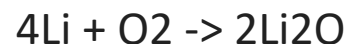


Chemical Reactivity of s-Block Elements

Reactions with Air: Group 1 (Alkali Metals)

Lithium (Li)

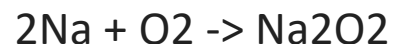
Forms Oxide



Small size stabilizes normal oxide.

Sodium (Na)

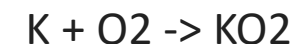
Forms Peroxide



Reacts with oxygen to yield sodium peroxide.

K, Rb, Cs

Form Superoxides



Large metal cations stabilize large super-oxide anions.

Reactions with Air: Group 2 (Alkaline Earth Metals)

Beryllium (Be) & Magnesium (Mg)

- Kinetics: Inert to oxygen at room temperature due to a protective surface oxide layer.
- Action: Burn brilliantly only when ignited.

Reaction:



Calcium (Ca), Strontium (Sr), Barium (Ba)

- Reactivity: Readily attacked by air to form regular oxides.
- Barium special case: Forms a peroxide under specific high-heat conditions.

Reactions:



Reactions with Nitrogen Gas (N₂)

Group 1: Only Lithium Reacts!

- Anomaly: Only Li reacts directly with N₂ due to its tiny size and high lattice energy.
- Rest of Group 1: Completely unreactive with nitrogen gas.

Reaction:



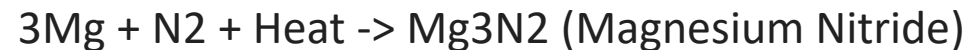
Group 2: All Elements React

- Universal Trend: All alkaline earth metals react with nitrogen upon heating to form ionic metal nitrides (M₃N₂).

Reaction:



Example:



Reactions with Water: Group 1 (Alkali)

Highly Vigorous & Highly Exothermic

All alkali metals decompose water to form strongly basic hydroxides and release Hydrogen (H₂) gas.

General Reaction Equation:



Reactivity Trend Down the Group (Li < Na < K < Rb < Cs):

- Lithium (Li): Reacts gently, non-explosively.
- Sodium (Na) & Potassium (K): React violently. The evolved H₂ gas immediately catches fire with a colorful flame.

Reactions with Water: Group 2 (Alkaline Earth)

Beryllium (Be)

- No Reaction

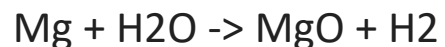
Be is completely unreactive with water or steam even at red heat due to its tiny atomic size and strong oxide layer format.

Magnesium (Mg)

- Hot Water / Steam Only

Does not react with cold water.

With Steam:



With Hot Water:

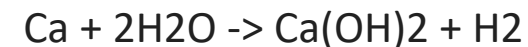


Ca, Sr, Ba

- Reacts with Cold Water

Reactivity increases down the group.

Reaction:



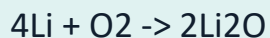
Calcium floats during the reaction as H₂ gas bubbles stick to its surface.

Oxides, Peroxides, Superoxides & Hydroxides

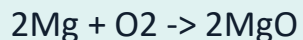
Normal Oxides (MO and M₂O)

PREPARATION

- Group 1 (Li only): Direct reaction with limited oxygen.



- Group 2 (Be, Mg, Ca, Sr, Ba): Heating metals in oxygen or thermal decomposition of carbonates/hydroxides.

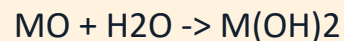


PROPERTIES

- Nature: Ionic crystalline solids (except BeO which is covalent and amphoteric).

- Basic Strength: Increases down the group. MgO is weakly basic, BaO is strongly basic.

- Reaction with Water: Forms highly alkaline hydroxides.

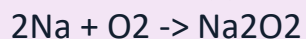


OXIDATION STATE: O_2^{2-} (-1)

Peroxides (M_2O_2 and MO_2)

PREPARATION

- Sodium Peroxide (Na_2O_2): Made by heating sodium metal in excess air/oxygen free of moisture.



- Barium Peroxide (BaO_2): Prepared by heating BaO with oxygen under pressure.



PROPERTIES

- Physical State: Diamagnetic and colorless when pure (Na_2O_2 is yellow due to superoxide impurities).

- Hydrolysis: React with cold water to give hydrogen peroxide (H_2O_2).



