

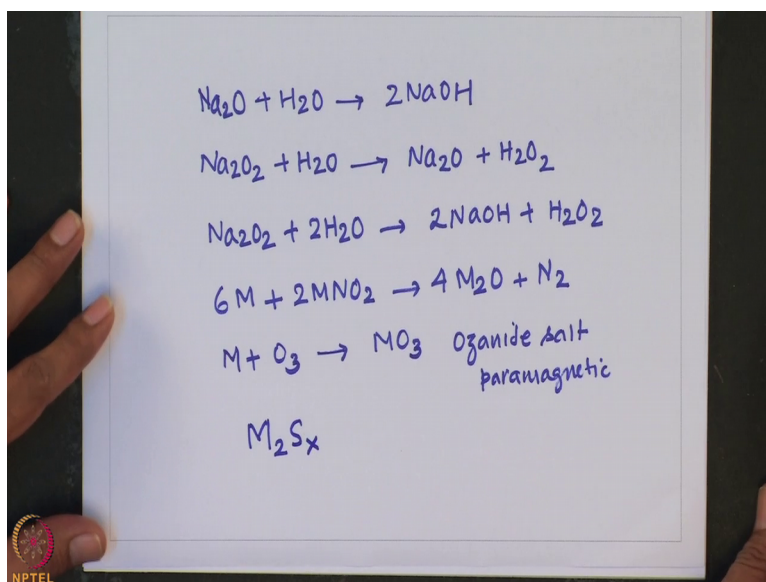
Main Group Chemistry
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Lecture – 17
Chemistry of Group 1 elements

Once again I welcome you to MSB lecture series on Main Group Chemistry. In my previous lecture I initiated discussion on chemistry of group 1 elements that is alkali metals. Today let me continue from where I had stopped.

I was discussing about the interaction of alkali metals with oxygen and sulphur. Let me recap whatever I said in my last class about how they interact with the oxygen and all these compounds react with oxygen to form oxide peroxide or super oxides. Lithium forms exclusively oxide whereas, sodium and potassium form oxide as well as peroxide and rest of the elements form super oxides, and these oxides are highly sensitive to moisture they readily react with moisture or water to give the corresponding alkali solutions.

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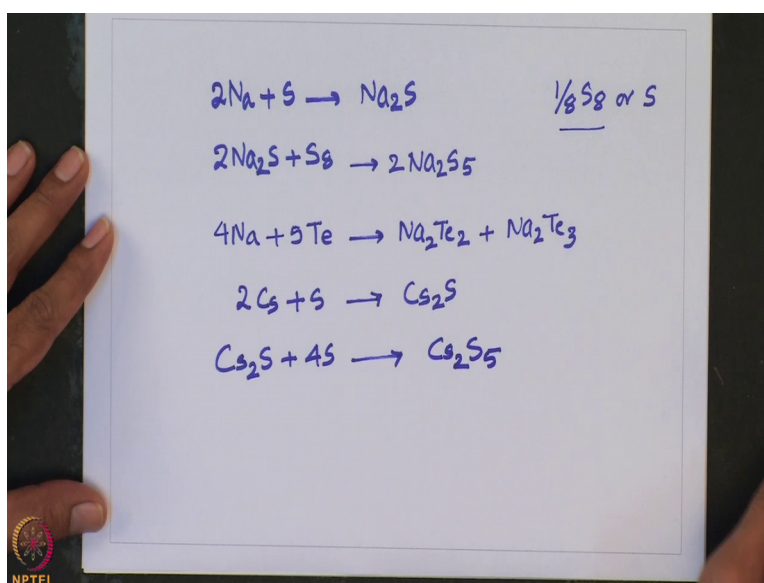


For example Na_2O , sodium oxide reacts with water to form sodium hydroxide. Similarly if you take sodium peroxide it reacts with one equivalent of water to form initially sodium oxide plus H_2O_2 and then if it is reacted with 2 equivalents of water it forms 2NaOH plus H_2O_2 . Similarly metal reacts with metal nitrate, metal nitrate to

form the corresponding metal oxide plus N₂ is liberated here and alkaline metals also react with ozone to form ozanide salt, see this is called ozanide salt. So, these ozanide salts are paramagnetic in nature. Of course, with sulphur form all these alkaline metals sulphides and poly sulphides of composition M₂S_x.

