

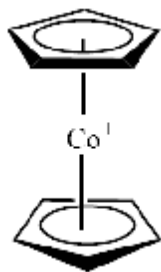
Chapter 10

Group IA (1)

Alkali Metals

Lithium, Sodium, Potassium, Rubidium and Cesium

Similar to H^+ in that they form M^+ . (other cations that are related are NH_4^+ (like K^+) and Tl^+ (Rb^+)).



Na^+ and K^+ are very important physiologically. Cells differentiate between them by specific complexation reactions.

Li^+ salts are used to treat manic depressive disorders.

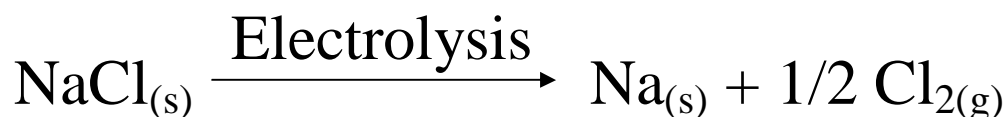
$K^+NO_3^-$ is used in fertilizers.

Na^+ as $NaOH$, Na_2CO_3 , Na_2SO_4 are among the top 50 chemicals in terms of production.

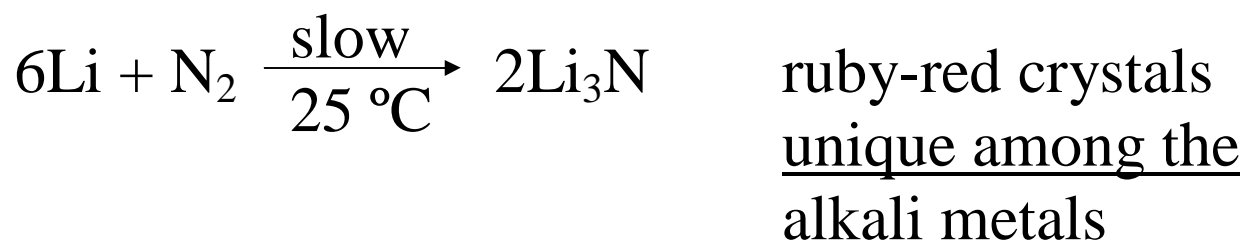
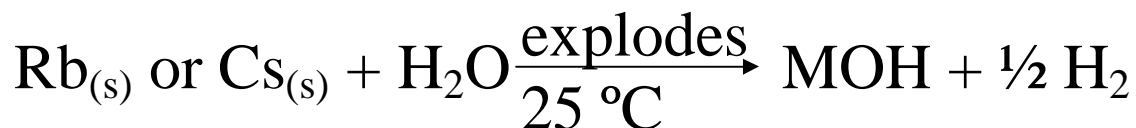
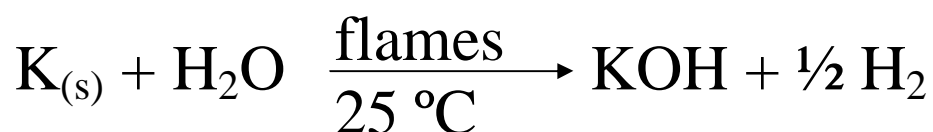
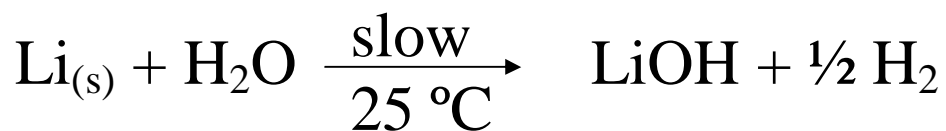
What Dictates the Chemistry of Alkali Metals?

