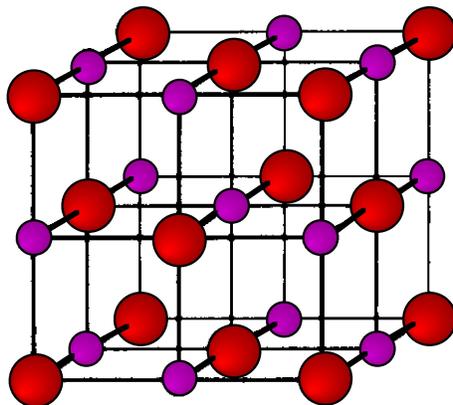


Figure 3.12: Unit cell structure of a rock salt lattice.

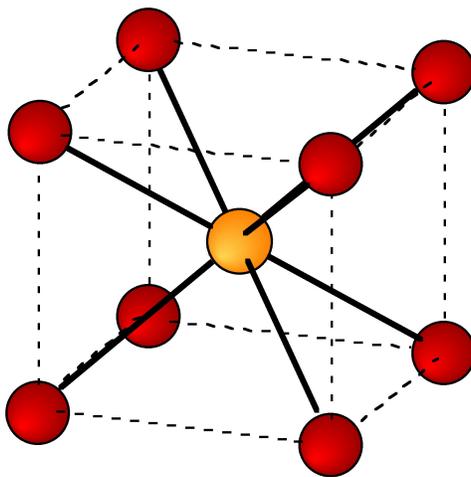


Figure 3.13: Unit cell of CsCl.

As an example, the structure of KBr can be predicted from the data in Table 3.7 and Table 3.9. The ionic radius of K^+ is 1.33 \AA , while that for Br^- is 1.96 \AA . The ratio of the ionic radii (r^+/r^-) is 0.67. Hence, KBr has a NaCl (rock salt) structure.

Exercise 3.2.1

What is the structure of NaH?

(Solution on p. 130.)

Exercise 3.2.2

What is the structure of RbF?

(Solution on p. 130.)

3.2.2 Complexes

The coordination complexes of the alkali metal cations (M^+) involve electrostatic, or ion-dipole, interactions (Figure 3.14) that have no preferred direction of interaction. Thus, the ionic radius of the cation (Table 3.7) controls the coordination numbers of the metal in its complexes (Table 3.11).

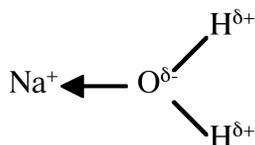


Figure 3.14: A schematic representation of the ion-dipole or electrostatic interaction of Na^+ with water.

Aquo ion	n
$[Li(H_2O)_n]^+$	4
$[Na(H_2O)_n]^+$	6
$[K(H_2O)_n]^+$	6
$[Rb(H_2O)_n]^+$	6 - 8
$[Cs(H_2O)_n]^+$	8

Table 3.11: Coordination number for alkali metal ions in aqueous complexes.

In general the alkali metal ions form complexes with hard donor such as oxygen (H_2O , ROH , RCO_2^- , etc.) or nitrogen (e.g., NH_3 , NR_3 , etc.). The aquo complexes readily exchange the water for other ligands, (3.13); however, the equilibrium constants are small when the ligand is similar in size to water.



As a consequence of the low equilibrium constants for monodentate ligands, the alkali metal cations, M^+ , favor coordination to polydentate ligands such as ethylenediaminetetraacetic acid (EDTA, Figure 3.15), polyethers, and even natural polyesters or polypeptides. In each case the polydentate ligand wraps itself around the cation.

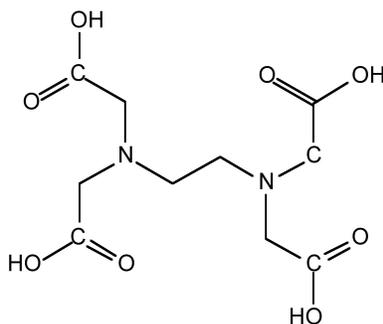


Figure 3.15: Structure of ethylenediaminetetraacetic acid (EDTA).