So, let me write few reactions involving sulphur or one can take sodium sulphide react with S₈.

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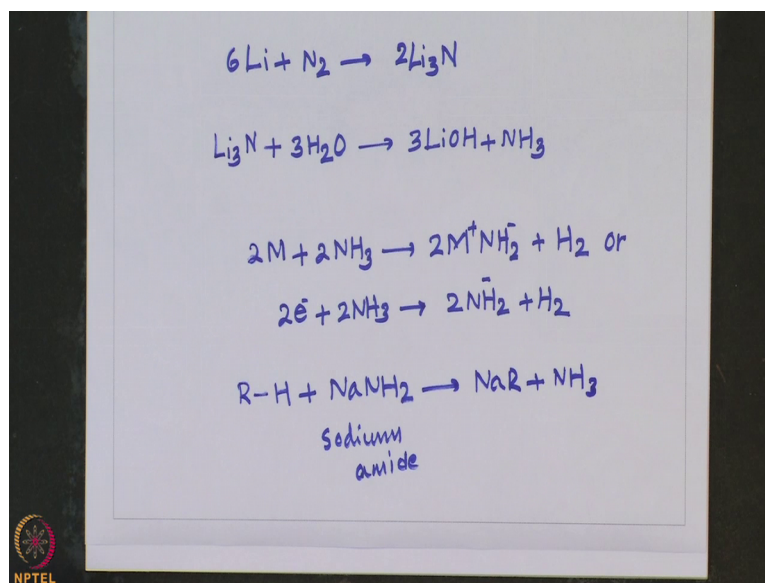


Of course, here also if I write S it indicates the reaction stoichiometry is 2 sodium is to 1 sulphur. In case if I am considering S as S₈ then what I should do is one-eighth of S₈ I should write or simply S.

So, here Na₂S reacts with S₈ to form 2 Na₂S₅ and similarly sodium can also react with the tellurium to give a mixture of Na₂Te₂ similar to sodium peroxide and Na₂Te₃. And cesium also reacts in a similar fashion plus and this cesium sulphide reacts with the excess of sulphur to give Cs₂S₅ similar to sodium analog, sodium reaction.

Lithium directly reacts with nitrogen to form lithium nitride.

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For example, treat 6 equivalents of lithium with nitrogen it gives 2 Li 3 N. So, you may be surprised to see this reaction happening in fact, lithium nitride is very stable because of very high lattice energy associated with lithium nitride due to the smaller lithium plus ion and the small highly charged nitride ion that is N 3 minus, despite having to break the strong n n bond that exist between 2 nitrogen atoms you know that between 2 nitrogen atoms in nitrogen is a triple bond with the energy 954, the bond strength is about 954 kilo joules per mole. That means, whatever the energy that is needed to break n n bond essentially comes from the lattice energy of formation of lithium nitride.

