Main Group Chemistry
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Lecture – 28
Chemistry of Group 13 Elements

Welcome to MSB lecture series on Main Group Chemistry. In my previous lecture I spoke on Oxides of Group 13 elements, today let me speak on halides of group 13 elements; boron, trihalides, or monomeric under ordinary conditions and posses trigonal planar structures. They are much more volatile than the corresponding compounds of aluminium. The trifluorides of aluminium, gallium, indium, and thallium are or non volatile solids.

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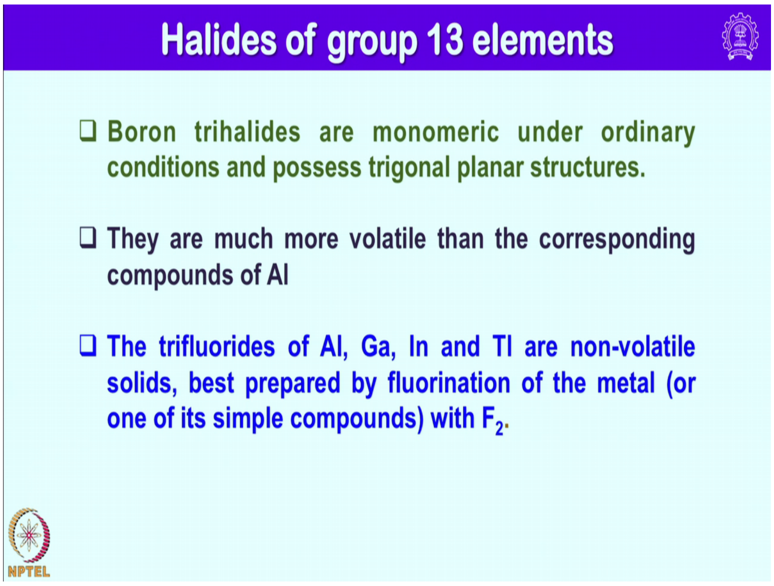

Halides of group 13 elements

- ❑ Boron trihalides are monomeric under ordinary conditions and possess trigonal planar structures.
- ❑ They are much more volatile than the corresponding compounds of Al
- ❑ The trifluorides of Al, Ga, In and Tl are non-volatile solids, best prepared by fluorination of the metal (or one of its simple compounds) with F_2.

Best prepared by the fluorination of the metal or one of its simple compounds with fluorine gas, in fact, when we talk about trihalides of group 13 elements all combinations of M and X occur in trivalent MX 3.

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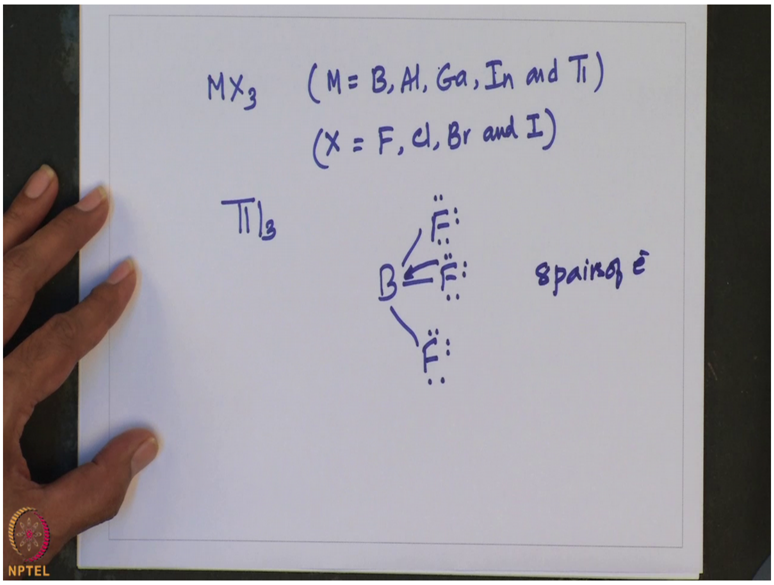

That means, when we consider MX 3 all combination are possible where M equals boron, aluminium, gallium, indium, and thallium; and X fluorine, chlorine, bromine, and iodine.

