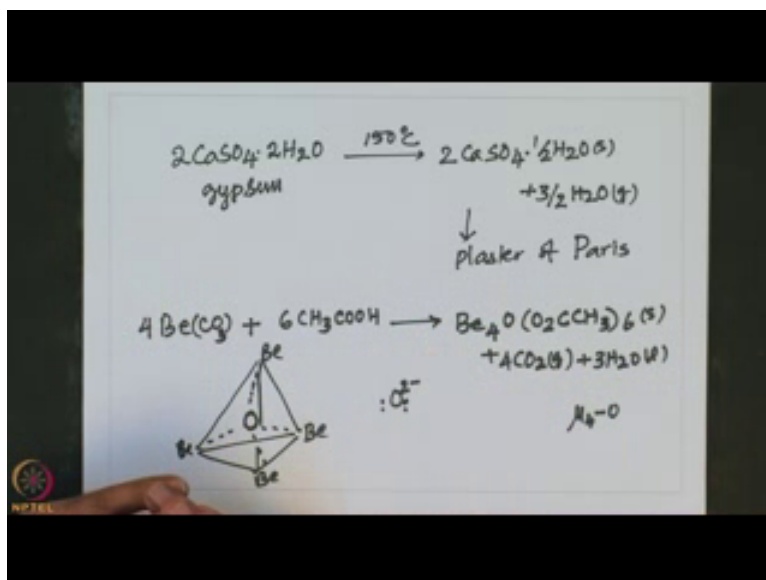


Main Group Chemistry
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Lecture - 23
Chemistry of Group 2 elements

Welcome to MSB lecture series on Main Group Chemistry. In my last lecture I was discussing about calcium sulphate dihydrate that is called gypsum and its conversion into plaster of Paris that is calcium sulphate having half equivalent of water. So, how it is done?

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Take calcium sulphate $2\text{H}_2\text{O}$ this is nothing but gypsum. So, this one on heating to 150 degree centigrade loses water considerably to form this, so here of course one and half molecules of water are lost in this one. So, this is called plaster of Paris. In case of beryllium we come across another interesting molecule called basic beryllium acetate. And of course, analogous lead acetate is also known basic lead acetate. How it is prepared? So that means, the structure is quite interesting.

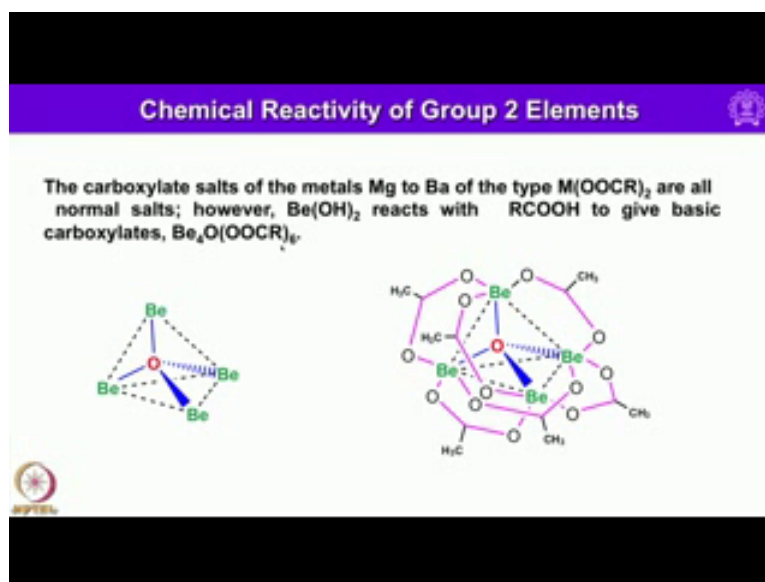
In case of basic beryllium acetate, I will give you the preparation later; in case of basic beryllium acetate also known as beryllium oxo ethanoate, it consists of a central oxygen atom surrounded by tetrahedron of 4 beryllium atoms. That means, imagine a beryllium tetrahedra very similar to white phosphorous at the centre plays oxygen and make the

bonds, then you have a μ_4 ; that means, oxygen connecting to 4 beryllium atoms which are disposed to 4 corners of a tetrahedron and which in turn are bridged by acetate ions. It can be prepared by the reaction of beryllium carbonate with acetic acid, in this one we get $\text{Be}_4\text{O}(\text{O}_2\text{CCH}_3)_6$ times, of course plus CO_2 comes out plus $3\text{H}_2\text{O}$ will also form, ok.