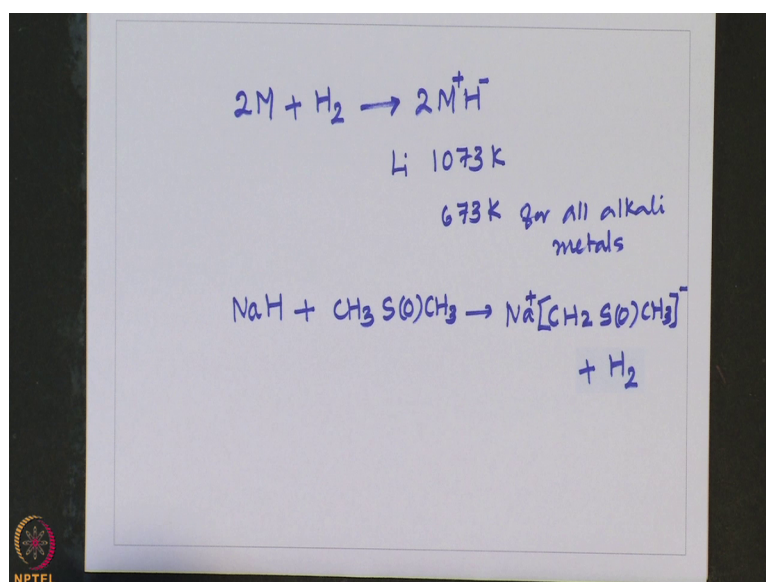
And despite this salt is stable this is proven to hydrolysis; that means, it undergoes hydrolysis to form lithium hydroxide and ammonia is liberated. And just like sodium hydroxide which is based in water sodium amide is a base in liquid ammonia because it is able to deprotonate acidic molecules such as R H; that means, it is essentially if the H is quite acidic in a organic molecule it can activate CH bond.

If we take one of these alkali metals and put into ammonia it forms, this indicated that sodium amide is a base with liquid ammonia. What actually happens here can also be written in this fashion two electrons when they are leached out from alkali metals that interacts with ammonia to form amide ions plus H 2 is liberated. As I mentioned this sodium amide can deprotonate if the H is sufficiently acidic in an organic molecule. For example, if I consider this reaction here this shows you how a alkyl sodium is generated.

So, this is also called sodium amide. So, this gives Na R plus NH₃ is formed. So, this way sodium amide comes very handy in organic reactions to make carbon carbon bonds.

Now, let us look into the interaction of alkali metals with hydrogen to form hydrides as I had already mentioned in my early lectures that hydrogen reacts with alkali metals and alkaline earth metals to form ionic hydrides. So, here most of the metals alkali metals react with hydrogen to form the corresponding hydride. For example, in case of lithium the temperature required is quite high, this is a general reaction of alkali metals with hydrogen to form metal hydride.

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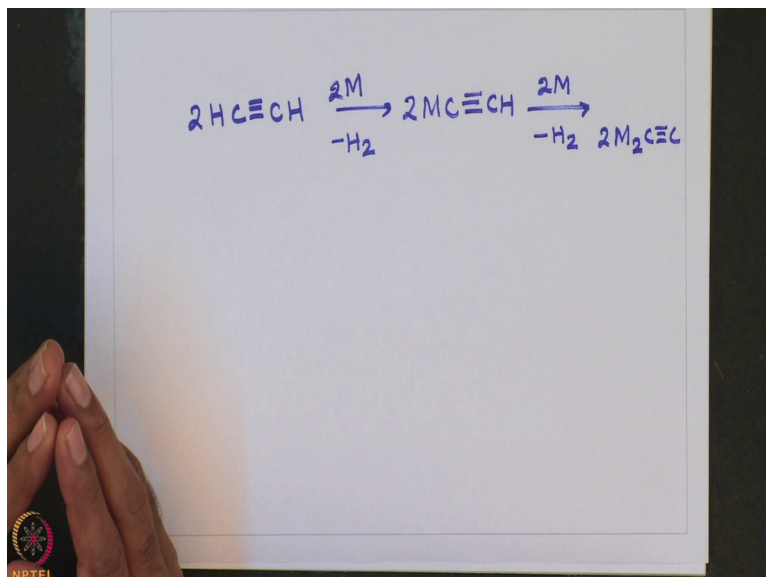


So, in case of lithium temperature required is 1073 Kelvin whereas, for other elements reaction happens at relative lower temperature for rest of the alkali metals one can perform reaction at 673 Kelvin, for all alkali metals. So, H minus is a very strong base can be used to deprotonate organic molecules containing relatively acidic CH groups very similar to sodium amide here alkali metal hydrides also can be used to deprotonate organic molecules provided the CH bond is relatively acidic.