- Low ionization energies to make +1 cations
- M^+ ions are spherical and hard (low polarizability)
- High 2nd ionization energies prevent the +2 oxidation state
- Most bonding interactions are ionic due to low polarizability (Li^+ is strongest in terms of polarizing ability due to size/charge ratio – in other words it forms the most covalent compounds)
- Li is least reactive, Cs is most reactive

Preparation of alkali metals is mainly by electrolysis of fused salts

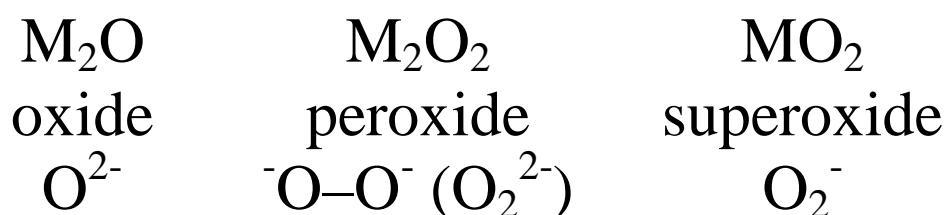
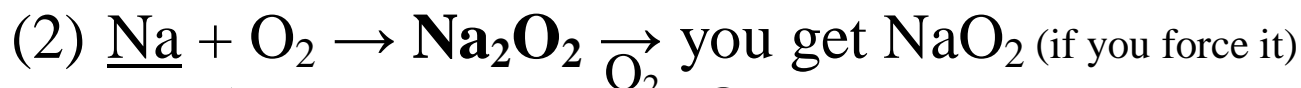


Reactivity Comparisons



A Fundamental Difference Can Be Observed in O₂ Reactions

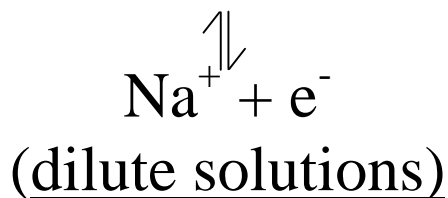
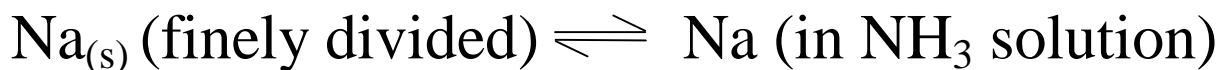
(main products in bold)



Q Why differences?

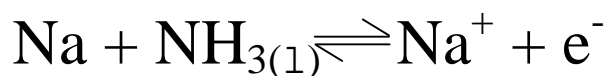
A The differences in reactivity with O₂ can be attributed to cation size.

Solutions of Alkali Metals in Ammonia NH_{3(l)}



Q What do these equilibria mean?

A That the NH_3 medium is able to “solvate” an electron. The solvated electron occupies a “cavity” in the $\text{NH}_3(l)$ where it is somewhat delocalized over a large volume so that the surrounding molecules are polarized. The polarized NH_3 molecules form the cavity due to NH_3 lone pair – e^- repulsions.



is stable without air or water, but eventually can react further to give:



This reaction is facilitated by photochemical and catalytic routes

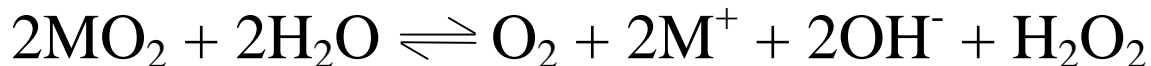
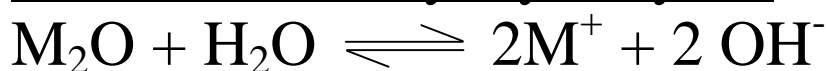
Binary Compounds (only two elements)

oxides – M_2O , M_2O_2 , MO_2

hydroxides – MOH (not really binary but these
are viewed as metal oxides as well)

salts – MX (X = halide for example)

Oxides, Peroxides and Superoxides of Alkali Metals are Easily Hydrolyzed



Hydroxides

- $NaOH$ etc., white, very hygroscopic
(deliquescent) solids (means they literally
dissolve in the moisture from the air)
- solids also absorb CO_2 from the atmosphere
(solutions do as well)