3.2.2.1 Macrocyclic ligands

Macrocyclic ligands represent a special class of polydentate ligand. They are defined as being a cyclic compound with nine or more members including all the heteroatoms and with three or more donor atoms, and are given the special name of cryptands when they are synthetic bi- and poly-cyclic multidentate ligands. Crown ethers is the name applied to macrocyclic ligands that consist of a ring containing several ether groups. Figure 3.16 shows several common macrocyclic ligands.

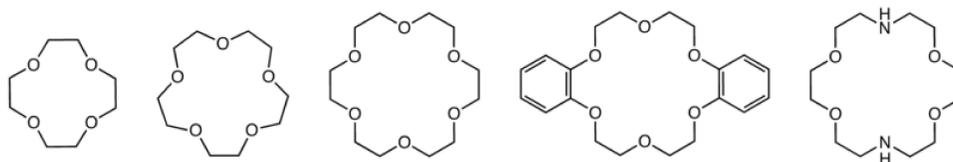


Figure 3.16: The structures of some common macrocyclic ligands.

Macrocyclic ligands are generally oxygen or nitrogen donor ligands, and they form highly stable 1:1 complexes with alkali metal ions in which all or most of the coordination sites on the metal are occupied, i.e., $[M(L)]^+$ rather than $[M(L)(H_2O)_n]^+$. Since the external surface of the macrocyclic ligands comprises of organic residue (e.g., CH_2 groups) the complexes are soluble in organic solvents. Thus, crown ethers are commonly used to solubilize salts (e.g., NaCl) in organic solvents. They have also been used to create solutions of nanoparticles, such as carbon nanotubes (Figure 3.17), that are ordinarily highly insoluble in common organic solvents (Table 3.12).

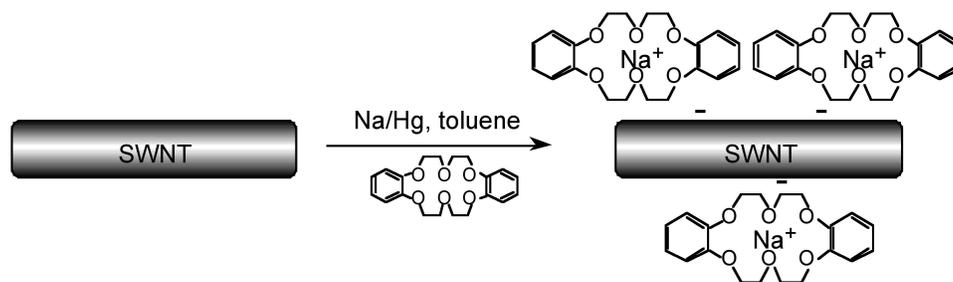


Figure 3.17: Representation of the reaction between Na/Hg amalgam, dibenzo-18-crown-6, and purified single walled carbon nanotubes (SWNTs) in toluene and the formation of the $[\text{Na}(\text{dibenzo-18-crown-6})]_n[\text{SWNT}]$ complex. Adapted from R. E. Anderson and A. R. Barron, *J. Nanosci. Nanotechnol.*, 2007, **7**, 3436.

Solvent	SWNT concentration (mg/L)
CH ₂ Cl ₂	14.05
DMF	11.42
hexane	4.65
toluene	3.79
EtOH	2.37
MeOH	2.37
CHCl ₃	0.30
H ₂ O	0.10

Table 3.12: The concentration of Na/dibenzo-18-crown-6 solubilized reduced single walled carbon nanotubes (SWNTs) in various solvents.

The most important factor in the coordination of various macrocyclic ligands to alkali metal ions is the relative size of the ion and the ligand cavity. For example, 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane is a potentially octa-dentate ligand; however, the binding efficiency is very dependant on the identity of the M^+ ion (Figure 3.18). The low binding constant for lithium is probably as a consequence that the ligand would have to distort to coordinate to the small cation. Conversely, the lower equilibrium for caesium is due to its being too large to fit completely into the ligand cavity.

