Chapter 7

Short Note on Diagonal Relationship in S block elements

Chetan Kumar, Department of Chemistry
Shri Jain Terapanthi College, Ranawas, Pali

Diagonal Relationship :

Second period elements **Lithium (Li), Beryllium (Be),** and **Boron (B)** show differences in properties with the elements of their group **[I A, II A, III A]**.Whereas the third period shows similarities in properties with the elements of **group II A, III A and IV A** respectively. This relationship shows similarity in properties of elements. This relationship shows similarity in properties of elements when moving diagonally in the periodic table. It is called **diagonal relationship.**

	IA	**IIA**	**IIIA**	**IVA**
Second period	Li	Be	B	C
Third Period	Na	Mg	Al	Si

Diagonal relationship is displayed by the elements due to two reasons -

1. Same Electropositive Character:

There is an increase in electropositivity as we move from top to bottom in a group whereas there is a decrease in electropositivity as we move from left to right in a period Hence the positive electrical properties remain almost constant when moving in diagonal form

2. Same Polarising Power:

The effective nuclear charge decreases and atomic size increases as we go down the group.which decreases the polarisation ability.Going from left to right in a period, the effective nuclear charge increases while the atomic size decreases,Due to which the polarization capacity of the elements increases.Therefore the polarisation capacity remains almost the same when moving diagonally. That is why there is similarity in the properties of elements.

Diagonal Relationship between Lithium and Magnesium:

There is similarity in properties between the element Li of group number one of the second period and the element Mg of group number 2 of the third period, this is called diagonal relationship. The reason for the similarity in the properties of Li and Mg is that their ionic radii are almost the same **[Li+ = 76pm, Mg2+ = 72pm]** and their polarization capacity is found to be the same. The following similarities are found in the properties of Li and Mg -

(i) Both are hard metals with **high melting points.**

(ii) The **atomic radius [Li=152pm, Mg=160pm]** and **ionic radius [Li+=76pm, Mg2+=72pm]** of both are almost the same.

(iii) **Electronegativity** of both is almost the same **[Li= 1.0, Mg= 1.2]**

(iv) Both react slowly with water to form hydroxides, which are weakly alkaline in nature.

(v) Both react with nitrogen to form nitrides, **Li3N** and **Mg3n2**.

(vi) Both the oxygen atoms react with the normal oxide **[Li2O and MgO].** They do not form **peroxide** or **superoxide**

(vii) On heating the carbonates of both decompose to liberate CO2.

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

$$MgCO_3 \rightarrow MgO + CO_2$$

ISBN: 978-93-344-1269-7

(viii) NO_2 and O_2 are formed on heating the nitrates of **Li** and **Mg**.

$$4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$$

$$2MgNO_3 \rightarrow 2MgO + 2NO_2 + O_2$$

(ix) **Phosphates**, **carbonates** and **oxalates** of both the elements are insoluble in water.

(x) Chlorides of **Li** and **Mg** are acid compounds, and alcohol and is soluble in **pyridine**. **Chloride hydrates** of both **[LiCl.2H2O and $MgCl_2.6H_2O$]** are formed.

Diagonal Relationship between Be and Al:

Beryllium, an element of group number two of the second period, shows similarities in properties with **aluminium** of group number 13 of the third period, the following are the reasons for this -

1. Their **polarizability** is almost the same, due to which they form compounds of covalent nature.

2. The values of standard oxidation potential of both are almost same.

$$Be \rightarrow Be^{+2} + 2e^- \quad E° = 1.85V$$

$$Al \rightarrow Al^{+3} + 3e^- \quad E° = 1.66V$$

3. The value of **electronegativities** of both is same **[Al = 1.5, Be = 1.5].**

Be. There are the following similarities in the properties of **Al** and **Na** -

(i) In nature both occur together in the same mineral beryl **[3BeO.Al2O3.6SiO2].**

(ii) The **oxides** and **hydroxides** of both are **amphoteric** in nature.

