NATIONAL OPEN UNIVERSITY OF NIGERIA

CHM 111

Introduction to Inorganic Chemistry

Module 4

CHM 111 Introductory Inorganic Chemistry Module 4

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Module 4

Unit 1 Reactivity of Alkaline Earth Metals

1.0 Introduction

In the Module 3, you studied some of the physical properties of the alkaline earth metals. In this unit, you will be studying their chemical properties. You will also study the stability of oxy salts of alkaline earth metals.

2.0 Objectives

At the end of this unit, you should be able to:

- write the equations showing the reactions of all the alkaline earth metals with oxygen
- describe the action of each member of the alkaline earth metals with acid
- describe the action of each member of the alkaline earth metals with water
- describe the structure of BeO
- describe using equations the formation of the metal halides
- describe the formation of hydrides by alkaline earth metals
- describe the thermal stability of oxy salts.

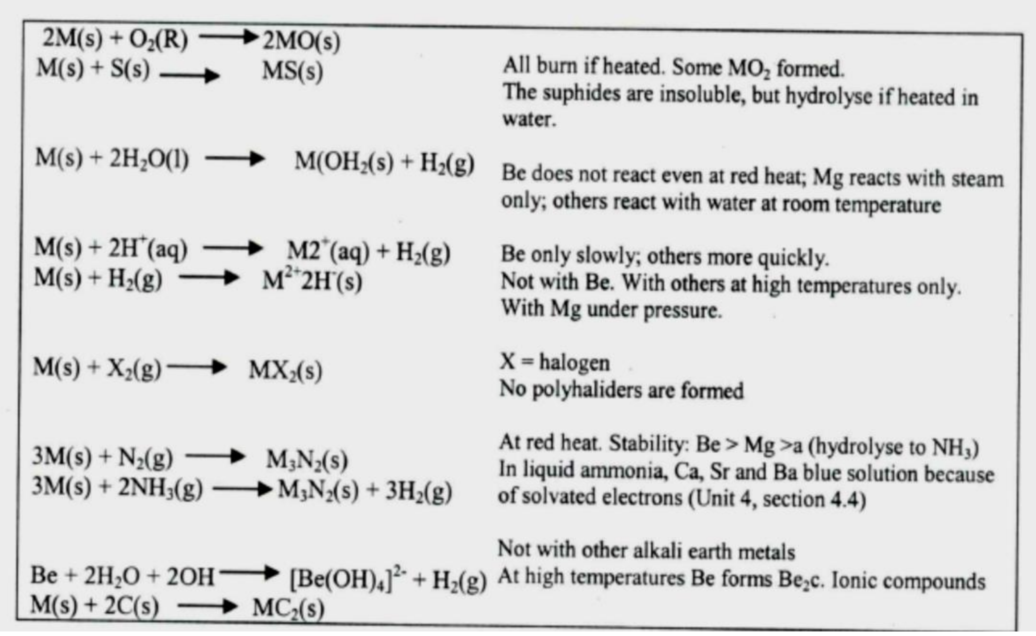
3.0 Main Content

3.1 Reactivity of Alkaline Earth Metals

Alkaline earth metals are less reactive than alkali metals as they are less electropositive than they are.

Table 3.1 shows some chemical reactions of by alkaline earth metals.

Table 3.1: Reactions of the Group 2 Metals



$2M(s) + O_2(R) \longrightarrow 2MO(s)$ $M(s) + S(s) \longrightarrow MS(s)$	All burn if heated. Some MO_2 formed. The suphides are insoluble, but hydrolyse if heated in water.
$M(s) + 2H_2O(l) \longrightarrow M(OH_2(s) + H_2(g)$	Be does not react even at red heat; Mg reacts with steam only; others react with water at room temperature
$M(s) + 2H^+(aq) \longrightarrow M2^+(aq) + H_2(g)$ $M(s) + H_2(g) \longrightarrow M^{2+}2H^-(s)$	Be only slowly; others more quickly. Not with Be. With others at high temperatures only. With Mg under pressure.
$M(s) + X_2(g) \longrightarrow MX_2(s)$	X = halogen No polyhaliders are formed
$3M(s) + N_2(g) \longrightarrow M_3N_2(s)$ $3M(s) + 2NH_3(g) \longrightarrow M_3N_2(s) + 3H_2(g)$	At red heat. Stability: Be > Mg >a (hydrolyse to NH_3) In liquid ammonia, Ca, Sr and Ba blue solution because of solvated electrons (Unit 4, section 4.4)
$Be + 2H_2O + 2OH \longrightarrow [Be(OH)_4]^{2-} + H_2(g)$	Not with other alkali earth metals
$M(s) + 2C(s) \longrightarrow MC_2(s)$	At high temperatures Be forms Be_2c. Ionic compounds

Reactivity of alkaline earth metals increases with atomic number down the group. Let us consider these re-activities at a time.