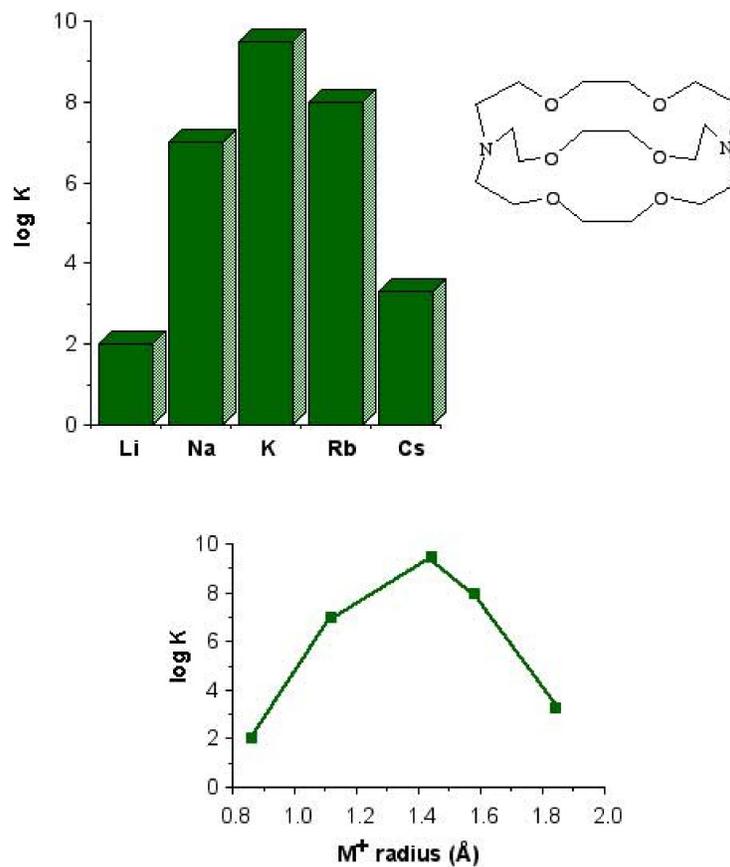


Figure 3.18: Relative stability constants ($\log K$) of alkali metal ions to 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane and relationship to the M^+ ionic radius.

One application of the size effect for macrocyclic ligands is the ability to selectively bind different metals. For example, the 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8,8,5]tricosane and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane ligands shown in Figure 3.19 have very different binding constants to Na^+ and K^+ , as a consequence of the relative size of the cation and the ligand cavity (Table 3.13).

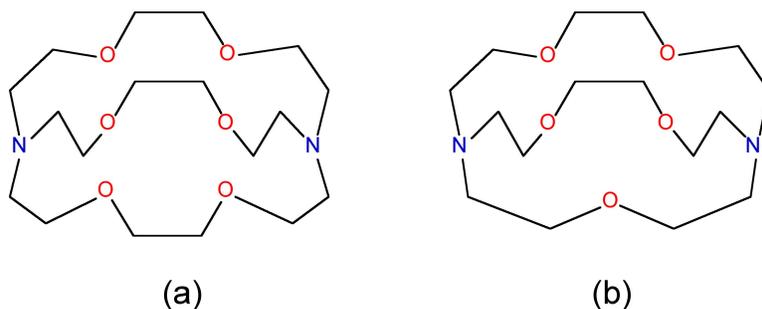


Figure 3.19: Structure of (a) 4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8,8,5]tricosane “[2,2,1]” and (b) 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane “[2,2,2]”.

Cation	[2,2,2]	[2,2,1]
Na ⁺	800	250,000
K ⁺	250,000	700

Table 3.13: Equilibrium constants for the M⁺ complexes for macrocyclic ligands with different cavity sizes. The structures of the ligands are shown in Figure 3.19.

3.2.3 Bibliography

- R. E. Anderson and A. R. Barron, *J. Nanosci. Nanotechnol.*, 2007, **7**, 3436.
- J. M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*. VCH (1995).