So in this one, this is also when we write O this should be written as $\mu_4\text{O}$. That means, essentially one can imagine a tetrahedron something like this, where we can place beryllium atoms; at the centre we have to put oxygen and establish bond with all the four. Of course, you should remember here O will be in the form of O^{2-} and lone pairs are there. And this makes covalent bonds with two berylliums and other two will be coordinate bond, but it is optimized all obvious like equivalent. So, this basic beryllium acetate is a colorless sublimable molecular compound, it is soluble in chloroform from which it can be even re-crystallized.

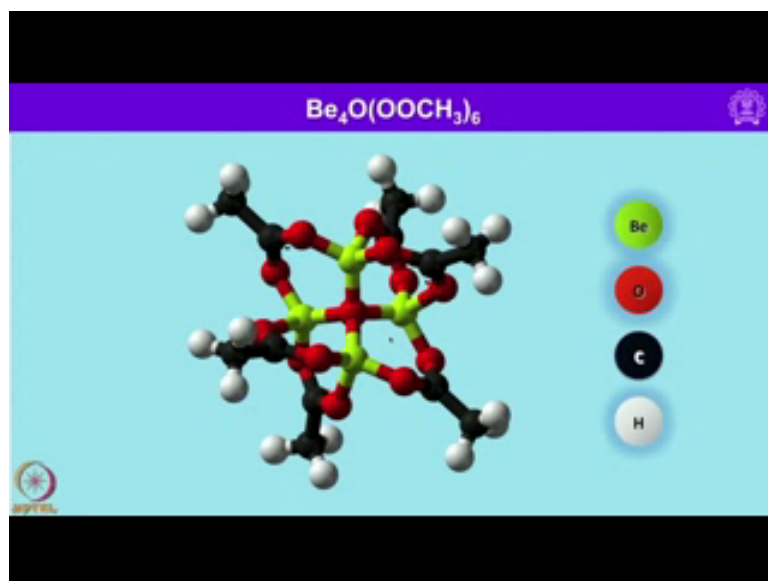
I am showing in next slide the structure of this one.

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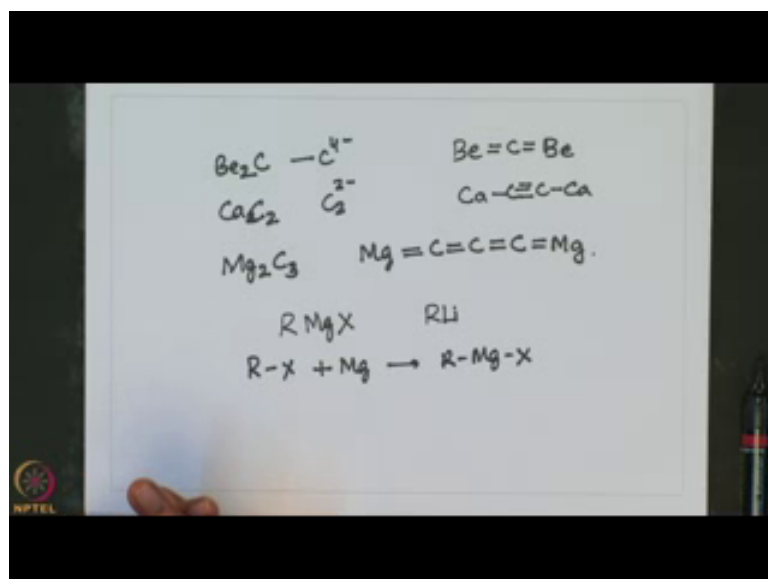
You can see here. So, in this one it is very clear. So, these 4 beryllium atoms are at 4 corners of a tetrahedron. At the middle we have oxygen atom, this is making bonds with all 4 beryllium atoms. Now, we have these acetate ions. These acetate ions will be bridging 2 beryllium in this fashion so that we have totally 6 acetate ions bridging over beryllium atoms having this composition here $\text{Be}_4\text{O}(\text{OOCR})_6$.

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This is how the structure looks like, the same structure I have shown here. So, let us look into the reactions of alkaline earth metals with the carbon. The group 2 metals form several types of carbides. I just gave introduction to the different type of carbides here.