- Oxidizing Agents: Powerful oxidizers, violently react with organic materials.

OXIDATION STATE: O_2^- (-1/2)

Superoxides (MO_2)

PREPARATION

- Formed by K, Rb, and Cs when burned in excess oxygen.
 $K + O_2 \rightarrow KO_2$
- Large cation stabilizes the large, unstable superoxide anion.

PHYSICAL PROPERTIES

- Color: Brightly colored crystalline solids (KO_2 is orange-yellow).
- Paramagnetic: Contain one unpaired electron in the antibonding π^* molecular orbital.

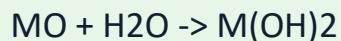
CHEMICAL REACTION

- Hydrolysis: Vigorous reaction releasing H_2O_2 and O_2 gas.
 $2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$
- CO_2 Absorber: Used in submarines/spacecraft to trap CO_2 and generate O_2 .
 $4KO_2 + 2CO_2 \rightarrow 2K_2CO_3 + 3O_2$

Hydroxides (MOH and M(OH)₂)

PREPARATION METHODS

- Reaction of oxides/peroxides with water:



- Direct reaction of active metals with water:



- Industrial method (NaOH via Chlor-alkali process):
Electrolysis of aqueous NaCl (brine).

KEY PROPERTIES & TRENDS

- Basic Strength: Group 1 hydroxides are stronger bases than Group 2. Extent increases down both groups due to decrease in ionization enthalpy.
- Solubility: Highly soluble in water for Group 1. For Group 2, solubility increases down the group: Be(OH)₂ is insoluble, Ba(OH)₂ is highly soluble.
- Thermal Stability: Group 1 hydroxides do not decompose on heating (except LiOH). Group 2 decompose into oxides:
 $Mg(OH)_2 \rightarrow MgO + H_2O$

Anomalous Behaviour of Lithium & Beryllium

Why do Li and Be show Exception Behaviour?

Exceptionally Small Size

Both Lithium (Li) and Beryllium (Be) atoms and ions are remarkably smaller than other members of their respective groups.

High Ionization Enthalpy

Extremely high ionization energies make them less electropositive compared to their heavier group congeners.

High Charge Density

High charge-to-size ratio leads to strong polarizing power, imparting significant covalent character to their compounds.

Absence of d-Orbitals

Unlike heavier elements, their valence shell lacks vacant d-orbitals, restricting their maximum covalency to 4.

Anomalous Behaviour of Lithium (vs Group 1)

Hardness: Much harder than other alkali metals, which are soft and cut easily with a knife.

Melting/Boiling Points: Significantly higher melting (454 K) and boiling points than Na, K, Rb, Cs.

Reaction with Air: Forms only normal oxide (Li_2O) and reacts directly with N_2 to form nitride (Li_3N).

Deliquescent Halides: Lithium chloride (LiCl) is deliquescent and forms hydrates ($\text{LiCl} \cdot 2\text{H}_2\text{O}$), others do not.

Thermal Decomposition: Lithium carbonate (Li_2CO_3) decomposes on heating to evolve CO_2 , unlike other stable alkali carbonates.

Anomalous Behaviour of Beryllium (vs Group 2)

Inertness to Water: Does not react with water or steam even at red heat, unlike other alkaline earth metals.

Covalent Nature: Beryllium compounds (like BeCl_2) are predominantly covalent and soluble in organic solvents.

Amphoteric Oxide/Hydroxide: BeO and Be(OH)_2 are amphoteric (react with acids and bases), while others are basic.

Coordination Capacity: Maximum coordination number is 4 due to only 4 available orbitals (others can exhibit 6).

Carbide Nature: Be_2C reacts with water to yield methane (CH_4), whereas other group carbides yield acetylene (C_2H_2).

Diagonal Relationships (Li-Mg and Be-Al)

Lithium (Li) $\leftrightarrow$ Magnesium (Mg)

- Similar atomic/ionic size (Li⁺=76pm, Mg²⁺=72pm).
- Both react directly with N₂ to form nitrides.
- Their carbonates decompose easily on heating.
- Both chlorides (LiCl, MgCl₂) are deliquescent and soluble in ethanol.