(iii) The **carbides** of both **[Be2C, Al4C3]** react with water to give **methane gas.**

(iv) Both react with alkali to give **hydrogen gas.**

$$Be + 2NaOH \rightarrow Na_2BeO_2 + H_2$$

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

(v) At high temperatures, **Be** and **Al** react with nitrogen to form **nitride** -

$$3Be + N_2 \rightarrow Be_3N_2$$

$$2Al + N_2 \rightarrow 2AlN$$

(vi) Both react with chlorine to form covalent chloride.These chlorides behave as Lewis acids.

(vii) Both the ions Be^{+2} and Al^{+3} have a strong **tendency** to form complex ions.

(viii) The **hydroxides** of both are **polymeric** in nature.

(ix) The **carbonates** of both are **unstable**.

(x) Both **Be** and **Al** do not give **flame test.**

Solvation Tendency :

Solvation is the process in which the molecules of the solvent combine with the molecules of the solute. The energy released in this process is called **solvation energy.**

If water is taken as the solvent then the process of solvation is called hydration. The energy released in this process is called **hydration energy**. When a salt is dissolved in water, water molecules remain combined with the metal ions. The number of water molecules associated with a metal ion is called the hydration number of that metal ion. **Li+, K+** and **Na+** get hydrated by water molecules and form tetrahedral formations surrounded by four water molecules. While **Cs+** and **Rb+** are octahedrally surrounded by six water molecules.

When the salts of alkali metals are put in water, they dissolve and give positive and negative ions, due to which they become conductors of electricity. In aqueous solution, conductivity is lowest due to Li^+ ions and highest due to **Cs+** ions -

$$Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$$

Order of electrical conductivity -

The reason for this order is that Li+ has high hydration due to its small size and Cs+ has very low hydration due to its large size.Hence the order of size of hydrated Li+, Na+, K+, Rb+ and Cs+ is as follows

$$Cs^+ < Rb^+ < K^+ < Na^+ < Li^+$$

Due to this the ionic conductivity of Li+ is low while that of Cs^+ is high.

ISBN: 978-93-344-1269-7

Solvation in alkaline earth metals -

The solvation tendency of the elements of II A group decreases from Be to Ba. Be^{+2} has the highest tendency to be hydrated while Ba+2 has the lowest tendency to be hydrated. Be^{+2} hydrates tetrahedrally to form $[Be(H_2O)_4]^{+2}$ ion.

Complexation Tendency of S-Block Elements:

Complex compound - A complex compound is a compound that contains a central metal atom surrounded by other molecules called ligands.

e.g. **Potassium Ferrocyanide $K_4[Fe(CN)_6]^{4-}$:**

$K_4[Fe(CN)_6] \leftrightarrows 4K^+ + [Fe(CN)_6]^{4-}$

It contains $[Fe(CN)_6]^{4-}$ complex ion. On dissolving $K_4[Fe(CN)_6]$ in water, $[Fe(CN)_6]^{4-}$ complex ion is formed.

In S block, complex compounds are formed by the elements of I A group and II A group. This tendency is found more in the elements of II A group whereas it is found less in the elements of I A group. The tendency to form complexes is more in those metal ions in which -

(a) the size of the cation is small

(b) the cation has higher charge

(c) vacant orbitals of lower energy are available

In the process of complexation, the atoms, molecules or ions that are attached to the metal ion donate electrons to form a covalent bond with the metal ion.

The tendency to form clusters decreases as we move from top to bottom in a group.

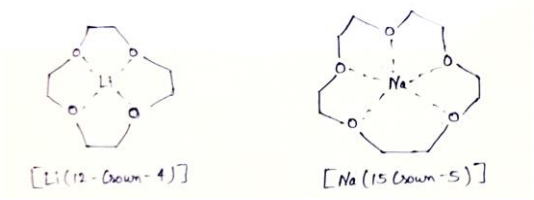
Due to the larger size of the elements of IA group than IIA elements and less amount of positive charge, the tendency of forming complex compounds in the elements of IIA group is relatively more than that of II A group elements.