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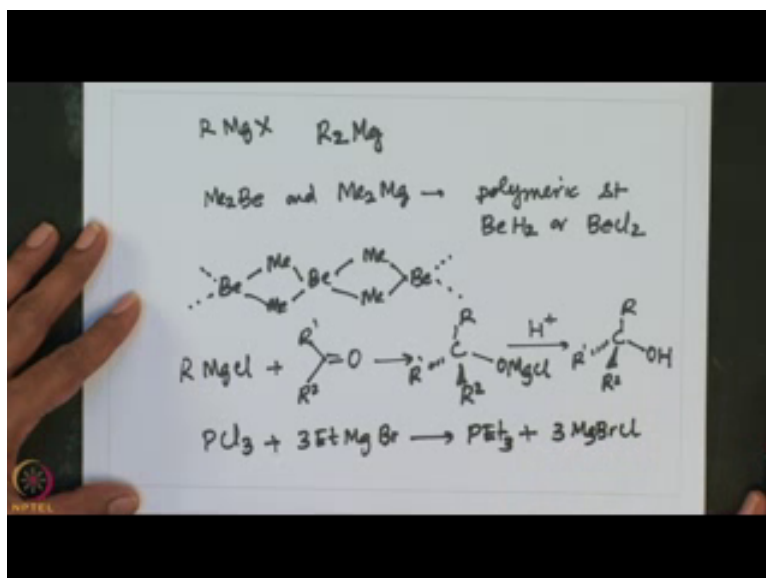
While discussing about the carbides I just mentioned that it forms something like this, where we have C 4 minus, whereas in case of calcium we have Ca 2. So, here we have essentially C 2 2 minus. And similarly in case of magnesium one can make a compound having this composition and the structure of this one can be written in this fashion. So, it

is very interesting to see what would happen and what are the products we get when we hydrolyze this Mg_2C_3 ; of course, if you are curious to know the structure of beryllium carbide and the structure will be something like this. In case of calcium carbide it has; this is how they make bonds.

So, the most important Organometallic compounds of group 2 metals are the Grignard reagents. Essentially they are having a general formula $R Mg X$, where R is an alkyl group, magnesium and hexagon halide, they are very similar to organolithium reagents; in terms of their reactivity and application in organosynthesis and essentially this Grignard reagent is made by treating alkyl halide with magnesium metal in a solvent such as diethyl ether or tetrahydrofuran $R X + Mg \rightarrow R Mg X$, ok

So, $R Mg X$ is always solvated by ether giving a tetrahedral geometry to magnesium and widely used in the preparation of organic compounds or in the formation of C-C bonds; carbon-carbon bond formation reactions Grignard reagents as well as lithium reagents are extensively used. Since I am devoting a few lectures to discuss the Organometallic chemistry of main group elements, I will be giving more details about the application of Grignard reagent as well as Organolithium reagents in organic reactions.

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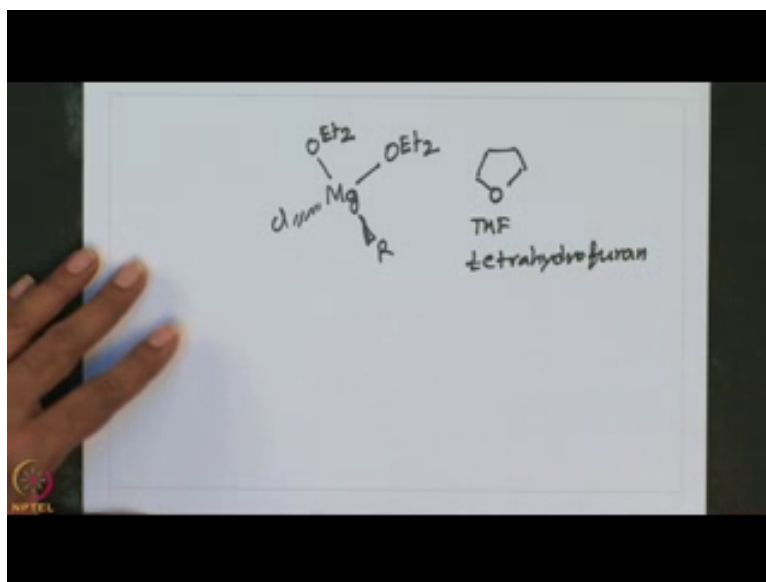
Besides making $R Mg X$ one can also make dialkyl magnesium compound, they are also known but they are less extensive when it comes to the application of these reagents in organic synthesis or carbon-carbon bond formation. And of course, when we look into

the structures of some of these compounds dimethyl beryllium and dimethyl magnesium they have the polymeric structure very similar to BeH_2 or BeCl_2 ; that means, one can conveniently write in this fashion. So, it goes like this.