So, all combinations are possible with an exception of thallium triiodide. The reason is very simple: any combination of highly oxidising and highly reducing species is unstable and here thallium plus 3 is essentially oxidising in nature and I minus is reducing. So, as a result what happens this one is unstable. Except for this one all combinations are possible.

And as I mentioned, all trivalent halides are planar molecules and they have an empty p orbital perpendicular to the plane in BF 3 and in fact also in BCl 3 this pi back donation filled X pi orbital. That means, you just recall chlorine or fluorine when they have acquired an electron they have s 2 p 6 electronic configuration. Out of that one, that means four pairs of electrons are available in the valence shell of any halide anion. Out of that one pair is utilised in bonding other three pairs are available for pi bonding. Out of that one of the fluorine can always donate through 2 pi; 2 pi or 2 pi 3 pi interactions to overcome some of the electron deficiency of boron atom.

And in this case essentially boron fluorine bonds have some multiple bond character more compared to BCl 3 here. In case of BCl 3 we are talking about 2 p and 3 p overlapping, and because of mismatch this overlapping is very poor. As a result what happens a poor back bonding one can anticipate from chlorine to boron. As a result what happens boron trichloride remains more stronger or powerful Lewis acid compared to BF 3.

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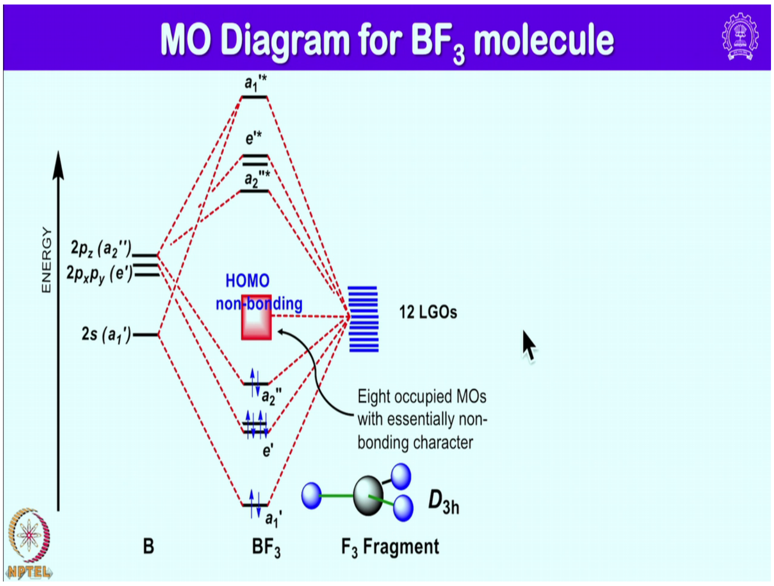

MO Diagram for BF_3 molecule

Eight occupied MOs with essentially non-bonding character

So, you just recall the MO diagram I showed for BF 3 molecule while discussing the bonding concepts that time I showed you this one, this I wrote MO diagram for BF 3. Here we just see B can utilize four valence orbital; so a 2 p orbitals and 2 s orbital, whereas here this F 3 fragment has 12 orbitals essentially each one has 3 p and 1 s, so as a total of we have 12 legand group orbitals. These legand group orbitals will combine with B to form this bonding and non-bonding. That means, essentially we have total of 16 atomic orbital. Out of 16 atomic orbitals 4 atomic orbitals are used for bonding and 4 for anti bonding and remaining 8 remain as non-bonding with 16 electrons.

You may be wondering from where these 16 electrons are coming; just go back to this BF Lewis dot structure of course this is planar. So, we have this kind of situation here. We have three pairs of electron on each let us assume one of the fluorine atom gives a pair of electron through back bonding p pi p pi.