Let me give an example here. Let us take sodium hydride and treat this one with dimethyl sulfoxide it gives. So, in this fashion all this hydrides can be used to activate CH bond and to carry out a variety of organic transformation in organic synthesis. So, let us look into the interaction of alkali metals with carbon fragments or organic molecules.

For example, acetylene reacts directly with alkali metals to form the corresponding carbides or alkyne derivatives.

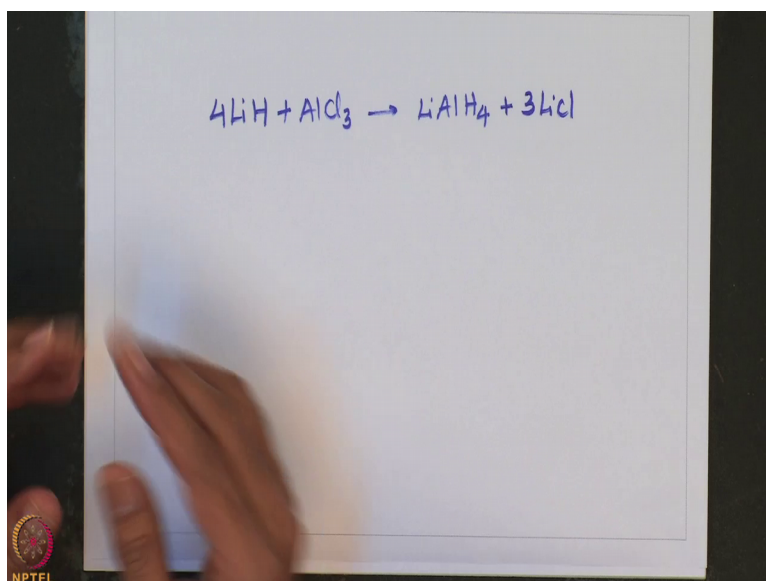
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Let us consider acetylene when an acetylene is treated with one equivalent of M, it forms and of course, here H₂ is liberated and then on subsequent treatment of this one with 2 more equivalents of metal what we get is, this one.

So, this is essentially a reaction in which ethyne or acetylene acts as an acid of course. The extensive organometallic chemistry is associated with alkali metals especially with lithium we call lithium organics lithium reagents for example, N butyl lithium, tertiary butyl lithium, secondary butyl lithium, methyl lithium, phenyl lithium. So, all those things they find numerous applications in a variety of organic transformations I would elaborate more on the reactivity of alkyl or aryl lithium or organo lithium reagents and their utility in organic chemistry when I discuss (Refer Time: 13:30) chemistry of main group elements that I will be doing after completing the chemistry of all main group elements group wise.

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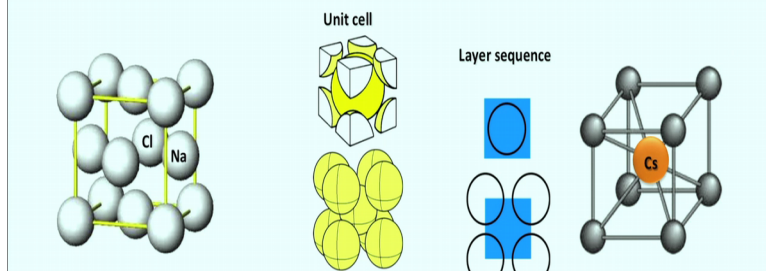


This lithium hydride, it can also be used to make other reducing agents. For example, when lithium hydride is treated with aluminum dichloride it leads to the formation of lithium aluminum hydride very important reagent to reduce or to convert many of the main group halides to the corresponding hydrides. Of course, already I showed you the utility of lithium aluminum hydride in main group chemistry to make the corresponding hydrides. For example, lithium aluminum hydride when it is treated with tetrachlorosilane it forms silane or tetrachlorosilane similarly lithium aluminum hydride also can be used to make PH bonds corresponding from PCl bonds.