One should remember beryllium is tetrahedral is surrounded by 4 methyl groups and we have here 3 centered 2 electron bonds. Just I would show you the application of Grignard reagent in organic synthesis one reaction I will show you here. Let us consider a simple R-Mg-Cl and treat this one with a ketone; initially it forms an intermediate of this type. So, this is how one can use in organic synthesis. For example: a ketone will be giving tertiary alcohol. Similarly one can also use in reaction such as for example; if we take P-Cl_3 and treat P-Cl_3 with 3 equivalents of ethyl magnesium bromide one can conveniently make triethylphosphine, of course plus 3 equivalents of Mg-Br-Cl will be formed.

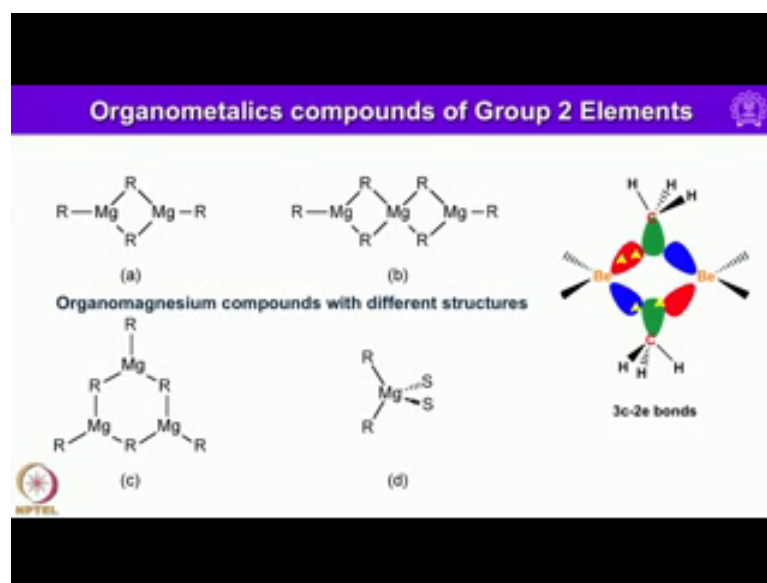
So, this is how one can utilize in making main group elements to carbon bond either employing Grignard reagent or lithium reagent.

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So, why the reaction has to be carried out in diethyl ether; it gives coordinative saturation most of the time Grignard reagents will be having. So now, it gives a kind of tetrahedral stable geometry to magnesium. So, here one can conveniently use diethyl ether or one can also use tetrahydrofuran. This is called THF: that is called tetrahydrofuran, this is a cyclic ether.

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I have shown some of the structures of Grignard reagents here. It can have simple dimeric structure in absence of any donor solvents such as ethers or one can also think of having a tri nuclear structure like this. And organomagnesium compounds also show cyclic structure like this. And most preferred one is this one, where in order to make it exist in monomeric form it has to be stabilized using donor solvents such as diethyl ether or THF.

In absence of any of these solvents they associate to form dimeric structure or trimeric structure or trimeric cyclic structure and essentially establishing 3 centered 2 electron bonds. And one can visualize 3 centered 2 electron bonds here, same analogy one can use using valence bond theory or hybridization concept, ok.

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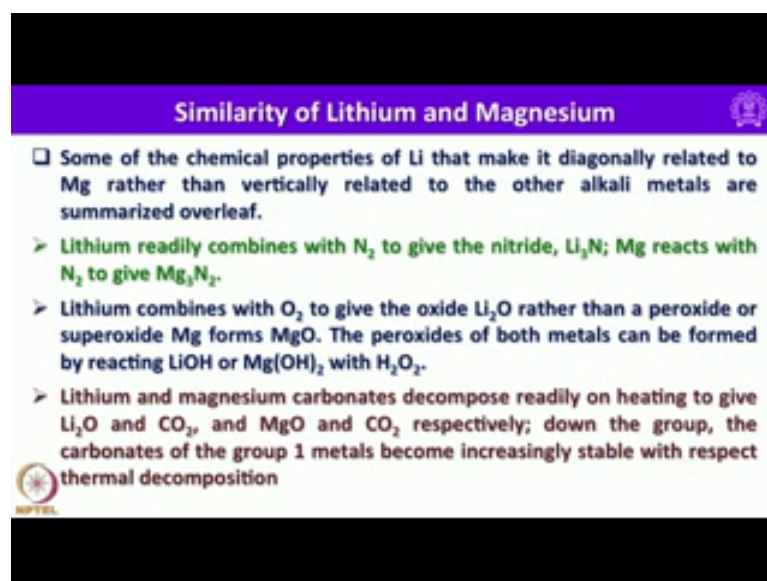
Diagonal relationship between Be & Al