Salts

MX X^- = many types of anions

most give colorless, crystalline ionic compounds

Anomalies arise with lithium compounds –

Why? Mainly due to its small size and its effect on lattice energies!

compare:

(1) LiH stable to 900°C

NaH decomposes at 350°C

(2) Li_3N stable

Na_3N does not exist at 25°C

(3) $\text{LiOH} \xrightarrow{\Delta} \text{Li}_2\text{O}$ i.e. it decomposes

$\text{MOH}_{(\text{s})} \xrightarrow{\Delta} \text{MOH}_{(\text{g})}$ i.e. they sublime

(4) LiOH is much less stable than the other MOH compounds

(5) $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$, thermally unstable carbonate (not so much for others)

(6) LiF is not very soluble (more covalent)

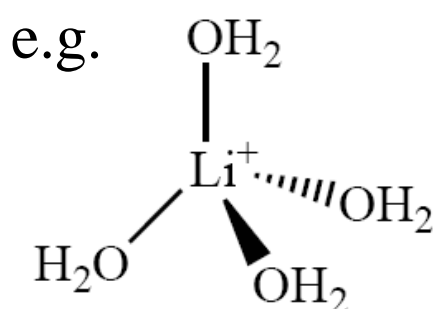
LiCl is soluble in pyridine

(unlike NaCl which is very soluble in water)

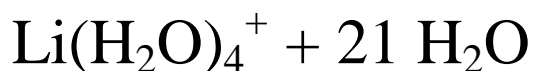
Solvation of M^+ alkali metal ions

issues:

- first coordination sphere
(How many waters are directly bound to M^+ ?)
- total coordination sphere
(How many total water molecules?)



$\text{Li}(\text{H}_2\text{O})_4^+$ is considered the first coordination sphere (found in the solid state).



additional water in the solvation shell

In other words Li^+ in H_2O exerts an influence on 25 H_2O molecules!

	<u>Li⁺</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Rb⁺</u>	<u>Cs⁺</u>
<u>Ionic Radii (Å)</u>	0.90	1.16	1.52	1.66	1.81
<u>Approximate Hydrated Radii (Å)</u>	3.40	2.76	2.32	2.28	2.28
<u>Approximate Hydration Numbers (# of H₂O)</u>	25.3	16.6	10.5	10.0	9.9
<u>Hydration Enthalpies (kJ/mol)</u>	519	406	322	293	264

Note that Li⁺, the smallest ion, exerts the most influence on water → it has the highest total hydration number.

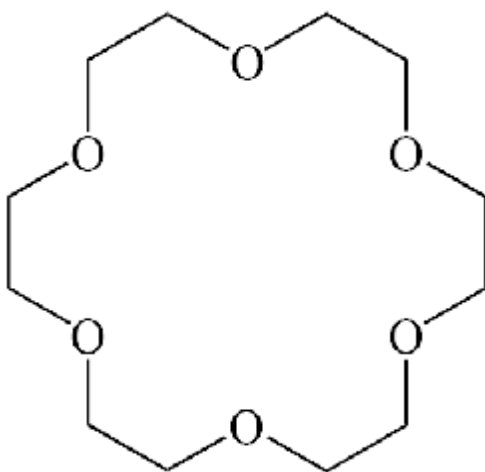
Q Why?

A greater charge density

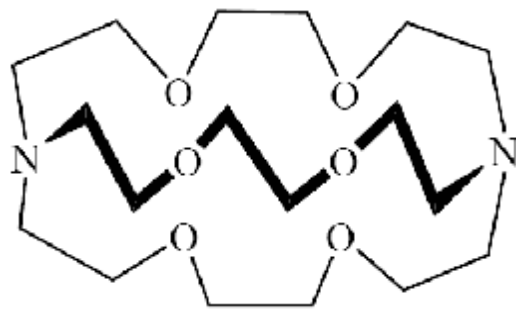
As a consequence, Li^+ , with its 25 hydration sphere H_2O molecules, will not associate with anions in ion-exchange resins very well!