3.3 The Anomalous Chemistry of Lithium³

While lithium shows many properties that are clearly consistent with its position in Group 1, it also has key differences to the other alkali metals. In fact, in many ways it is more similar to its diagonal neighbor magnesium (Mg) than the other Group 1 metals.

3.3.1 Charge/radius

The ionic radius for the +1 cation of lithium is very small in comparison with its next highest homolog, sodium (Table 3.14). This results in a correspondingly high value for the charge density (z/r). As may be seen from Table 3.14 the charge density for lithium is significantly higher than that of its Group 1 relations.

³This content is available online at <<http://cnx.org/content/m31918/1.1/>>.

Element	z	r (Å)	z/r (Å ⁻¹)
Li	+1	0.68	1.47
Na	+1	0.97	1.03
K	+1	1.33	0.75
Mg	+2	0.66	3.03

Table 3.14: Comparison of charge densities for lithium, sodium, potassium, and magnesium.

As a result of the high charge density, the Li⁺ ion is a highly polarizing ion. One of the main consequences of this is that lithium tends to form polar covalent bonds rather than ionic interactions. For example, alkyl lithium compounds (RLi) contain covalent Li-C bonds in a similar manner to the Mg-C bonds in Grignards (RMgX, where X = Cl, Br).

3.3.2 Lattice energy

Lithium compounds have high lattice energies as compared to the other Group 1 metals (Table 3.15). As a consequence Li₂O, Li₃N, and LiF are all insoluble in water, whereas their sodium compounds are highly soluble.

Compound	Lattice energy (kJ/mol)
LiF	-1046
NaF	-923
KF	-821
MgF ₂	-2957

Table 3.15: Comparison of lattice energies for compounds of lithium, sodium, potassium, and magnesium.

3.3.3 Coordination number

The small size of lithium results in a lower coordination number (4) for compounds and complexes than observed for the other Group 1 metals. However, lithium and magnesium complexes and organometallic compounds both have most commonly four-coordinate metal centers (in the absence of large steric constraints).

3.3.4 Chemical reactivity

A review of some of the reactions of lithium, magnesium and the other Group 1 metals shows the anomalous behavior of lithium and its similarity to magnesium. Both lithium and magnesium reacts with carbon or nitrogen to form the corresponding carbide and nitride. Whereas sodium and the other Group 1 metals show no reaction under ambient conditions. The combustion of either lithium or magnesium in air results in the formation of the oxides, Li₂O and MgO, respectively. In contrast, sodium forms the peroxide, Na₂O₂.

It is not only in the reactivity of the elements that this relationship between lithium and its diagonal neighbor exists. Many of the compounds of lithium have a similar reactivity to those of magnesium rather than sodium. For example, the carbonates of lithium and magnesium decompose under thermolysis to yield the oxides, (3.14) and (3.15), in contrast, sodium carbonate (Na₂CO₃) is stable to thermolysis.





3.4 Organolithium Compounds⁴

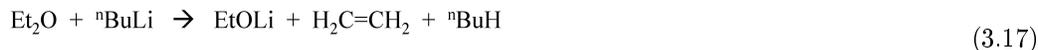
One of the major uses of lithium is in the synthesis of organolithium compounds, RLi. They have great importance and utility in industry and chemical research. Their reactivity resembles that of Grignard reagents, but they are generally more reactive.

3.4.1 Synthesis

The best general method for RLi synthesis involves the reaction of an alkyl or aryl chloride with lithium metal in benzene or an aliphatic hydrocarbon (e.g., hexane), (3.16).



While it is possible to use diethyl ether (Et_2O), the solvent slowly attack the resultant alkyl lithium compound, (3.17).



Metal-hydrogen exchange, (3.18), metal-halogen exchange, (3.19), and metal-metal exchange can also be used, (3.20).



All organolithium compounds are produced as solutions and are hence used in synthetic protocols by volume of solution. It is therefore important to know the exact concentration of RLi in solution. The simplest approach to quantify the amount of organolithium is to react a known volume with water, (3.21), and then titrate (with acid) the resultant base that is formed.