- Be^{2+} ionic radius ~ 31 pm; charge/size ratio = Al^{3+}
- As a result they have similarities in their properties
- Al forms an oxide film and as a result resistant to acid attack
- Be does the same
- $\text{Be}(\text{OH})_2$ dissolves in excess of alkali to form beryllate ion, $[\text{Be}(\text{OH})_4]^{2-}$
- Al does the same
- Chlorides of both Be and Al have bridged structures
- Both the chlorides in monomeric form are strong Lewis acids
- Used in Friedel Craft reactions
- Both have strong tendency to form complexes, BeF_4^{2-} and AlF_6^{3-}

So, let us look into the diagonal relationship between beryllium and aluminum. In fact, beryllium has more resemblance to aluminum rather than calcium or magnesium. Beryllium 2 plus ionic radius if you look into it, it is 31 picometer. And charge to size ratio is quite high, and that is comparable to Al 3 plus ion; as a result they have very similar properties and also reactivity. Aluminum forms an oxide film and as a result resistant to acid attack. Beryllium also forms the same: it forms a beryllium oxide layer and thus prevents from further attack. And beryllium hydroxide dissolves in excess of alkali to form beryllate: that means tetrahydroxyberyllate. Aluminum does the same it forms tetrahydroxy aluminate.

And chlorides of both beryllium and aluminum have bridged structures. Of course, aluminum has dimeric structure, whereas beryllium has a polymeric structure both the chlorides in monomeric form are strong Lewis acids; both are electron deficient in nature. And both of them are used in Friedel Craft reaction to make carbon-carbon bond. Both have strong tendency to form complexes. For example, tetrafluoroberyllate or hexafluoroaluminate something like that.

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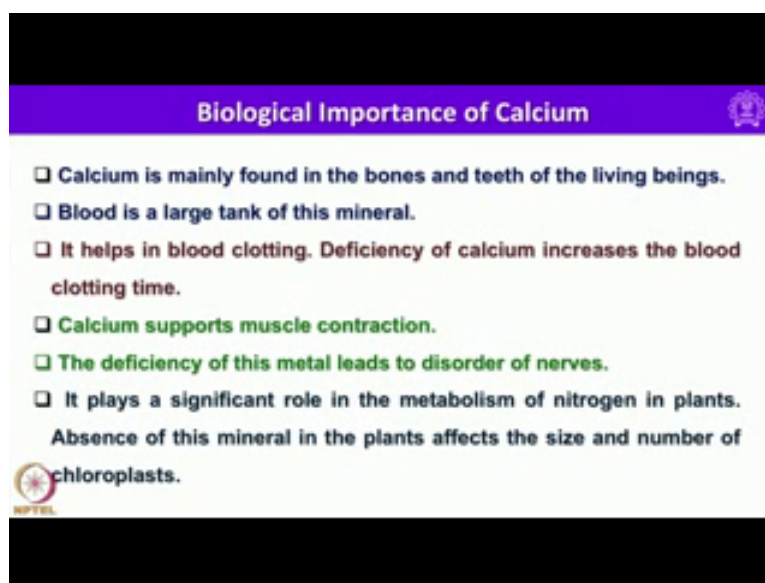
Similarity of Lithium and Magnesium

- Some of the chemical properties of Li that make it diagonally related to Mg rather than vertically related to the other alkali metals are summarized overleaf.
- Lithium readily combines with N_2 to give the nitride, Li_3N ; Mg reacts with N_2 to give Mg_3N_2 .
- Lithium combines with O_2 to give the oxide Li_2O rather than a peroxide or superoxide Mg forms MgO . The peroxides of both metals can be formed by reacting $LiOH$ or $Mg(OH)_2$ with H_2O_2 .
- Lithium and magnesium carbonates decompose readily on heating to give Li_2O and CO_2 , and MgO and CO_2 respectively; down the group, the carbonates of the group 1 metals become increasingly stable with respect to thermal decomposition

And now let us look into the similarity between lithium and magnesium; similar to beryllium and aluminum we have similarities between lithium and magnesium. That means some of the chemical properties of lithium that make it diagonal related to magnesium rather than vertically related to other alkali metals. I am summarizing now.


The lithium readily combines with nitrogen to give nitride that is Li_3N . Similarly magnesium reacts with nitrogen to form magnesium nitride Mg_3N_2 . And lithium combines with oxygen to give oxide Li_2O rather than peroxide or a super oxide. Similarly magnesium forms magnesium oxide not super oxide. The peroxides of both metals can be formed by reacting lithium hydroxide or magnesium hydroxide with hydrogen peroxide. Lithium and magnesium carbonates decompose readily on heating to give lithium oxide and carbon dioxide. Similarly magnesium carbonate on heating gives magnesium oxide and carbon dioxide; so the carbonates of the group one metals becomes increasingly stable with respect to thermal decomposition.