(a) All the metals liberate hydrogen form acids, although beryllium reacts slowly. Beryllium liberates hydrogen when treated with sodium hydroxide solution. The reaction can be represented thus:

$$Be + 2H_2O + 2OH^- \longrightarrow [Be(OH)_4]^{2-} + H_2(g).$$

This shows the anomaly in the behaviours of beryllium, in having amphoteric properties

(b) All the alkaline earth metals burn in oxygen to form oxides, MO. Oxides can also be formed by thermal decomposition of MCO^{3-}, $M(OH)_2$, $M(NO_3)_2$ and MNO_4 . With the exception of Beryllium oxide which is covalent, all other oxides are ionic in nature.

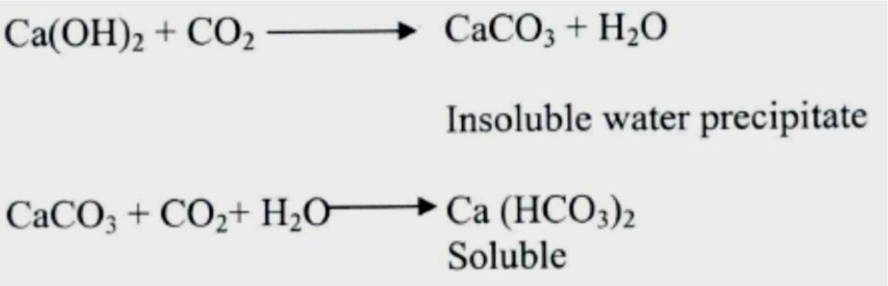
BeO has a wurtzite (hexagonal ZnS) structure (Figure 1.1). In this structure, each ion has four nearest neighbours distributed tetrahedrally around it. Others have sodium chloride type of structure, i.e. each metal ion, M^{2+}, is surrounded by six 0 2- ions and each 0^{2-} is surrounded by six metal ions (Figure 1.2). CaO is prepared on a large scale by heating calcium carbonate in lime kilns and is used in the manufacture of Sodium Carbonate, Calcium carbide, bleaching powder, glass and cement.

(c) Barium peroxide, BaO_2 is formed by passing air over heated BaO, at 800K. Strontium peroxide SrO_2, is obtained in a similar way at high temperature and pressure. Calcium peroxide, $Ca0_2$ is obtained as a hydrate by treating $Ca(OH)_2$ with hydrogen peroxide H_20_2 and then dehydrating the product.

Magnesium peroxide, MgO_2 is obtained only in the crude form by using hydrogen peroxide but no peroxide of beryllium is known. These peroxides are ionic solids having (0-0) 2-ion and can be considered as salts of very weak acids, H_20_2 . The peroxides on treatment with dilute acids form H_20_2.

(d) Alkaline earth metals react less readily with water than alkali metals to give hydrogen and metal hydroxides. Beryllium does not react with water or steam even at red heat. Magnesium reacts with hot water and Ca, Sr and Ba reacts with cold water to form the corresponding hydroxides. Beryllium hydroxide, $Be(OH)_2$ is amphoteric; the basic strength increases in the order Mg to Ba. Aqueous solutions of calcium and barium hydroxides are known as lime water and baryta water respectively.

$Ca(OH)_2$ reacts with CO_2 to form first an insoluble $CaCO_3$ which further reacts with CO_2 to give soluble bicarbonate.



$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Insoluble water precipitate

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2$$

Soluble

Calcium and barium bicarbonates are stable only in solution and decompose on removal of water to give carbonates. This property of bicarbonates is the reason for **STALACTITE** formation (The downward growth of $CaCO_3$ formed on the roof of a cause by the tricking of water containing calcium compounds) and **STALAGMITE** (he upward growth from the floor of a cave; by the tricking of water containing calcium compounds) formation.