So, then still we are left with 0 1 2 3 4 5 6 7 8; that means, 8 pairs of electrons; 8 pairs of electrons are still left. And these 8 pairs of electrons are essentially occupying here. This one pair whatever is there that is participating in bonding can be seen here in this one. This is the one that is responsible for that is essentially coming from p z; that is perpendicular to the plane of the molecule; where p x and p y are combined with s to form sp 2 hybrid orbitals.

So, you can sees here. And, in case if you write similar MO diagram for BH 3 we are considering h 3 fragment here. So, in this case here this will not be there because it accounts for only 6 electrons: 3 electrons from s 2 p 1 of boron and 1 electron is from hydrogen. So, that essentially comes for 6 electrons. So, this one is essentially coming from one of the fluorine lone pairs. So, that is making it multiple bond character in one of that one so that essentially gives or satisfy the octet of boron. And remaining 16 electrons are placed here they are non-bonding.

So, B X 3 are monomers the structures of AlX 3; that means, aluminium trichloride fluoride dependent on the type of halide we are using. Aluminium triflouride is a high melting polymeric solid build from fluorine bridged AlF 6 octahedra. The structure of AlCl 3 in the solid state has 6 coordinate aluminium centres with chloride bridges. However, if the liquid and gas phase aluminium trichloride remains dimeric that is called Al 2 Cl 6 with dative bonds between aluminium and chlorine in the bridging unit; I will be showing those structures soon. Aluminium tribromide and aluminium triiodide are dimeric in all states. ok.

So, before I show the structures let us see how one can prepare some of this group 13 halides. All boron trihalides except BI 3 may be prepared by direct reaction between the elements. However, the preferred method for BF 3 preparation is the reaction of B 2 O 3 with calcium fluoride in sulphuric acid. You should remember calcium fluoride is a powerful formicating agent. So, let me write these reaction methods through a balanced chemical equation.

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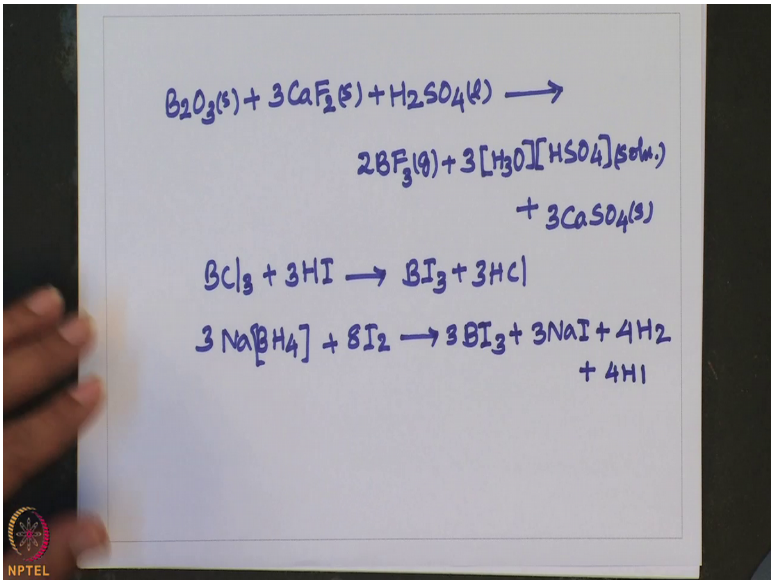

$B_2O_3(s) + 3CaF_2(s) + H_2SO_4(l) \longrightarrow$

$2BF_3(g) + 3[H_3O][HSO_4](soln.)$

$+ 3CaSO_4(s)$

$BCl_3 + 3HI \longrightarrow BI_3 + 3HCl$

$3\,Na[BH_4] + 8I_2 \longrightarrow 3BI_3 + 3NaI + 4H_2$

$+ 4HI$

Similarly, the reaction between boron and chlorine or bromine yields BCl 3 and BBr 3. For example, in case of BCl 3 when it is treated with a HI it can give BI 3 plus 3 HCl. Or one can also start with sodium borohydride plus 8 equivalence of iodine it gives. So, this is how one can prepare this much triiodide.