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Biological Importance of Calcium

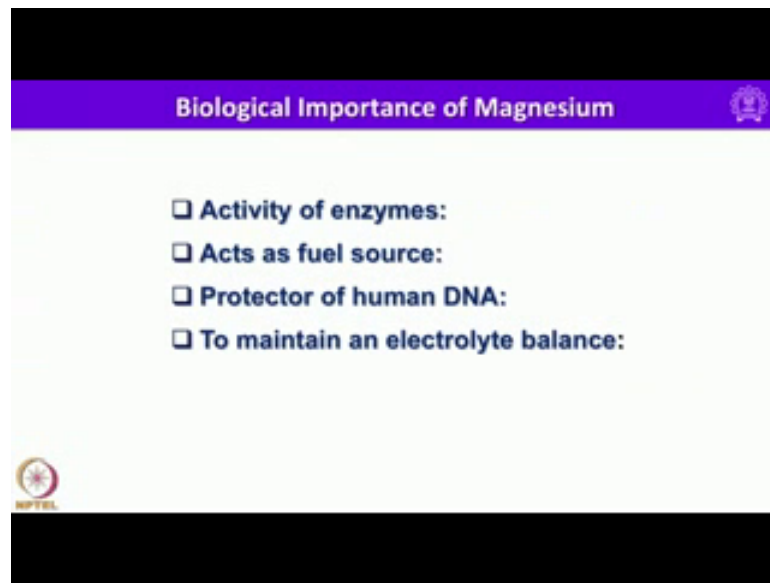
- ❑ Calcium is mainly found in the bones and teeth of the living beings.
- ❑ Blood is a large tank of this mineral.
- ❑ It helps in blood clotting. Deficiency of calcium increases the blood clotting time.
- ❑ Calcium supports muscle contraction.
- ❑ The deficiency of this metal leads to disorder of nerves.
- ❑ It plays a significant role in the metabolism of nitrogen in plants. Absence of this mineral in the plants affects the size and number of chloroplasts.

 NPTEL

Now, let us look into the biological importance of group 2 metals. First let us focus our attention on calcium. Calcium is mainly found in the bones and teeth of living beings. Blood is a large tank of this mineral; in fact it has all minerals that are essential for human to survive. It helps in blood clotting. Deficiency of calcium increases the blood clotting time.

So, calcium supports muscle contraction. The deficiency of this metal leads to disorder of nerves. It plays a significant role in the metabolism of nitrogen in plants. Absence of this mineral in the plants affects the size and number of chloroplasts.

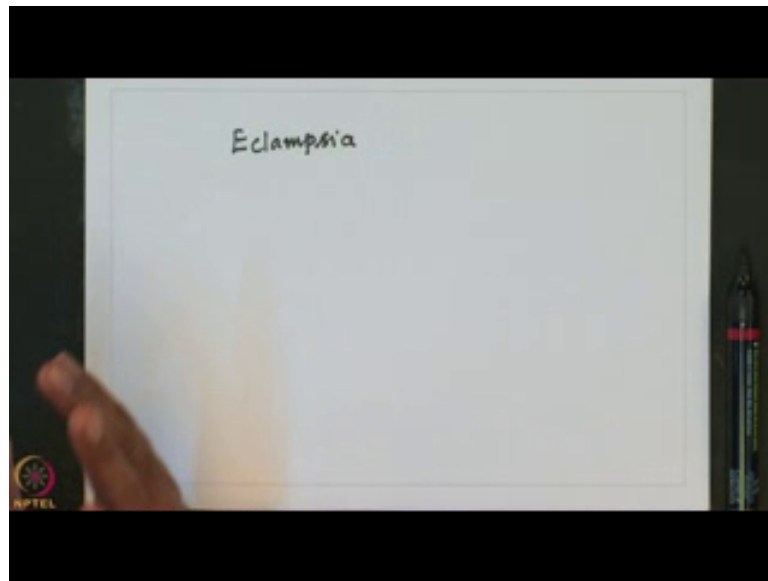
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And when it comes to the biological importance of magnesium it is not lagging behind, it plays a major role in the activity of enzymes, and also it acts as a fuel source, and it is a protector of human DNA, and also it has a major role in maintaining electrolyte balance.