(e) Metal halides, are obtained by direct combination with halogens as well as by the action of halogen on metals. Beryllium halides are covalent and other metal halides are ionic. Beryllium halides are hygroscopic and fume in air due to hydrolysis. They sublime and do not conduct electricity. Anhydrous beryllium halides are polymeric. Beryllium chloride vapours contain $BeCl_2$ and $(BeC1_2)_2$ but the solid is polymerised and can be represented as $(BeC1_2)_2$ (Figure 3.3).

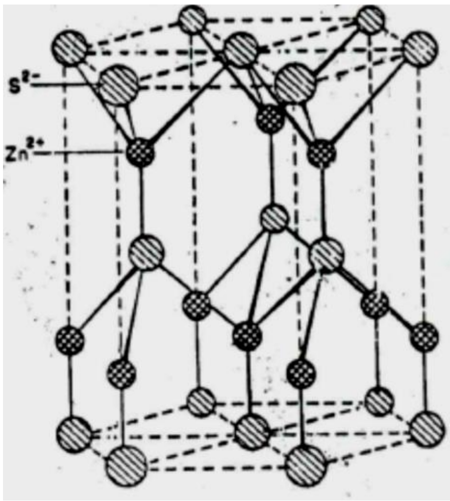


Fig 1.1: Wurtzite (ZnS) Structure

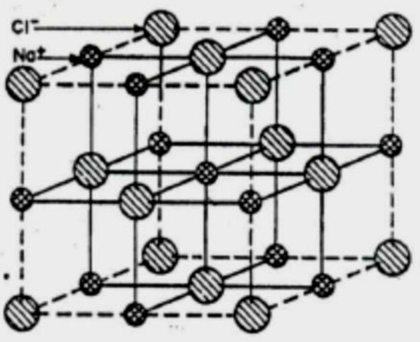


Fig 1.2: Rock Salt (NaC1) Structure

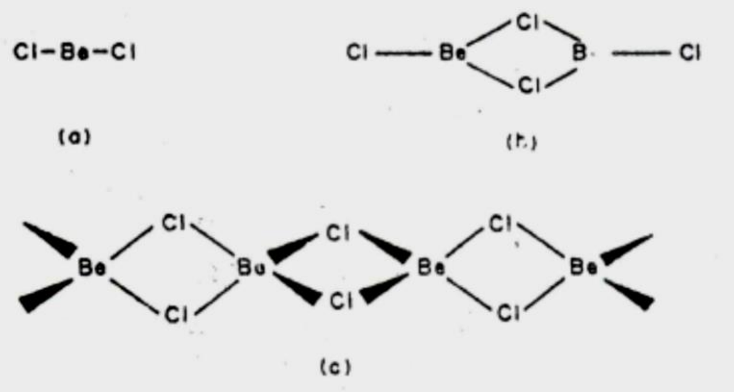


Fig 1.3: Beryllium Chloride (a) Monomer (b) Dimmer and (c) Polymer

The halides are hygroscopic and form hydrates. $CaC1_2$ is a well known drying agent and anhydrous $MgC1_2$ is important in the electrolytic extraction of Mg.

(f) All the Group 2 elements except beryllium form hydrides, MH_2, by direct combination with hydrogen.

Beryllium hydride can be formed by reducing beryllium chloride with lithium aluminium hydride $LiA1H_4$. All these hydrides are reducing agents which react with water to liberate hydrogen. Calcium strontium and barium hydrides are ionic and contain the hydride ion H- .Beryllium and magnesium hydrides are covalent and polymeric $(BeH_2)n$ has an interesting structure. The polymeric solid contains hydrogen bridges between beryllium atoms (Figure 1.4)