Beryllium (Be) $\leftrightarrow$ Aluminium (Al)

- Similar charge/size ratio (polarizing power).
- Both are rendered passive by concentrated nitric acid.
- Oxides (BeO, Al₂O₃) are high-melting amphoteric solids.
- Chlorides form polymeric, vapor-phase bridged structures (BeCl₂, Al₂Cl₆).

s-Block Metal Complexes & Crown Ethers

Coordination Chemistry, Structural Layouts & Host-Guest Interaction

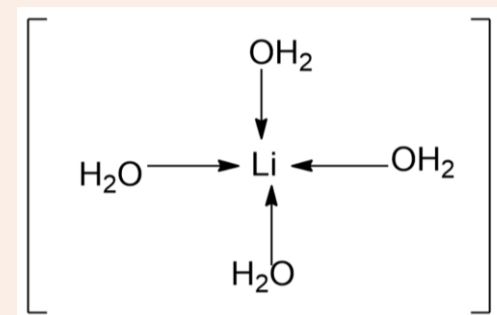
Complex Formation Tendency & Basic Shapes

General Trends & Reactivity Scales

- For complexation the metal ion must have (i) small size of cation (ii) high charge on cation and (iii) availability of vacant d-orbitals with appropriate energy
- Low Tendency: s-block metals traditionally have weak complexation traits due to large atomic size, low charge density and they don't have vacant d-orbitals to accept electrons donated by ligands.
- Reactivity Scale: The tendency decreases down the group as ionic radius expands: $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$.
- Group 2 vs Group 1: Alkaline earth metals form complexes more readily than alkali metals due to higher nuclear charge and smaller size.

Structural Layout: Aquo Complex

- Alkali metals form stable complexes with ligands like H_2O , NH_3 , Ph_3PO , CH_3CONH_2 , dioxane and pyridine. Complexes like $[\text{M}(\text{H}_2\text{O})_4]^+$ (where $\text{M} = \text{Li}^+, \text{Na}^+$ and K^+) and $[\text{M}(\text{H}_2\text{O})_6]^+$ (where $\text{M} = \text{Rb}^+, \text{Cs}^+$).
- Tetrahedral Configuration Representation:

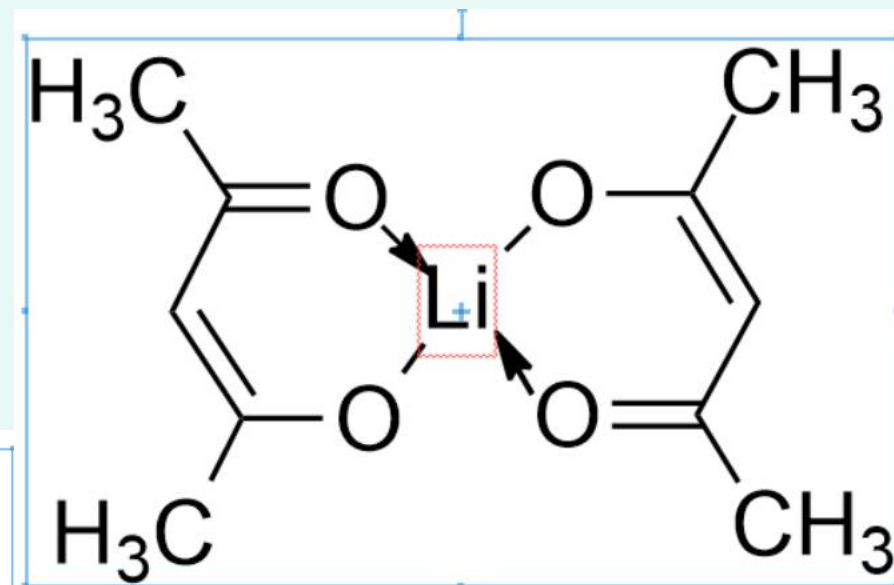
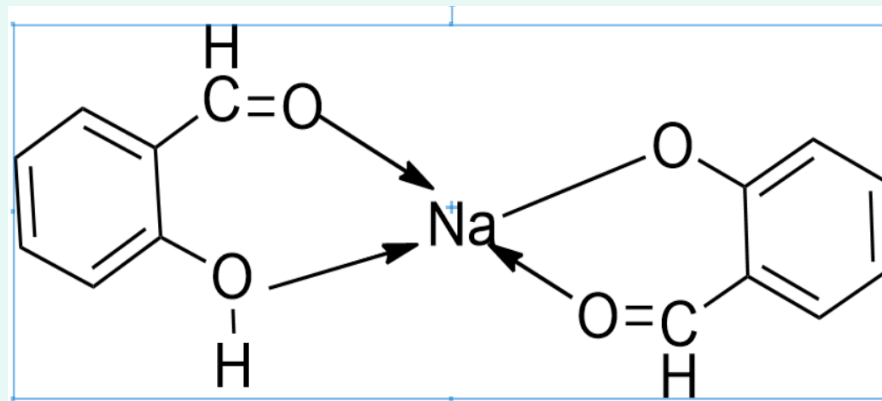
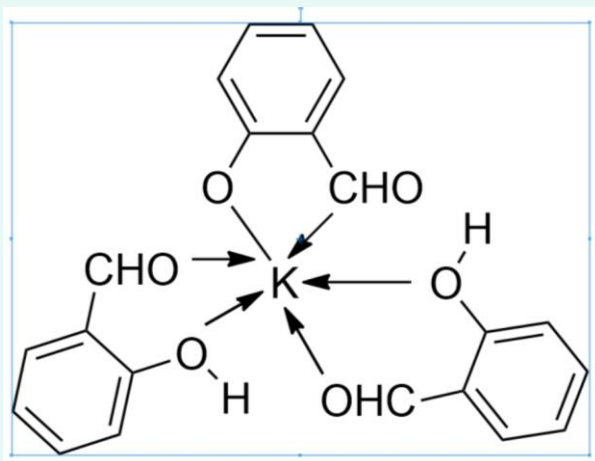