Let us look into the nature of these halides of boron.

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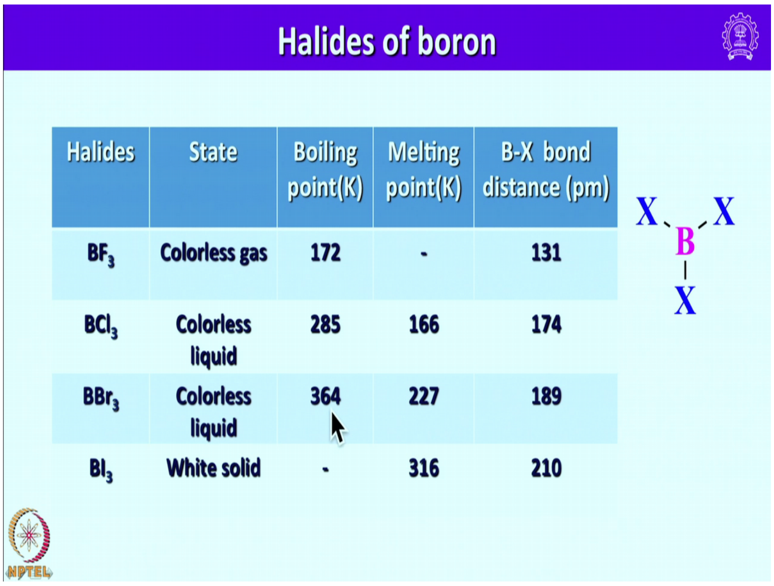

Halides of boron

Halides	State	Boiling point(K)	Melting point(K)	B-X bond distance (pm)
BF_3	Colorless gas	172	-	131
BCl_3	Colorless liquid	285	166	174
BBr_3	Colorless liquid	364	227	189
BI_3	White solid	-	316	210

And BF 3 is colourless gas boiling point 172 Kelvin and B X bond distance BF bond distance is 131 picometre. BCl 3 is a colourless liquid boiling point 285 Kelvin, melting point 166 Kelvin, and bond distance is 174. BBr 3 again colourless liquid with boiling point 364 Kelvin and melting point is 227 Kelvin and here BBr distance is 0189 picometre. Boron triiodide is a white solid with melting 316 Kelvin and boron to iodine bond distance is 210 picometre.

So, all are planar molecules.

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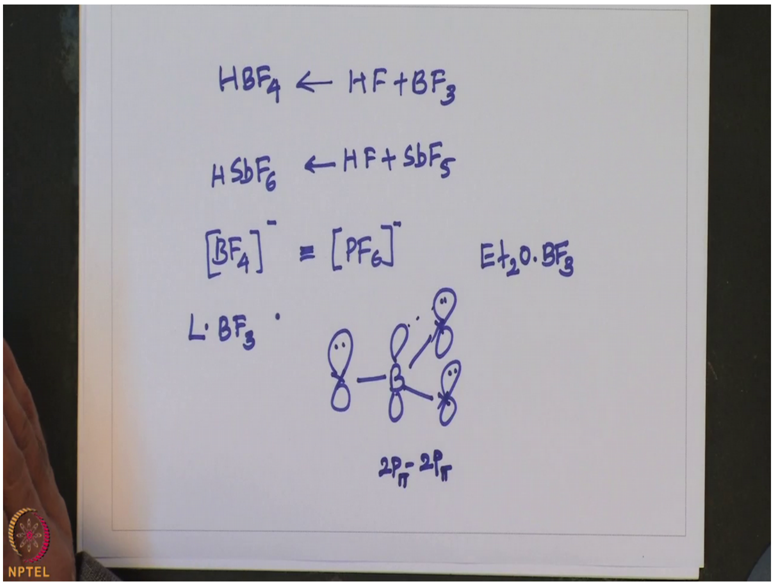

And tetrafluoroboric HBF 4 is essentially a very strong acid and it can be prepared by conveniently mixing HF with BF 3. It is a very strong proton donor; however the very strong proton donor is essentially a combination of HF plus SbF 5. This is HbF 6. This is a much more stronger proton donor compared to this one. And if you consider BF 4 anion, this is very similar to PF 6 anion, and they coordinate very weekly to metal centres until is often used as an innocent anion to precipitate larger cations; especially those of transfer metal complexes.