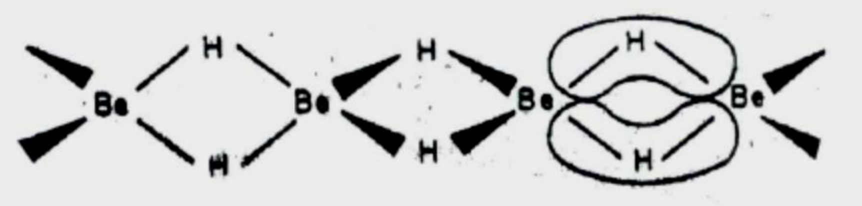


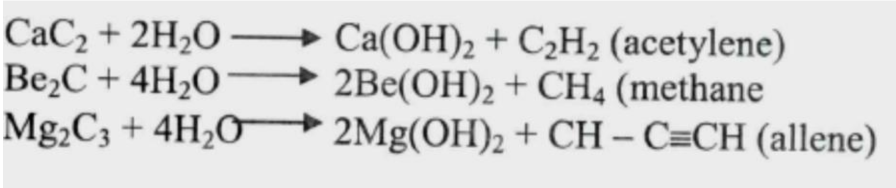
Fig. 1.4: Beryllium Hydride Polymer

Each beryllium atom is bonded to four hydrogen atoms and each hydrogen atom forms two bonds as it bridges two Be atoms. Since Be has two valence electrons and H only one, it means that there are no enough electrons to form the usual type of bonds in which two electrons are shared between two atoms. Instead of this, center bonds are formed in which a "banana — shaped" molecular orbital covers three atoms Be..........H......:Be containing the two electrons. The monomeric molecule BeH_2 if formed with normal bonds would have only four electrons in the outer shell of the beryllium atom and would be electron deficient. This would make the molecule very unstable. That is why BeH_2 exists as a cluster compound in which each atom shares its electrons with several neighbouring atoms and receives a share in their electrons in order to acquire a stable configuration.

(g) All the metals in the Mg - Ba series or their oxides react directly with carbon to give the carbides (acetylides), MC_2. These carbides are ionic in nature and have a NaC1 type of structure (Figure 1.2) with M^{2+} replacing Na^+ and C--.=-C 2- replacing Cl-. Beryllium forms methanide, Be_2C, with carbon, and acetylide BeC_2 with acetylene

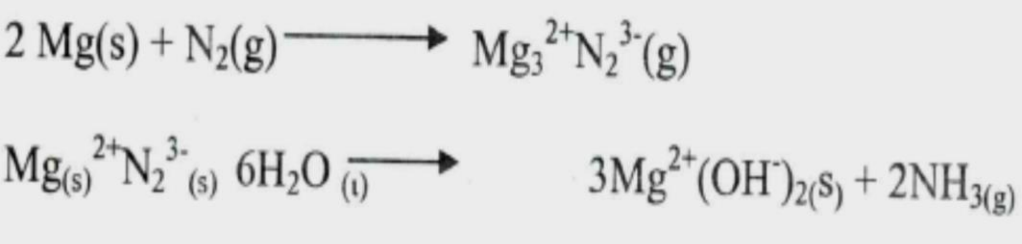
]

Magnesium on heating with carbon forms Mg_2C_3, which is an allylide since with water it liberates all ylene (methyl/acetylene). The naming of carbides depends on the hydrocarbon they liberate on reaction with water. If acetylene is liberated it is called acetylide. If methane is librated it is methanide etc.:



$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2 \text{ (acetylene)}$$
$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4 \text{ (methane}$$
$$Mg_2C_3 + 4H_2O \longrightarrow 2Mg(OH)_2 + CH - C{\equiv}CH \text{ (allene)}$$

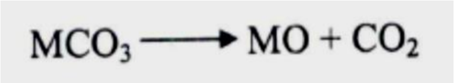
Alkaline earth metals burn in nitrogen to form nitrides, M_3N_2 it requires a lot of energy to convert. The stable N_2 molecule into nitride ion, N^{3-}, and this is recovered from the very high lattice energies of the alkaline earth metal nitrides. Beryllium compound is rather volatile while others are not. They are all colourless crystalline solids which decompose on heating and react with water to liberate ammonia and form either the metal oxide or hydroxide, e.g.:



$$2\,Mg(s) + N_2(g) \longrightarrow Mg_3{}^{2+}N_2{}^{3-}(g)$$
$$Mg_{(s)}{}^{2+}N_2{}^{3-}{}_{(s)}\ 6H_2O_{(l)} \longrightarrow 3Mg^{2+}(OH^-)_{2(s)} + 2NH_{3(g)}$$

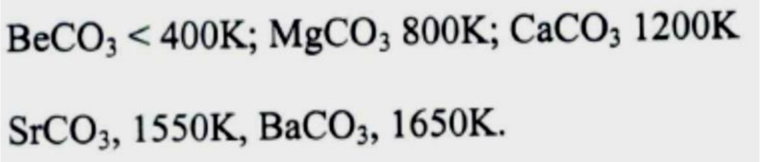
3.2 Thermal Stability of Oxy Salts

All Group 2 elements form oxy salts. The thermal stability of the oxy salts. The thermal stability of the oxy salts increases with the increase in electro-positivity of the metal, it increases down the group. The salts of group 2 are thermally less stable than those of group 1. The carbonates of alkaline earth metals are stable at room temperature. On heating, they decompose into the corresponding oxides and carbon-dioxide.



$$MCO_3 \longrightarrow MO + CO_2$$

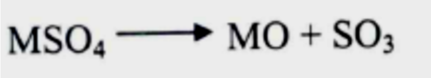
The temperatures at which the carbonates decompose are:



$BeCO_3 < 400K$; $MgCO_3$ 800K; $CaCO_3$ 1200K

$SrCO_3$, 1550K, $BaCO_3$, 1650K.