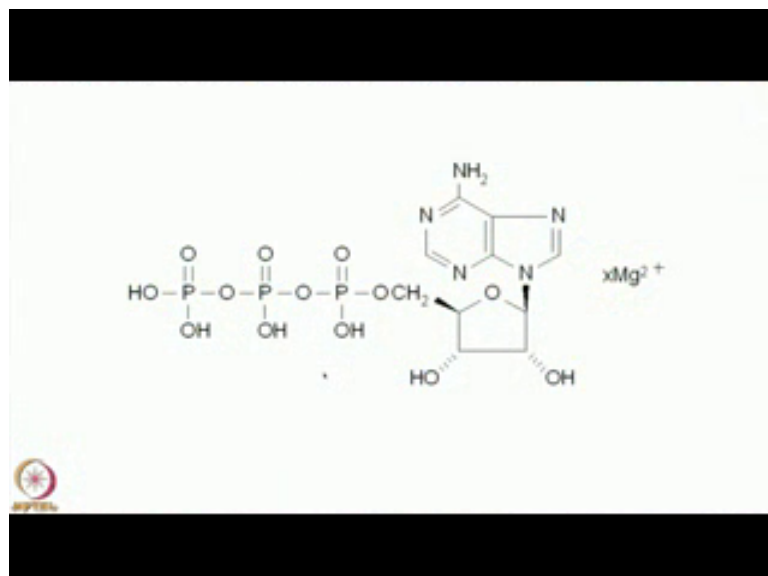
So, in human biology you may be curious to know the fact that magnesium is the eleventh most abundant element by mass in the human body. Its ions are essential to all living cells where they play a major role in manipulating important biological polyphosphate compounds such as ATP DNA and RNA. And hundreds of enzymes does require magnesium ion to perform their function. Magnesium compounds are used medicinally as common laxatives and also anti acids; for example, milk of magnesia. And in a number of situations where stabilization of abnormal nerve excitation and blood vessel spasm is required, this is used. And one term called eclampsia; then let me write here.

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So, is essentially a severe complication of pre-eclampsia; it is a rare but serious condition where high blood results in seizures during pregnancy for women. Magnesium ions are so to the taste and in low concentration they help to impart a natural thoughtness to fresh mineral waters. And in vegetation magnesium is the metallic ion at the centre of chlorophyll; that is responsible for the production of food. And also magnesium is an additive to fertilizers; essentially to enrich plants with magnesium.

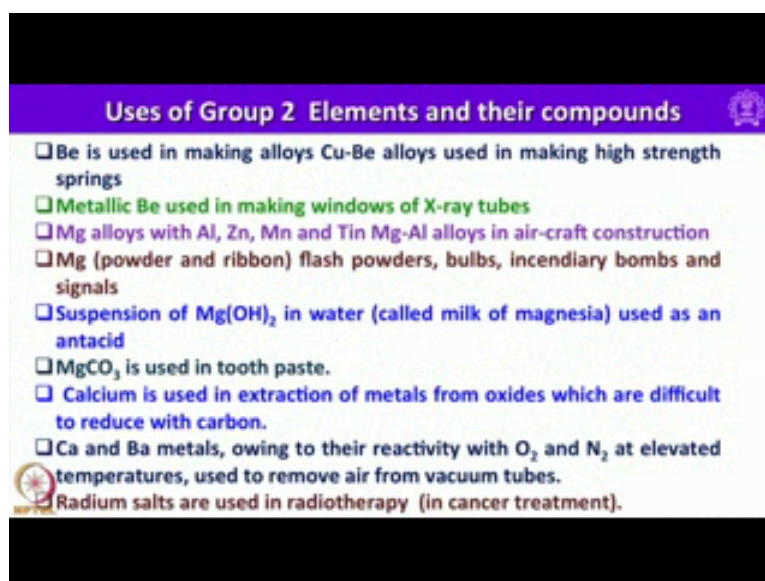
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Of course, this is a commercially available ATP complex of magnesium, and it is also considered as a protector of human DNA. So, DNA synthesis is not possible without the sufficient supply of this ion; that is magnesium ion; it is responsible for the stability and proper functioning of DNA. To maintain an electrolyte balance it is one of the most important mineral. In order to maintain a healthy electrolyte balance in our body deficiency of magnesium ion leads to the improper functioning of sodium potassium pump. I already explained what is sodium potassium pump while describing the chemistry of group one elements and especially while looking into the importance of alkali metals in biology.

So, let us look into the activity of enzymes where magnesium plays a major role. Magnesium as an enzyme co factor plays an important role in the breakage of glucose and fat molecule, in the production of enzymes, proteins, and regulation of cholesterol as well. It also acts as a fuel source; that means it plays an important role in the production of energy within the cells without the sufficient supply of magnesium ion nutrients cannot be converted into usable energy or ATP. Of course, ATP means adenosine triphosphate which is the fundamental unit of energy in human body. Production of ATP is significant to perform various actions, such as cell reproduction, protein synthesis etcetera.