- This dense configuration is stabilized entirely by strong ion-dipole electrostatic attractions.

Complex Formation Tendency & Basic Shapes

General Trends & Reactivity Scales

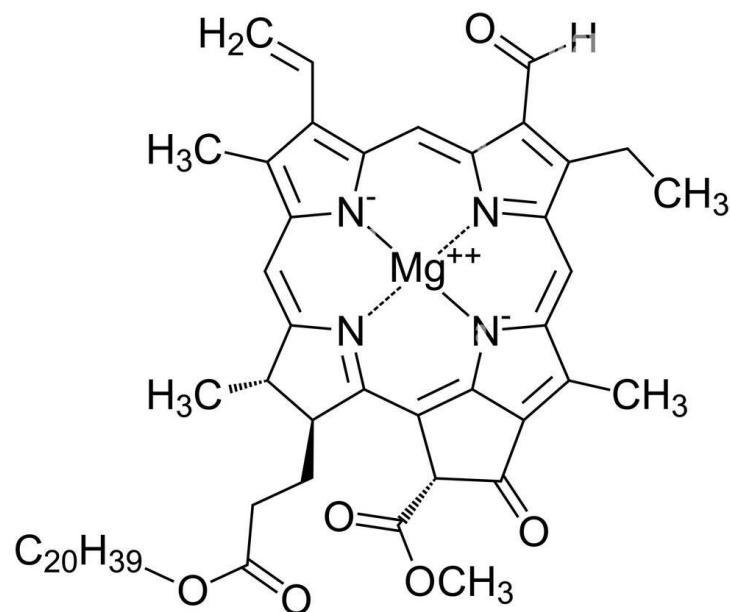
- Group I ions are also formed stable complexes with organic chelating agents. Example: - Salicylaldehyde, β -diketone, acetyl acetone, benzoyl acetone, methyl salicylate, o-nitrophenol. All these are multi-dentated ligands which form alkali metal chelate complexes.



Biological & Industrial Structural Clusters

Chlorophyll Ring Matrix (Mg^{2+})

- Porphyrin Cage: Magnesium sits at the exact geometric center of a highly rigid nitrogen-based porphyrin ring structure.
- Coordination: It forms four coordinate bonds with the nitrogen faces, holding a perfect square planar geometry.
- Structural Layout View:

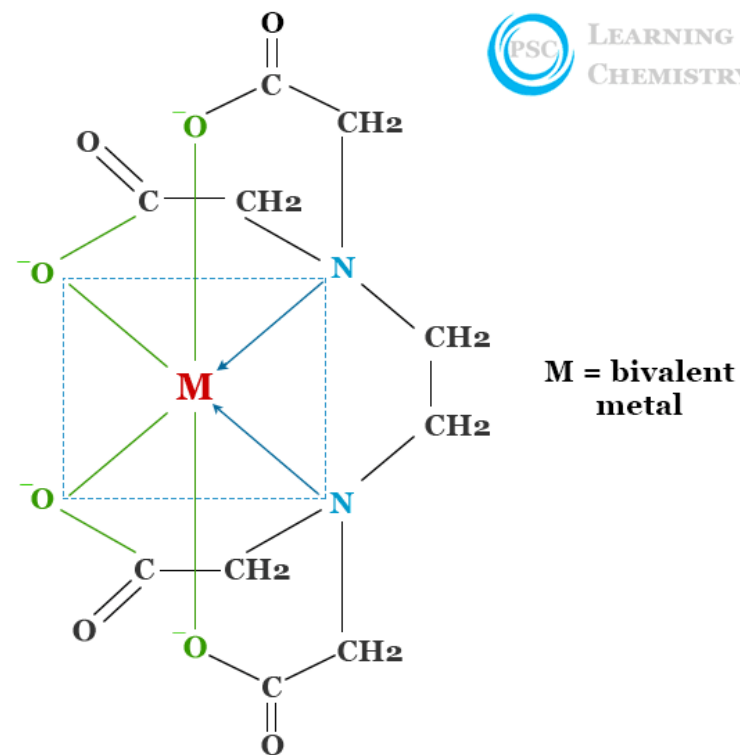


Chlorophyll *b*



EDTA Chelates (Ca^{2+} / Mg^{2+})

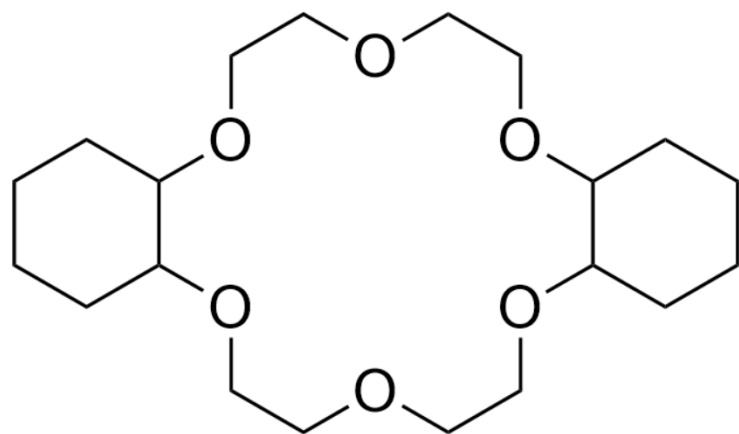
- Hexadentate Caging: Ethylenediaminetetraacetic acid (EDTA) acts as a powerful hexadentate ligand.
- Octahedral Structure: It completely wraps around Group 2 elements like Ca^{2+} or Mg^{2+} , locking them into an octahedral cage.
- Water Hardness Testing: This absolute wrapping matrix forms the complete analytical basis for determining water hardness via EDTA titrations.
- Simplified View:



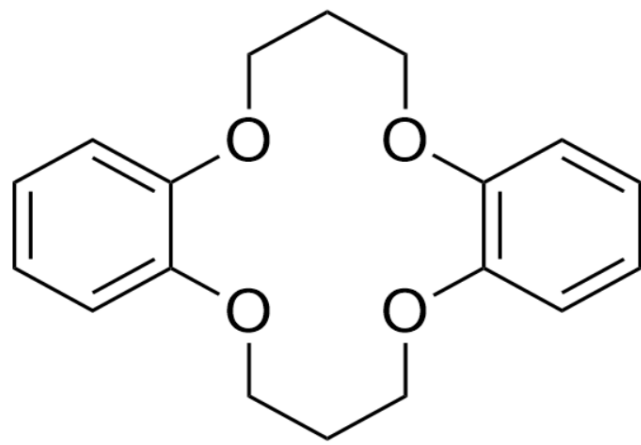
Introduction to Crown Ether Architecture