The sulphates are more stable than the carbonates. On heating they decompose into oxides and sulphur trioxide



$$MSO_4 \longrightarrow MO + SO_3$$

The order of decomposition temperature of the sulphate is:

$BeSO_4$' 850K; Mg SO_4' 1150K; $CaSO_4$' 1400K; $SrSO_4$' 1650K.

Alkali metal nitrate decompose into nitrites on heating whereas alkaline earth metal nitrates decompose on heating to metal oxide, nitrogen dioxide and oxygen.

eg $2Ca(NO_3)_2 \longrightarrow 2CaO + 4NO_2 + O_2$

4.0 Conclusion

We can conclude this unit by stating that the alkaline earth metals are generally less reactive than the alkali metals. Some of the reactions of the alkali earth metals include their action on acid to liberate hydrogen and their reaction with oxygen to form oxides which with the exception of that of beryllium are ionic in nature.

5.0 Summary

In summary, you have learnt the following in this unit:

- that alkaline earth metals are less reactive two than alkali metals
- that the alkaline earth metals react with acids to liberate hydrogen
- that all alkaline earth metals burr in oxygen to form oxides
- that the structure of BeO is the wurtzite (hexagonal ZnS) type, and that of other oxides is the NaCl of structure
- that the alkaline earth metals react less readily with water
- that the result of the reaction between alkaline earth metals and water is the formation of hydrogen and metal hydride oxides
- that alkaline earth metals combine directly with halogens to form metal halides which are hygroscopic in nature and some e.g. $CaCl_2$ are used as drying agents
- that all Group 2 elements with the exception of beryllium forms hydrides (MH_2) by direct combination with hydrogen
- that all the metals in the Mg — Ba series or their oxides react directly with carbon to give the carbides (acetylides) MC_2.

Self-Assessment Exercise

1. Explain why noble metals like Au, Pt, Rh and Ir are not attached by nitric acid, but Au and Pt are dissolved by AQUA REGIA.
2. What are the usual coordination number e.g Be^{2+} and Mg^{2+}? What is the reason for the difference?

6.0 Self-Assessment Exercise

1. Explain in brief why the hydride bridge is $(BeH_2)n$ is considered to be electron deficient but not the halide bridge in $(BeC1_2)n$.
2. Which is more stable to heat, beryllium carbonate or barium carbonate and why.

7.0 References/Further Reading

Cotton and Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry*. Cambridge: Cambridge University Press.

Unit 2 Complexing Behaviour of Alkaline Earth Metals

1.0 Introduction

In Unit 1, you studied the chemical properties of alkaline earth metals. You learnt about the reactions of the alkaline earth metals with oxygen, water and acids. You also studied the thermal stability of their oxy salts. In the course of our studies, you must have noticed that the first member of the alkaline earth metal always behave differently from the rest. In this unit, you will be studying the anomalous behaviour of beryllium. You will also be studying the complexation behaviour of the alkaline earth metals in this unit.

2.0 Objectives

At the end of this unit, you should be able to:

- list at least one complex that is formed by each member of the alkaline earth metals
- describe the structure of the complexes formed by members of the group
- list the properties in which beryllium differs from other members of the alkaline earth metals.

3.0 Main Content

3.1 Complex-Forming Behaviour of Alkaline Earth Metals

An interesting property of the alkaline earth metals is their complex behaviour. As we have seen earlier, complex formation is favoured by small, highly charged cations with suitable empty orbitals of approximately the right energy with which the Ligand orbitals can combine. Alkaline earth metal form more complexes as compared to alkaline metals. The tendency to form complex (mostly with 0 and N donors) decreases with increasing atomic number. Thus, of the heavier ions, only Ca^{2+} forms a complex with ethanol.

Beryllium having the smallest ion in the group tends to form complex most readily. It mostly forms complexes with tetrahedral arrangement because of the available orbitals as shown in Figure 2.1.