Complexation of Cations by Crown Ethers and Cryptates

M^+ alkali metals are not easily dissolved in their salts into non-aqueous solvents. They need polar (usually H_2O molecules) to stabilize them in their solvated forms. To circumvent this, chemists have used the two types of molecules shown below.

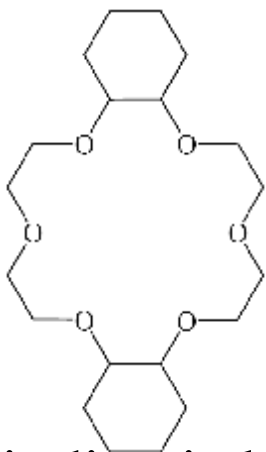


18-crown-6



2,2,2-crypt

crown ethers - (cyclic ethers)



the number of O atoms and the total number of atoms in the ring are specified in the name:

“18-crown-6”

dicyclohexyl 18-crown-6

Binding is largely electrostatic in the cavity of the cyclic ether.

Important to have a close size match of the cavity and the ion if you want binding to be tight.

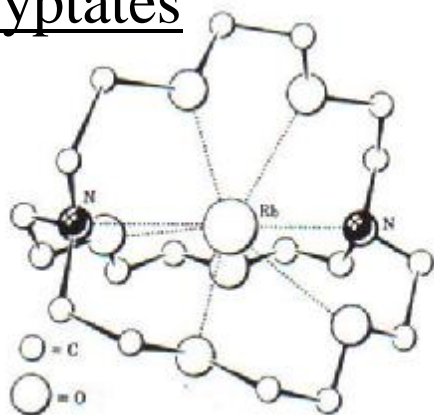
18-crown-6

$\text{Li}^+ < \text{Na}^+, \text{Cs}^+ < \text{Rb}^+ < \text{K}^+$

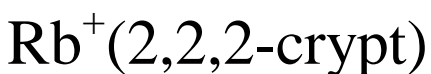
Binding
is less

Best size
match!

Cryptates



More potent and selective agents for binding alkali cations (and others). Both N and O atoms are present; they are polycyclic which means they can fully surround a cation.



These are very important reagents in organometallic chemistry for getting salts to dissolve in non-polar or low polarity solvents.

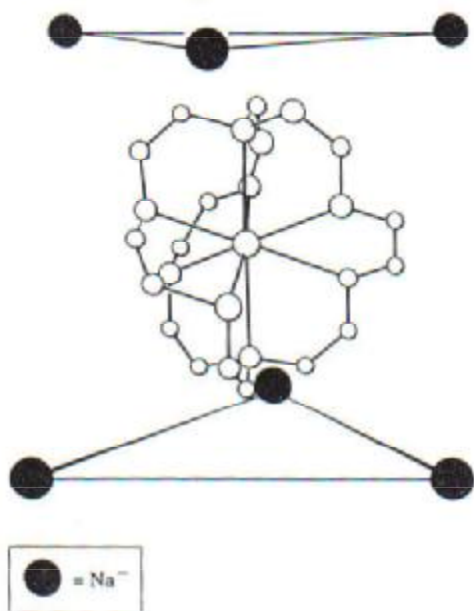
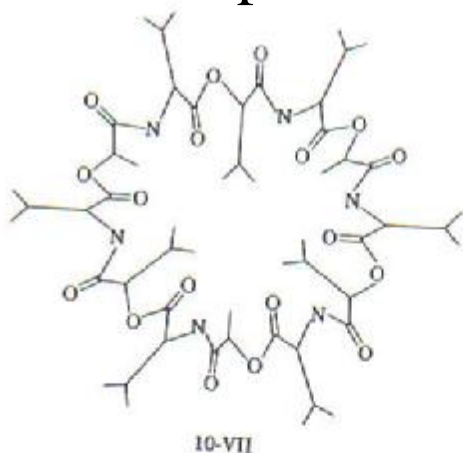


Figure 10-2 Part of the unit cell of the crystalline sodide $[\text{Na}(2,2,2\text{-crypt})]^+\text{Na}^-$ showing a single sodium cation at the center of the 2,2,2-crypt ligand and the six nearest neighbor Na^- (sodide) anions. [Reprinted in part with permission from F. J. Tehan, B. L. Barnett, and J. L. Dye, *J. Am. Chem. Soc.*, 96, 7203-7208 (1974). Copyright © (1974) American Chemical Society.]