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Compounds with halogens

- Alkali metal halides are well-known compounds.
- CsCl, CsBr and CsI have the same structure



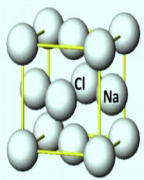
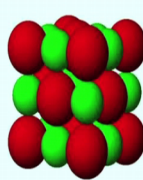
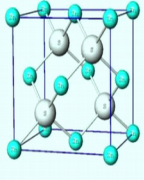
- In CsCl structure, the cation and anion are both eight coordinate
- In NaCl, they are six coordinate; both have a ratio of 1:1

Now, let me look into the compounds with halogens. With halogens alkaline metals react to form all type of halides for example, all alkaline metals react with all halogens to make all combinations lithium can react with all halogens starting from fluorine, chlorine, bromine, iodine to form the corresponding halides in the same cesium also can form, but they have little different properties whereas, reactivity as well as their structures.

All alkali metals react with halogens to form the corresponding halides and here cesium chloride, cesium bromide and cesium iodide has the same structure whereas, sodium chloride has a different structure the structure of sodium chloride is face centered cubic whereas, that of cesium chloride, cesium bromide and cesium iodide is body centered cubic b c c. And in cesium chloride structure the cation and anion are both 8 coordinate that you can see from this one here cesium is 8 coordinated, similarly if I continue this lattice this halides are also 8 coordinated having 8 adjacent alkali metal ions whereas, in case of sodium both chlorine as well as sodium or 6 coordinate having a ratio of 1 is to 1 that you can see from the structure here both are octahedrally surrounded by the opposite ions. Some chlorine is surrounded by sodium ions and sodium each, sodium is surrounded by 6 chloride ions.

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Predicting the structures using radius ratio rules

The structure adopted by a salt M^+X^- can be predicted by considering the relative sizes of the cation (radius r_+) and anion (r_-), the so-called radius ratio rules:

r^+/r^-	Structure type
0.225-0.414	ZnS (sphalerite)
0.414-0.732	NaCl
>0.732	CsCl

Radius ratio rules provide a reasonably general means of assessing the likely structure adopted by an ionic solid, but give incorrect predictions when:

- there is a significant covalent bonding
- The radius ratio is near borderline
- Ionic radii are not known accurately; the values vary with the coordination number (how many nearest neighbour ions) of the ion

So that means, since we have several halogen compounds of alkali metals all combination is possible then how to predict the structure. We have a an empirical

formula to predict the structure using simply radius ratio rule; that means, here the structure adopted by a salt $M^+ X^-$ can be readily predicted simply by considering the relative sizes of cation and the anion and this is nothing, but the radius ratio rule.

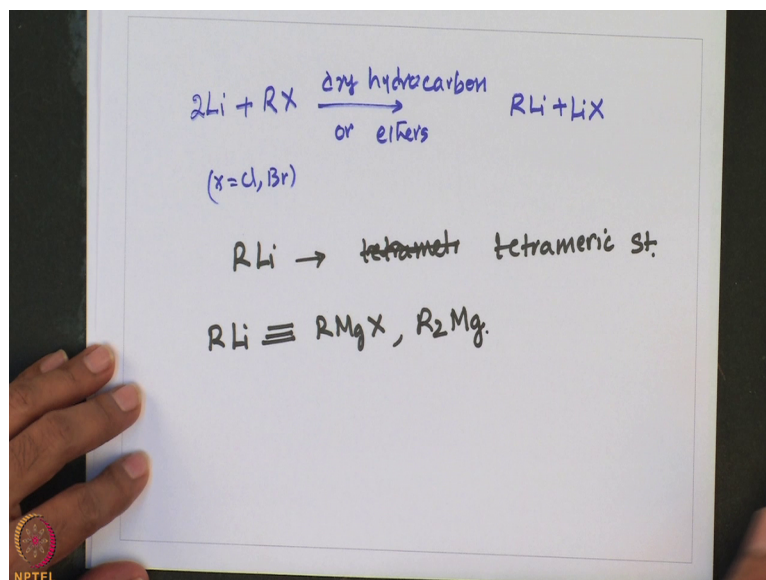
What it says let us see. I have listed the radius ratio values for different structure types for example, when the radius ratio range is between 0.225 to 0.414 they assume sphalerite structure that is zinc sulphide structure. When the value is between 0.414 and 0.732 they assume sodium chloride structure, here they assume that is face centered cubic structure when the value is greater than 0.732 they prefer cesium chloride structure or body centered cubic structure; so how far this ratio is reliable to depict the structure of alkali metal halides.