Host-Guest Chemistry and Ring Layouts

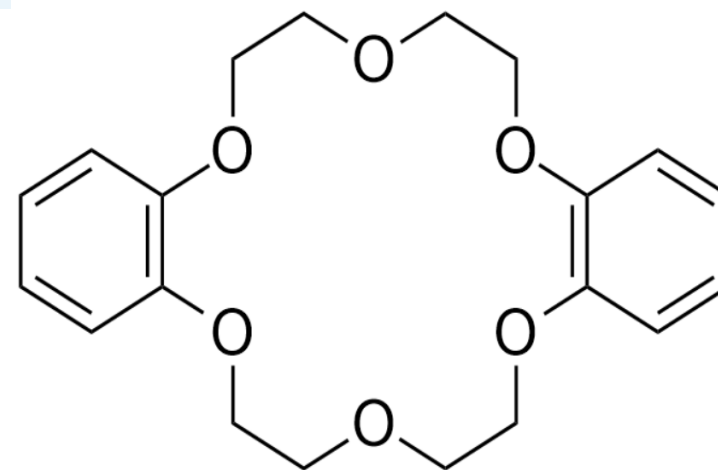
- Definition: Crown ethers are cyclic polyethers containing repeating (-CH₂-CH₂-O-) units that mimic a royal crown structure.
- Nomenclature Rule: Expressed in a standardized X-Crown-Y style format (where X is the total number of ring atoms, and Y is the total number of oxygen donor sites).
- Dual Surface Polarities: The outer carbon loops are highly lipophilic (organic-soluble), while the central inner core cavity contains dense oxygen electron lone pairs, rendering it highly hydrophilic.
- Unique Trapping Mechanism: This structural contrast sets up an electrostatic trap that selectively cages positive metal ions.



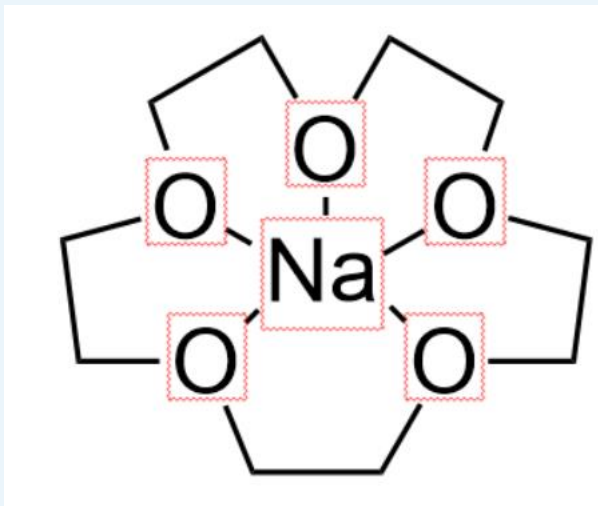
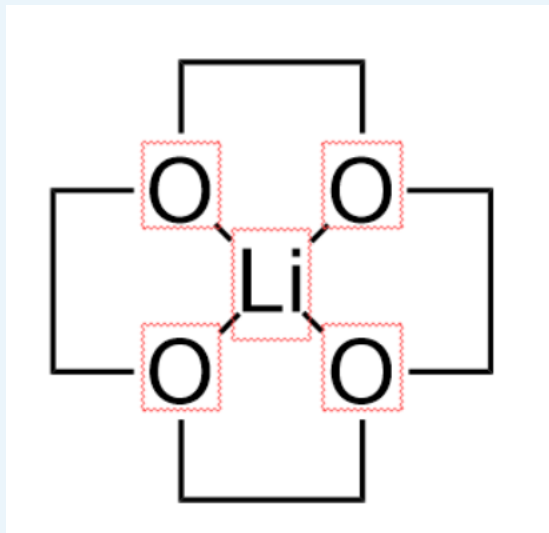
Cyclohexyl-18crown-6