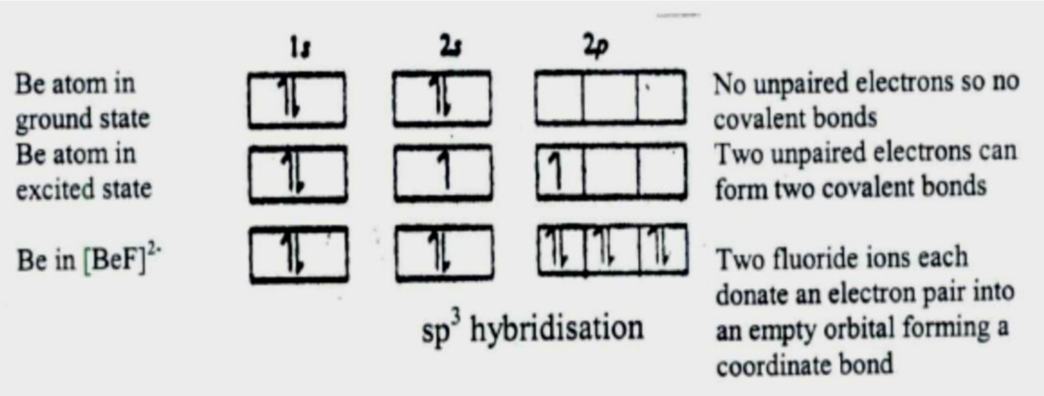


Fig. 2.1: The Tetrahedral Structure of Hetrafluoroberyllates

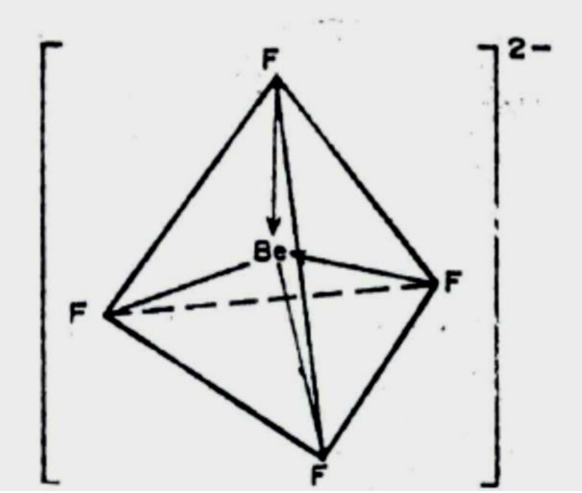


Fig. 1.2: TetrafluoroberyllaLe Complex Ion $(BeF_4)^{2-}$

The arrows in Figure 1.2 above indicate that two F - ions from coordinate bonds with BeF_2 . However, once these are formed, all the Be-F bonds tend to become similar.

Beryllium forms white crystalline molecular oxide — carboxylates of which basic **Beryllium Acetate** Viz $[OBe_4 (CH_3 C00^-)_6]$ is typical. It is used for the purification of Be because of its volatility and solubility in organic solvents. Beryllium forms a number of chelates with legands like oxalates, $[Be (C_20_4)_2]^{2-}$ (Figure 2.3) and B-diketonate anions.

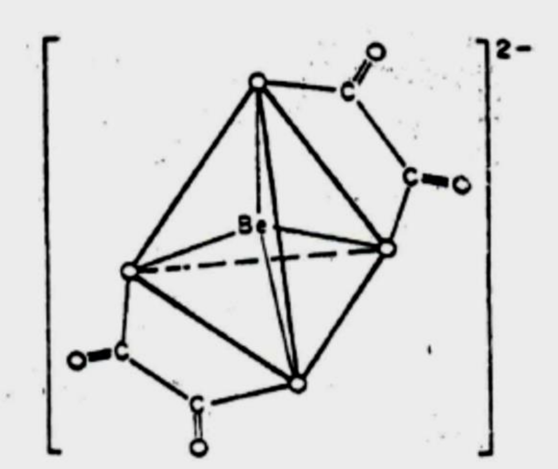


Fig 2.3: Beryllium Oxalate Complex Ion $[Be(C_20_4)_2]_2$

In the hydrated salt, example $BeCO_3.4H_20$ and $BeSO_4.4H_20$ beryllium ions exist in the form $[Be (H_20_4)]^{2+}$ where they show a coordination number of four. Magnesium is known to form a very important complex occurring in nature as in chlorophyll; a green pigment of plants which produces sugar in the presence of sunlight, carbon dioxide and water in a process known as photosynthesis.