So, boron trifluoride forms a range of complexes with ethers, nitrous, and amines. That means, essentially there are all having donor atoms such as nitrogen or oxygen. And of course, commercially BF 3 is available as etherate. Multiple bonding or partial double bond character comes can be seen from this diagram here. You can see here: as I said when in a typical planar molecule if you consider. So, these are all p z orbitals: we have electrons here, and here this is empty p z orbital. So, here one can see interactions and these results in multiple bond character. And in case of boron we can anticipate 2 P; 2 P interaction 2 P pi 2 P pi interactions.

The formation of partial bonds in trigonal planar B s three molecule can be considered in terms of the donation of electron density from the filled P atomic orbitals and the X atoms that is a halide into the empty 2 P atomic orbitals on boron. So, reaction of B X 3 with Lewis base results in a change from a trigonal planar to tetrahedral molecule. In that case what happens essentially instead of forming sp 2 hybridization it forms sp 3 hybridization having 3 sp 3 orbits having 1 electron each and 1 sp 3 having no electron. So, this without any electron will interact with filled 2 P orbits of fluorine or 3 P orbits of chlorine to form multiple bonding or have a pi bonding like this.

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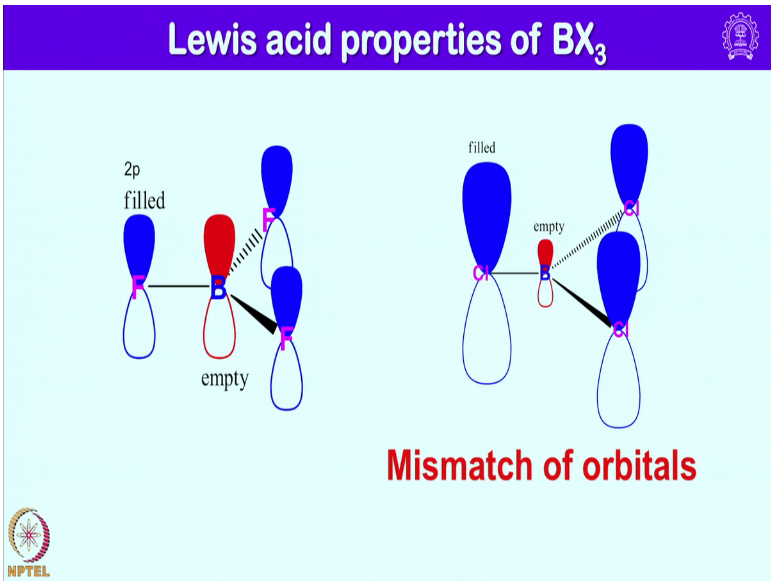

Lewis acid properties of BX_3

Mismatch of orbitals

You can see clearly here. Of course, when we talk about multiple bonding between boron and fluorine is much more stronger compared to boron and chlorine, because here we are talking about 2 p with 3 p interaction. Because of the mismatch of the orbital overlapping is not very efficient, whereas in case of boron trifluoride we are talking about 2 p 2 p interaction here the overlapping is more efficient. As a result what happens BF 3 somehow overcomes the electron deficiency compared to BCl 3 as result BF 3 is slightly less Lewis acidic in nature compared to BCl 3.