The radius ratio rules provide a reasonably general means of assessing the likely structure adopted by an ionic solid. However, it can give incorrect predictions only when there is a significant covalent bonding is there for example, if we consider lithium halides most of them because of its charged sized ratio that significantly differs from rest of the alkali metals there is some covalent character as a result in that case this rule may not predict precisely and because of covalent bonding present in it. The radius ratio near border line, when we have this ratio near border line for example, when we have 0.414 or you know it can have zinc sulphide structure or sodium chloride structure and again when the value is around 0.732 again it can have either sodium chloride structure or cesium chloride structure; that means, one has to be extremely careful when the values are border line and the ionic radii are not known accurately, the values vary within the coordination number of the ion. So, in those what happens the prediction may not be precise; however, it gives say a rough method to estimate the structure type of alkali metal halides.

Let us look into the preparation of some of the organo lithium reagents. You may be surprised that I did not give the method of preparation of alkali metal halides of course, most of the alkali metal halides do occur in nature and however, if one has to make any of this alkali metal halide one can conveniently use the neutralization reaction. For example sodium hydroxide on treatment with hydrochloric acid gives sodium chloride plus water. So, one can use this method and most commonly this kind of methods are used to prepare alkali metal halides.

Now, let me look into the preparation of organo lithium reagents. Several methods we have one method I will show you, and rest of the methods as I said I will be discussing when I start lecture on organometallic compounds of alkali metals.

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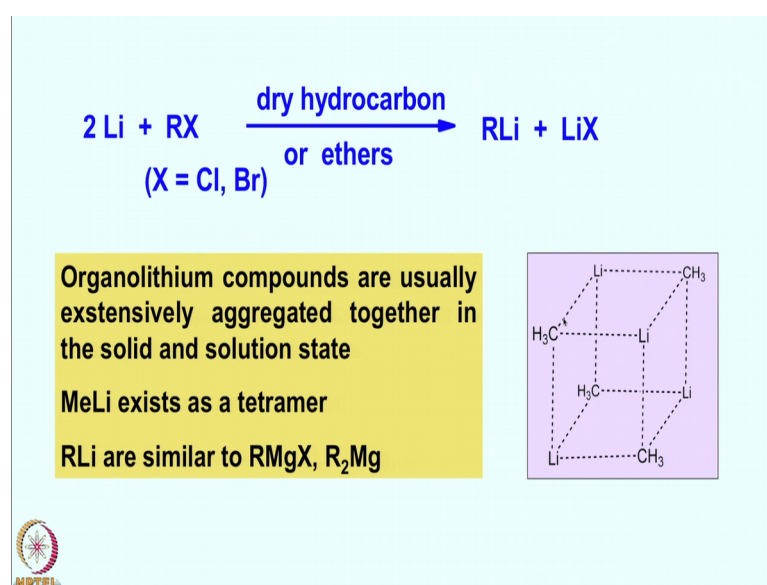
When 2 equivalents of lithium is treated with an organic halide one has to remember that these reactions have to be carried out strictly under inert atmospheric conditions using dry hydrocarbons and thoroughly dried glassware or dry ethers such as diethyl ether or tetrahydrofuran and here x can be preferably Cl or Br, here it forms RLi plus LiX. So, this LiX is insoluble and this can be filtered off and if the solution would contain alkyl lithium.