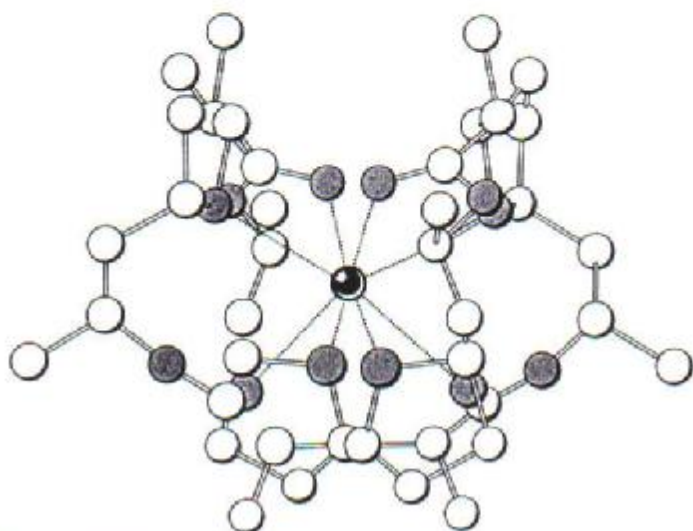
Biological systems use a similar strategy for transporting alkali metals

Nature uses cyclic peptides like the ones shown below to transport M^+ across membranes.

For example:



valinomycin



nonactin
 K^+

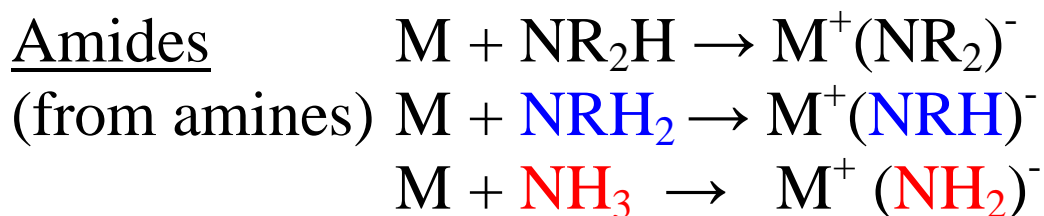
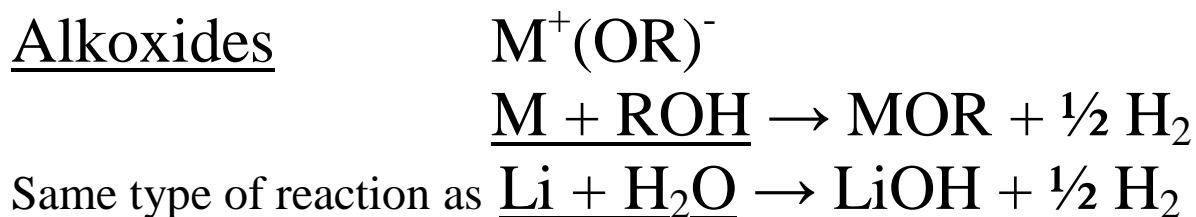
Figure 10-3 The structure of the nonactin complex of K^+ .
[Reproduced by permission from D. A. Fenton, *Chem. Soc. Rev.*, 1977, 6, 325-343.]