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Uses of Group 2 Elements and their compounds

- Be is used in making alloys Cu-Be alloys used in making high strength springs
- Metallic Be used in making windows of X-ray tubes
- Mg alloys with Al, Zn, Mn and Tin Mg-Al alloys in air-craft construction
- Mg (powder and ribbon) flash powders, bulbs, incendiary bombs and signals
- Suspension of $Mg(OH)_2$ in water (called milk of magnesia) used as an antacid
- $MgCO_3$ is used in tooth paste.
- Calcium is used in extraction of metals from oxides which are difficult to reduce with carbon.
- Ca and Ba metals, owing to their reactivity with O_2 and N_2 at elevated temperatures, used to remove air from vacuum tubes.
- Radium salts are used in radiotherapy (in cancer treatment).

So, with this let us look into the uses of group 2 elements and their compounds. We come across extensive utility of main group elements and their compounds in day to day life. For example: beryllium is used in making a variety of alloys. Copper beryllium alloy used in making high strength springs; of course, springs comes very handy in lot of day to day materials. Metallic beryllium used in making windows for X-ray tubes. And magnesium can conveniently combine with aluminum zinc and manganese and also tin to make a variety of alloys with different properties.

Magnesium aluminum alloys are used in the aircraft construction. And magnesium powder or ribbon is used in bulbs, incendiary bombs, and signals. And suspension of magnesium hydroxide in water is also called milk of magnesia used as an antacid. And magnesium carbonate is also used in toothpaste. And calcium is used in extraction of metals from oxides which are difficult to reduce with carbon prior to the reduction to scavenge most of the main group elements calcium is used in metallurgy. Calcium and barium metals owing to the reactivity with oxygen and nitrogen at elevated temperature used to remove air from vacuum tubes.

So, in order to achieve very high vacuum to get rid of trace amount of oxygen or nitrogen, so they are treated with calcium and barium at very high temperature. Radium salts are used in radiotherapy; that is in cancer treatment. Magnesium oxide finds important application as refractory material. The refractory materials are extensively used in furnace. These magnesium oxide it has a very high melting point of 3073 Kelvin and can withstand high temperature up to 2300 Kelvin for long periods and is relatively inexpensive. As a result for inner layering of furnace magnesium oxide is used in the form of bricks as refractory material. Magnesia is fabricated in bricks for lining furnaces in steel making, incorporating chromium oriented refractory bricks increases the resistance to thermal shocks. So, that means one can also make an alloy and use it as a refractory material.

Magnesia bricks are also widely used in night storage radiators. Magnesium oxide conducts heat extremely well, but also has the ability to store it without much loss of it. In a radiator, the bricks of made up of magnesium oxide absorb heat which is generated by electrically heated filaments during periods of off break and then radiate the thermal energy over relatively longer period. So that means, essentially they store and that can be

dissipated later to maintain a certain temperature inside the oven. And in some cases in the radiator essentially it is used to absorb excess heat that is generated.

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The slide features a purple header with the text "MgO: refractory material" and a small logo on the right. Below the header, there are two bullet points in a light blue font. The first bullet point states: "MgO (Magnesia) is fabricated into bricks for lining furnaces in steelmaking." The second bullet point states: "Magnesia bricks are also widely used in night-storage radiators: MgO conducts heat extremely well, but also has the ability to store it." At the bottom left of the slide, there is a small circular logo with the text "NPTEL" below it.

Magnesium oxide can be fabricated into bricks for lining furnaces in steelmaking, I mentioned already. And as I said; so that means, they are conveniently used in night storage radiators. And in fact, another important property of magnesium oxide is it conducts heat extremely well, but also has a remarkable ability to store it without much leakage of temperature.

When one looks for a commercial viable refractory oxide, magnesium oxide comes very handy it can be conveniently fabricated to bricks and several other type of material; that I will show you in the next slide.

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You can see here: this is magnesium oxide in the powder form, it can be molded into any of these shapes, and this is a typical a furnace I have shown. Here if you look into it furnace inside is layered with this magnesium oxide, and here it can be used where the temperature of furnace goes up to more than 3000 degree centigrade.

So, let me stop at this juncture. And in my next lecture, let me come up with more applications of group 2 elements and their compounds in day to day life.

Thank you very much, and have a pleasant reading of inorganic chemistry.