So, organo lithium compounds are extensively aggregated together in the solid state and solution state as well. For example, methyl lithium exists as a tetramer. Why these compounds have a tendency to associate or aggregate to form higher oligomers is because, here just if you can see methyl lithium or organo lithium reagents it is mono coordinated when it is mono coordinated at least 3 more vacant sites are there as a result what happens it is considered as electro deficient. In order to overcome the electron deficiency it will try to undergo association very similar to what we come across in case of BH_3 becoming di borane or aluminum tri chloride becoming Al_2Cl_6 . So, in this case all alkyl lithium reagents prefer to have dimeric or tetrameric structure. Methyl lithium prefers a tetrameric structure and the reactivity and its utility is more or less similar to (Refer Time: 22:25) reagent such as RMgX or di organo reagent such as R_2Mg .

So, if we take generally RLi where R is an alkyl group or aryl group, they associate in case of methyl lithium N butyl lithium secondary N butyl lithium. So, they exist in the form of a tetrameric structure in solid state and when it comes to the reactivity reactivity is very similar to (Refer Time: 23:08) reagent of course, I will be discussing more about (Refer Time: 23:12) reagent along with the chemistry of group 2 elements and also R₂Mg.

So, this is how the methyl lithium structure looks like.

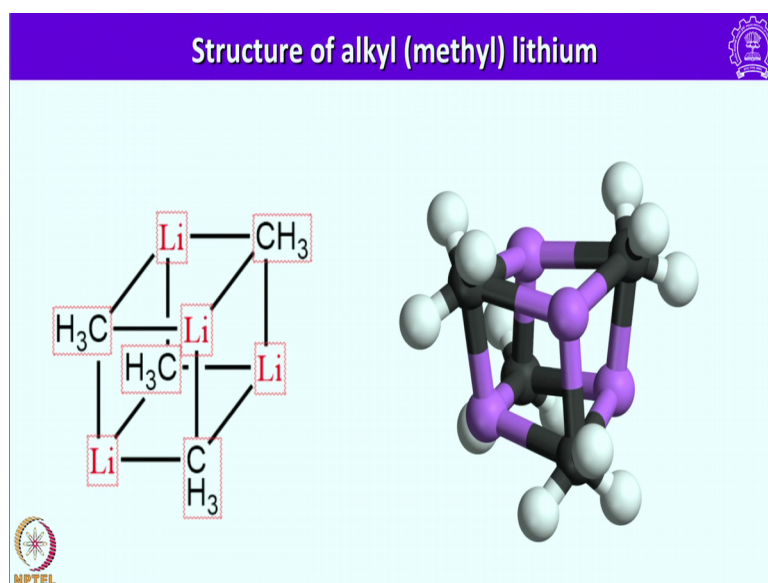
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You can see here it has a cubian structure where alternate carbons are occupied by lithium and methyl groups and here if it is essentially 2 electron 4 centered bonds are there. And this can also be explained using valence bond theory through hybridization concept as well as molecular orbital theory. I would give more insight into the structure of methyl lithium to start with or in general alkyl lithium compounds.

As I said again while discussing organometallic chemistry of main group elements and this how it looks like here.

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So, methyl lithiums, 4 methyl lithiums will associate to form a tetramer having a cubane structure and this can also be visualized here in this all type diagram. You can see here these are this represent 3 hydrogen atoms on carbon and we have lithium here and it will give you clear idea that one of the sp^3 hybrid orbital of methyl a moiety having one electron interacts with the 3 lithium atoms out of 3 lithium atoms one of the lithium atoms readily give one electron to each methyl groups. So, that we have essentially 2 electrons are associated with each methyl lithium and we do not have any excess electrons as a result 2 electrons are shared between a 4 atoms.

So, alkali metal complexes form relatively very few complexes with neutral ligands and lithium salts are more soluble in solvents such as ethanol, ethers than those of other group members. Lithium is 4 coordinate and sodium and potassium are 6 coordinate. Let me discuss more details in my next lecture.

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