Alkali Metal Organometallics

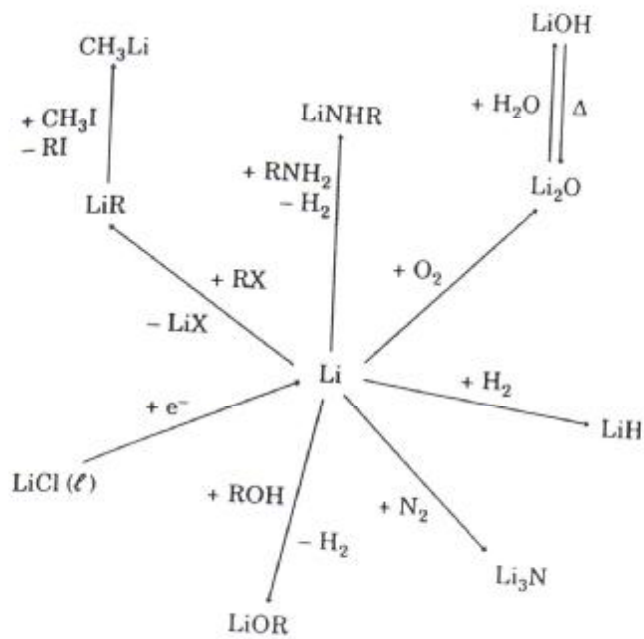
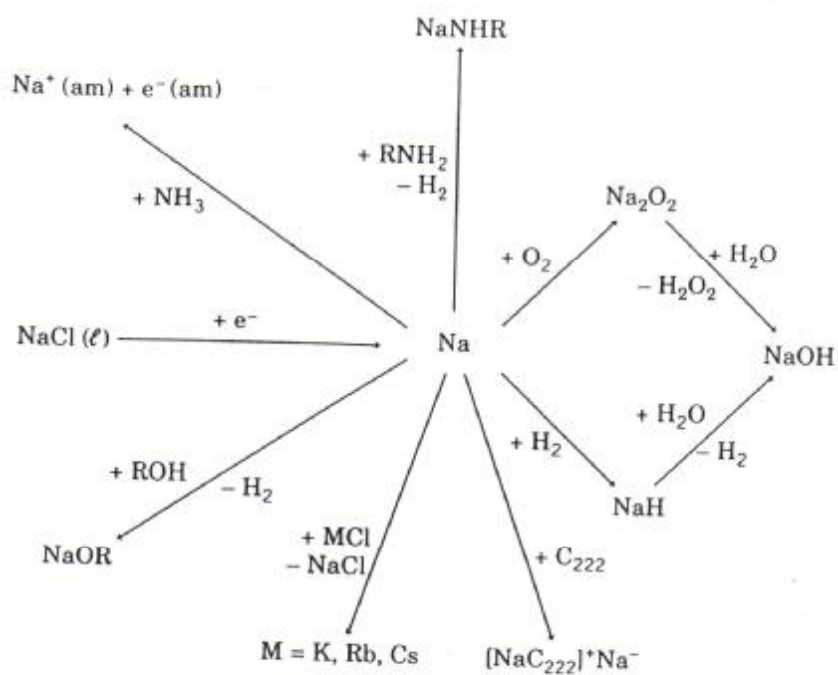


Li^+R^- $\text{R} = \text{Me, Bu, etc.}$, are used to deliver R^- groups in reactions. They react very swiftly with O_2 , H_2O and are pyrophoric which means that they burn in air.

Other Common Compounds Often Used In Organometallic Chemistry Alcohols, amines, and other X-H bonds are highly reactive towards the neutral alkali metals M.