$$6CO_2 + 6H_2O \xrightarrow[\text{sunlight}]{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6} + 6O_2$$

Magnesium in chlorophyll is coordinated by four nitrogen atoms in the heterocyclic porphyrin ring system (Figure 2.4)

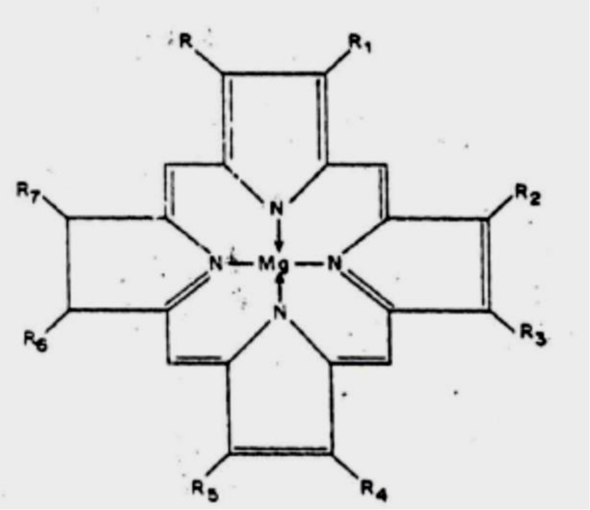


Fig. 2.4: Skeleton of Chlorophyll II Molecule

The rest of the alkaline earth elements from calcium to barium form complexes only with strong complexation agent such as acetylacetone, ethylene diaminetetra acetic acid [EDTA] etc. In fact titrations are performed using EDTA in buffer solution to estimate the amount of Ca^{2+} and mg^{2+} present in water to determine the hardness of water.

3.2 Anomalous Nature of Beryllium

Beryllium, the first member of the alkaline earth metal group, differs from the members of the group just as lithium differs from three members of its group. In facts beryllium differs more from magnesium than lithium does from sodium. As we shall see in the later units, the anomalous nature of the first member of s- and p-block groups becomes more pronounced toward the middle of the table.

Beryllium also shows a diagonal resemblance to aluminium in the same way as lithium does to magnesium. The properties in which beryllium differ from magnesium it shares with aluminium in general. Let us now look at these properties one at a time.

1. The cohesive properties of beryllium are much greater than those of magnesium and other elements in the group. As a result, it is much harder and has higher melting points.

2. It has smaller atomic radii higher electron affinity and higher ionization energy.

3. Its higher polarizing power leads to all its compounds being largely covalent with lower melting and boiling points, and enthalpies of formation (example BeF 2, m.p 1073 K while for the rest of the group is about 1573 k). All the compound of Be are more soluble in organic solvents than the corresponding magnesium compounds. They hydrolyse in water and in this respect they rather resemble aluminium.

4.0 Conclusion

In conclusion, you have seen in this unit that alkaline earth metals form more complex than the alkali metals of Group I. We have also seen that complex formation favour smaller cations. The ability to form complexes decreases with increasing atomic number. Thus, Be forms more complexes than Mg, Ca, and Ba. Beryllium shows behaviours which differ from that expected from a member of Group 2.

5.0 Summary

In this unit, you have studied the following:

- alkaline earth metals form complexes
- beryllium being smaller in size than the other member of the group forms more complexes
- magnesium forms important complexes that occur in nature. An example of such a complex is the one found in chlorophyll, the green pigment found in plant
- beryllium the first member of the alkaline earth metal shows anomalous behaviour that is, it behaves differently than it is expected to do as a member of the group
- this anomalous behaviour is manifested in it having much higher melting and boiling points. It also has smaller atomic radii, higher electron affinity and higher ionisation energy.

Self-Assessment Exercise

Explain why noble metals like Au, Pt, Rh and Ir are not attacked by nitric acid, but Au and pt are dissolved by Aqua regia.

6.0 Self-Assessment Exercise

Why do alkaline earth metals form more complexes as compound to the alkaline metals? Give only two reasons.

7.0 References/Further Reading

Cotton and Wilkinson (n. d.). *Basic Inorganic Chemistry*. John Wiley and Sons.

Wilson, J. G. & Newell, A. B. (n. d.). *General and Inorganic Chemistry.* Cambridge: Cambridge University Press.