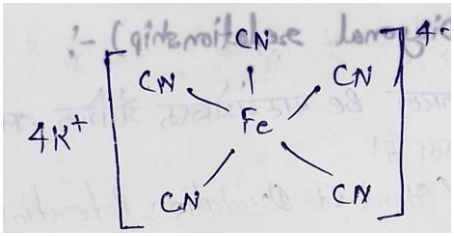
Complexes of Alkali Metals -

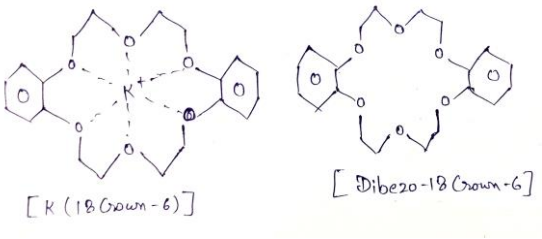
The tendency of the elements of group IA to form complexes decreases from Li to Cs as their size increases, hence the order of their complexation tendency is -

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

In the aqua complexes of alkali metals the co-ordination number for Li+ is 4 whereas for Rb^+ and Cs^+ it is 6. Alkali metals also form **polyether complexes**.







Complexes of Alkaline Earth metals :

The ability of alkaline earth metals to form complexes is higher than that of alkali metals because the charge on them is higher than that on alkali metals but their ionic size is smaller. In these, the order of packing capacity from Be+2 to Ba+2 is as follows -

$Be^{+2} > Mg^{+2} > Ca^{+2} > Sr^{+2} > Ba^{+2}$

Be^{+2} The ion has the highest capacity for complexation. The complex compounds of Be^{+2} are as follows :

- Tetra Fluoro Baryllates

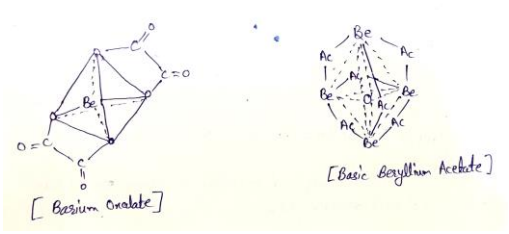
- Barium Oxalate

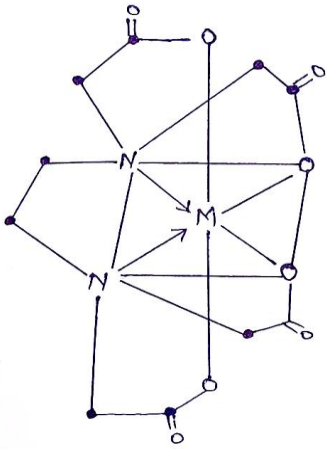
- Cationic Barium Ion

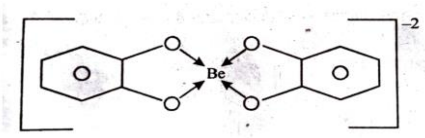
- Bis (Ethylenediamine) beryllium (II) ion

- Basic Beryllium Acetate

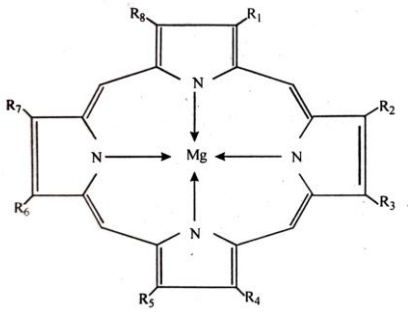
ISBN: 978-93-344-1269-7





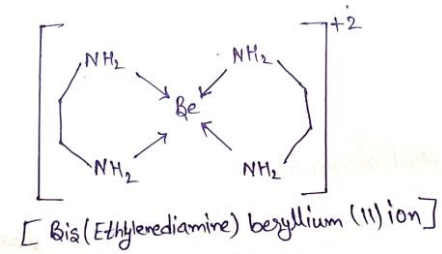


Cationic Barrilliet Ion



Chelate ring of chlorophyll

Mg forms some complex halides, such as **$[MgCl_4]^{2-}$** its most important complex compound is chlorophyll which has a structure in the form of a **chelate ring. Mg^{+2}** And **Ca^{+2}** complexes with **EDTA** i.e. **ethylene diamine tetra acetate ion** to form a compound.



ISBN: 978-93-344-1269-7