Dibenzo-14crown-4

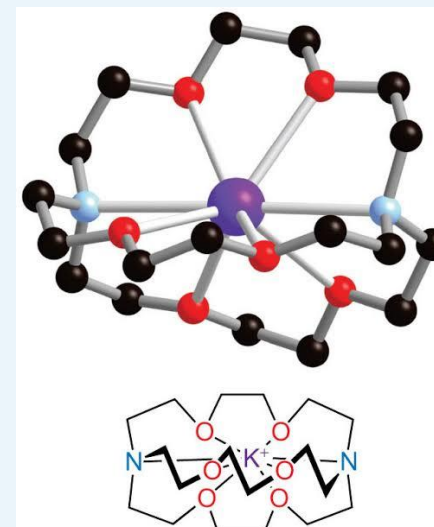
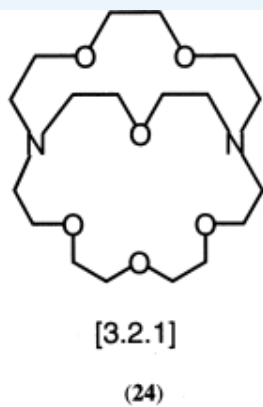
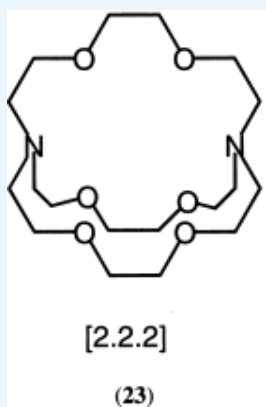


Dibenzo-18crown-6



Cation	Polyether Ring
Li	14-Crown-4
Na	15-Crown-5
K	18-Crown-6
Rb	21-Crown-7

Cryptates: - The polycyclic ligands which have donor atoms other than oxygen such as N and/or O or P and S. These are called Cryptates. The name Cryptates comes from the Greek word for hidden. In these structures the metal ion is hidden in the structure. The Cryptates are even more selective and stronger complexing agents than crown ethers.



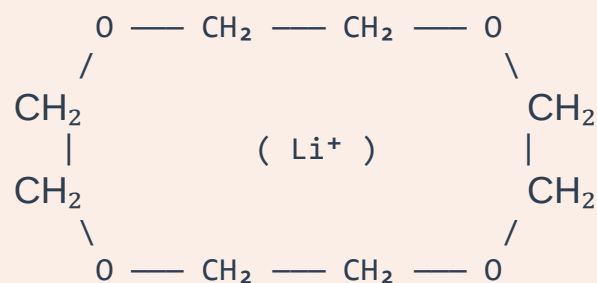
Size Complementarity (The Lock & Key Model)

Crown Ether Type	Cavity Diameter (Å)	Best Fit Metal Cation	Ionic Diameter (Å)
12-Crown-4	1.2 – 1.5 Å	Lithium (Li ⁺)	1.34 Å
15-Crown-5	1.7 – 2.2 Å	Sodium (Na ⁺)	1.94 Å
18-Crown-6	2.6 – 3.2 Å	Potassium (K ⁺)	2.66 Å

2D Structural Mapping of Complexes

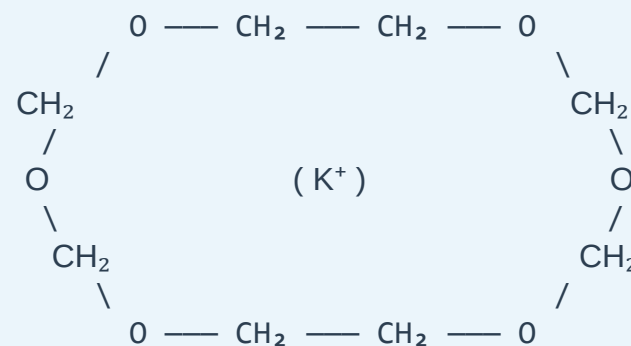
12-Crown-4 with Li^+ Structure

The tiny lithium ion coordinates tightly with four symmetrical oxygen faces lying perfectly in a single plane.



18-Crown-6 with K^+ Structure

Six coordinating oxygen points encapsulate the larger potassium ion directly in the central void.



Applications Driven by Structural Design

Phase Transfer

- Purple Benzene: Solubilizes highly inorganic salts like KMnO_4 in purely organic solvents (benzene).
- The crown sequesters K^+ , carrying the colored MnO_4^- anion directly into the non-polar phase layout.

Naked Nucleophiles

- High Reactivity: Caging the cation leaves the accompanying anion completely unencumbered or 'naked'.
- This enhances nucleophilic velocity dramatically for difficult reactions using F^- or CN^- ions.

Bio-Mimicking

- Ion Channels: Mimics natural macrocyclic antibiotics like Valinomycin.
- Crucial for advanced analytical fields including ion-selective sensors and precise metal isotope separations.