However, while the concentration of freshly prepared samples of organolithium reagents can be theoretically measured in this way, real samples always contain some amount of LiOH or other bases. A simple titration inevitably results in an over estimation of the organolithium reagent. To overcome this a *double titration* method is used.

⁴This content is available online at <<http://cnx.org/content/m32444/1.2/>>.

3.4.1.1 Gillman double titration method

The careful addition of a known volume of an organolithium reagent solution (between 0.5 and 1.5 mL) to an excess of water yields a solution of LiOH that can be titrated with a standardized solution of hydrochloric acid, using phenolphthalein as the indicator. The presence of any LiOH in the original organolithium solution will be incorporated into this titration, and thus the result will be a measure of the *total base content* in the solution, i.e., (3.22).

$$\begin{array}{l} \text{Total base} \\ \text{content} \end{array} = \begin{array}{l} \text{LiOH formed from} \\ \text{the reaction of RLi} \\ \text{with H}_2\text{O} \end{array} + \begin{array}{l} \text{LiOH present as} \\ \text{impurity in the} \\ \text{RLi solution} \end{array} \quad (3.22)$$

In order to determine the amount of LiOH present as impurity in the organolithium solution it is necessary to react the RLi without the formation of base, then titrate the resulting solution. To do this, an aliquot (the same amount as used before) of the organolithium is reacted slowly with 1,2-dibromoethane ($\text{BrCH}_2\text{CH}_2\text{Br}$) dissolved in dry diethyl ether (Et_2O). After 5 min of stirring, the solution is diluted with an excess of water and then titrated with a standardized solution of hydrochloric acid, again using phenolphthalein as the indicator. The difference of the two titrations gives the exact concentration of the organolithium.

Example 3.1

An aliquot of $n\text{BuLi}$ in hexanes (0.50 mL) was added to degassed water (20 mL). After any visible reaction had ceased, a few drops of a phenolphthalein solution in water/methanol are added resulting in a pink color indicative of a basic pH. The resulting mixture is titrated with standardized hydrochloric acid ($[\text{HCl}] = 0.1034 \text{ N}$) until complete disappearance of the pink color (7.90 mL).

A second aliquot of $n\text{BuLi}$ in hexanes (0.50 mL) is added to 1,2-dibromoethane (0.20 mL, Et_2O). After 5 min of stirring, the mixture was diluted with water (20 mL) and after addition of the phenolphthalein indicator titrated (with vigorous stirring due to the biphasic nature of the system) with standardized hydrochloric acid ($[\text{HCl}] = 0.1034 \text{ N}$) until complete disappearance of the pink color (0.25 mL).

The concentration of $n\text{BuLi}$ is calculated as follows:

$$\begin{array}{l} \text{Step 1.} \\ \text{Step 2.} \\ \text{Step 3.} \end{array} \begin{array}{l} [\text{total base}] = \frac{\text{volume HCl} \times [\text{HCl}]}{\text{volume } n\text{BuLi}} = \frac{7.90 \times 0.1034}{0.50} = 1.633 \\ [\text{residual base}] = \frac{\text{volume HCl} \times [\text{HCl}]}{\text{volume } n\text{BuLi}} = \frac{0.25 \times 0.1034}{0.50} = 0.013 \\ [n\text{BuLi}] = [\text{total base}] - [\text{residual base}] = 1.633 - 0.013 = 1.620 \text{ M} \end{array}$$

3.4.2 Properties

Alkyl lithium compounds are either low melting solids or liquids, and often with high volatility (depending on the substituent) due to the covalent nature of the bonding. They are soluble in aliphatics, aromatics, and ethers. However, while the reaction with ethers is generally slow, (3.17), alkyl lithium compounds can polymerize tetrahydrofuran (THF).

Organolithium compounds react rapidly with air and water (both vapor and liquid). The reaction with water is the basis of the Gillman double titration method for determining the concentration of organolithium reagents in solution.