What is happening here? Redox chemistry of course. M is oxidized, H^+ is reduced



Chapter 11

Group IIA (2) Elements

Alkaline Earth Elements

Beryllium, Magnesium, Calcium, Strontium,
Barium, Radium

Be important element in a negative sense –
 very toxic if its compounds are inhaled
 (destroys lungs)
 minor element in terms of technical
 importance

Mg, Ca, Sr, Ba are in many common minerals
and in the ocean

e.g. limestone which is CaCO_3
 dolomite which is $\text{CaCO}_3 \cdot \text{MgCO}_3$

Ra all isotopes of this element are
 radioactive

<u>Group IA</u> <u>Alkali Metals</u>	→	<u>Group IIA</u> <u>Alkaline Earth Metals</u>
larger atomic radii	→	smaller atomic radii (increased effective nuclear charge)
lower melting and boiling point	→	higher melting and boiling point
lower densities	→	higher densities
lower ionization energies	→	higher ionization energies
lower hydration energies	→	higher hydration energies
lower lattice energies	→	higher lattice energies

Chemistry of Group IIA (some highlights)

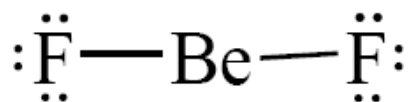
Be very small ionic radius

Be^{2+} 0.31 Å compared to:

(Li^+ is 0.60 Å; Na^+ is 0.96 Å; K^+ is 1.33 Å;
 Mg^{2+} is 0.65 Å; Ca^{2+} is 0.99 Å; etc.)

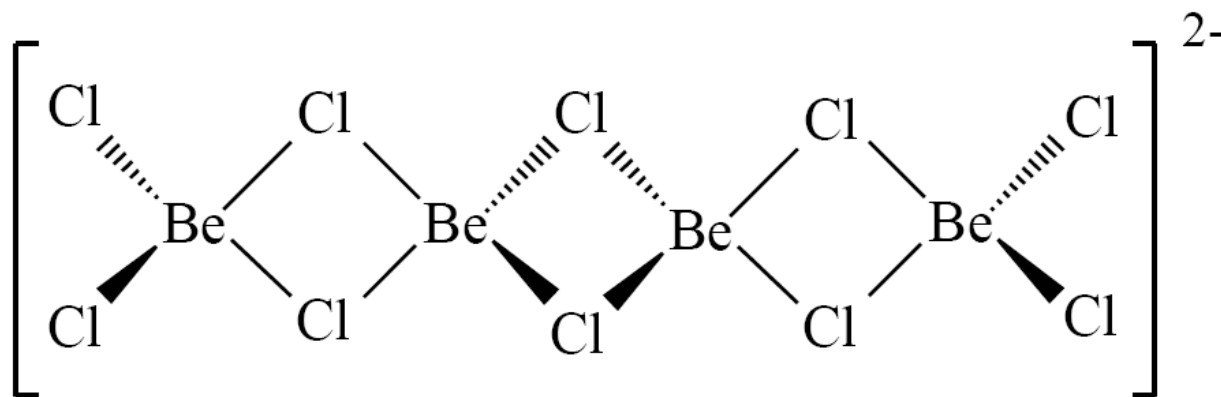
Due to the very small size of Be^{2+} , it cannot exist as a simple cation in its compounds.

Consequently, even BeF_2 and BeO are more covalent than they are ionic unlike other M^{2+} species.



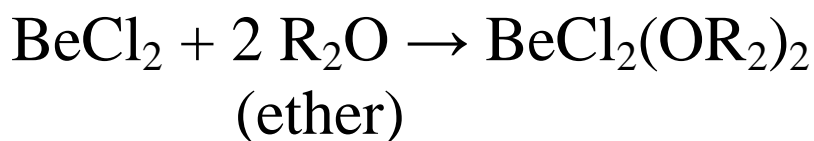
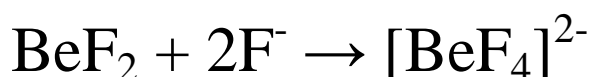
- linear
- coordinatively unsaturated
- exists only in the gas phase

Polymerization of BeX_2 compounds is common
 $[\text{BeF}_2]_n$, $[\text{BeCl}_2]_n$, etc.,



a portion of $[\text{BeCl}_2]_n$ is above

Since BeX_2 compounds are so coordinatively unsaturated, they are useful as Lewis acids in many reactions



assumes tetrahedral coordination