3.4.3 Structure

The structure of organolithium compounds is dominated by their highly oligomeric nature as a result of 3-center 2-electron bridging bonds. In all cases the extent of oligomerization is dependant on the identity of the alkyl (or aryl) group. The alkyl-bridged bond is similar to those found for beryllium and aluminum compounds.

In the vapor phase any particular organolithium derivative show a range of oligomeric structures. For example, the mass spectrum of EtLi shows ions associated with both tetramers (e.g., $[\text{Et}_3\text{Li}_4]^+$) and hexamers (e.g., $[\text{Et}_5\text{Li}_6]^+$). The structures of the different oligomers have been predicted by molecular orbital calculations (Figure 3.20).

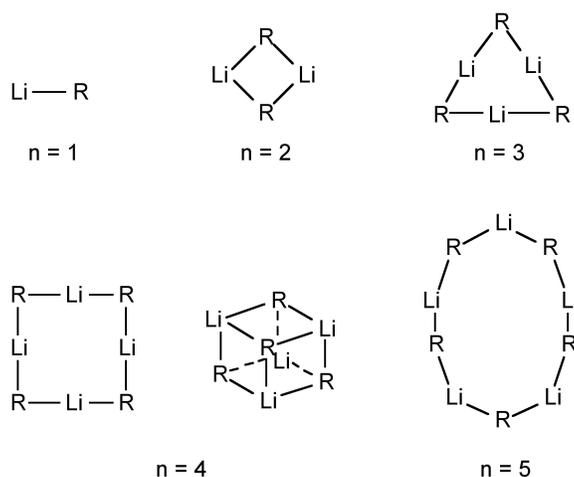


Figure 3.20: Proposed vapor phase structures for various oligomers of RLi.

Solution molecular weight measurements indicate the oligomerization is present (in the absence of a coordinating ligand such as Et_2O or an amine). The extent of oligomerization depends on the steric bulk of the alkyl group (Table 3.16). Oligomerization and solution structures have also been investigated by ^7Li and ^{13}C NMR spectroscopy.

R	$[\text{RLi}]_n$	R	$[\text{RLi}]_n$
Me	4	Et	6
^nBu	6	^tBu	4

Table 3.16: Extent of oligomerization (n) for organolithium compounds $[\text{RLi}]_n$ in benzene solution.

There are a large number of X-ray crystallographically determined structures for organolithium derivatives. The archetypal example is MeLi, which exists as a tetramer in the solid state (Figure 3.21). The lithium atoms are arranged as a tetrahedron and the carbon atoms are positioned on the center of the facial planes, i.e., the carbon is equidistant from each of the lithium atoms. In contrast, EtLi has a similar tetrahedral structure, but the α -carbon of the ethyl groups are asymmetrically arranged such that it is closer to one lithium atom than the other two.

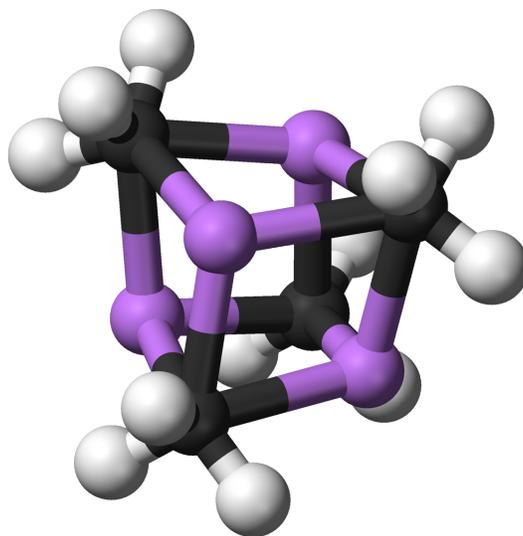


Figure 3.21: Solid state structure of MeLi. Copyright: Ben Mills (2007).

It is possible to prepare monomeric organolithium compounds by the addition of amines, especially chelate ligands such as ethylenediamine (en) and tetramethylethylenediamine (TMED). The reactivity of RLi is increased dramatically by the addition of such Lewis bases. For example, PhCH₂Li shows an increased reactivity of 10⁴ with the addition of TMED.

The bonding in organolithium compounds is difficult to describe:

- Based upon the relative electronegativity of Li (0.98) and C (2.5) it would be expected to have significant ionic character.
- Organolithium compounds form electron deficient oligomers typical of covalent bonding and clearly not as a result of ionic aggregation.
- The spin-spin coupling, $J(\text{C-Li})$, observed by NMR spectroscopy (10 – 15 Hz) are consistent with a covalent bond.
- Organolithium compounds undergo radical reactions.

However, the overall description of the bonding in RLi is that of a covalent interaction with significant polar (ionic) character, i.e., $\text{M}^{\delta+}\text{-C}^{\delta-}$.

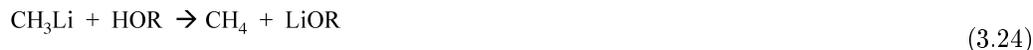
3.4.4 The use of organolithium compounds in organic synthesis

Organolithium compounds perform many of the reactions commonly observed for Grignard reagents. However, lithium reagents are generally more reactive than their Grignard analogs.

3.4.4.1 Hydrolysis

Organolithium compounds react with water to give the hydrocarbon and lithium hydroxide, (3.23). Lithium alkyls also react with other hydroxylic compounds such as alcohols and carboxylic acids, (3.24).



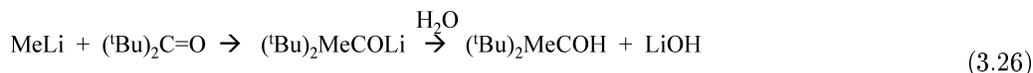


One important use of the hydrolysis reaction is specifically deuteration, (3.25).



3.4.4.2 Reaction with carbonyls

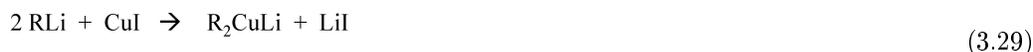
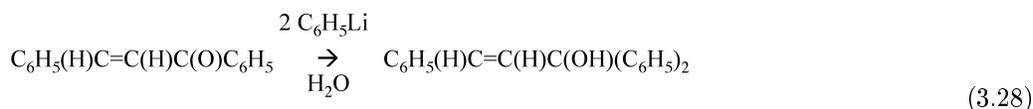
Organolithium compounds react with organic carbonyls (aldehydes, ketones, and esters) to yield the alcohol on hydrolysis, (3.26). This synthetic route is particularly useful since lithium reagents are far more reactive than the analogous Grignard, allowing reactions to be carried out at lower temperatures and minimizing enolization side reactions.



The high reactivity of alkyl lithium compounds means that they react with carboxylic acids to yield the ketone rather than the lithium carboxylate.



Organolithium compounds generally react with α,β -unsaturated ketones to give the 1,2-addition product, (3.28). However, lithium dialkylcuprates, which are formed from the alkyl lithium and copper(I) iodide, (3.29), add exclusively by the 1,4-addition, (3.30).



3.4.4.3 Transmetalation

One of the most useful methods of preparing organometallic compounds is the exchange reaction of one organometallic compound with a salt of a different metal, (3.31). This is an equilibrium process, whose equilibrium constant is defined by the reduction potential of both metals. In general the reaction will proceed so that the more electropositive metal will form the more ionic salt (usually chloride).



Lithium reagents may be used to prepare a wide range of organometallic compounds.



3.4.5 Bibliography

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Solutions to Exercises in Chapter 3

Solution to Exercise 3.2.1 (p. 117)

The ionic radius of Na^+ is 0.97 \AA , while that for H^- is 1.54 \AA . The ratio of the ionic radii (r^+/r^-) is 0.67 . Hence, NaH has a NaCl (rock salt) structure.

Solution to Exercise 3.2.2 (p. 117)

The ionic radius of Rb^+ is 1.47 \AA , while that for F^- is 1.33 \AA . The ratio of the ionic radii (r^+/r^-) is 1.10 . Hence, RbF has a CsCl structure.