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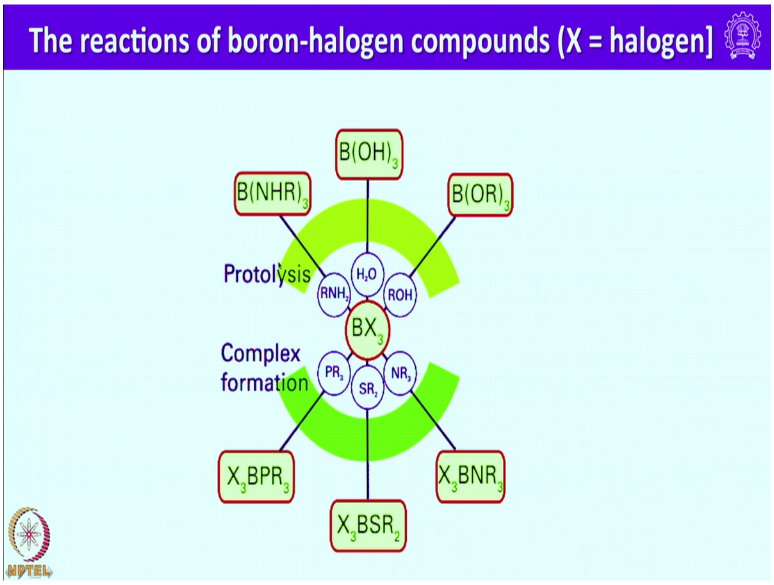

The reactions of boron-halogen compounds (X = halogen]

So, this shows the reactions of boron halogen compounds. For example, you can see and here B X 3 can react with water to form boric acid B OH thrice or you treat that one with alcohol to form corresponding alkoxides or (Refer Time: 15:15) oxides or one can treat with amines to form adducts, or one can also treat with dialkyl sulphide or diaryle sulphide to form the adduct again similar to amine adducts. And one its react should with phosphine also forms adduct.

And similar adducts are also known with carbon monoxide as well. And on treatment with amine it undergoes protolysis to form this kind of compounds B NHR 3 times. These are some reactions of boron halogen compounds. And boron chlorides bromides and iodides are susceptible to hydrolysis by mild proton sources such as water alcohol or even amines that you saw. So, just let me show one reaction here, although I had shown in that previous slide.

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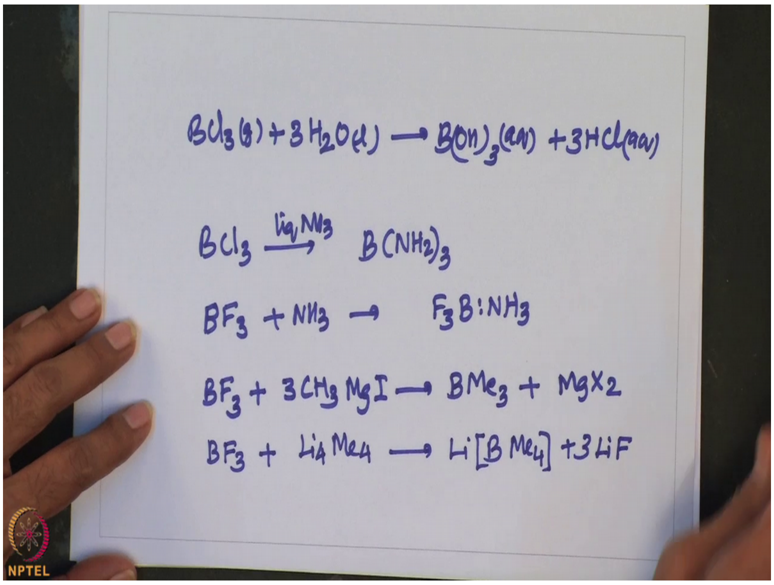

$$BCl_3(g) + 3H_2O(l) \longrightarrow B(OH)_3(aq) + 3HCl(aq)$$

$$BCl_3 \xrightarrow{liq\ NH_3} B(NH_2)_3$$

$$BF_3 + NH_3 \longrightarrow F_3B{:}NH_3$$

$$BF_3 + 3CH_3MgI \longrightarrow BMe_3 + MgX_2$$

$$BF_3 + Li_4Me_4 \longrightarrow Li[BMe_4] + 3LiF$$

And it is BF 3 forms an adduct with NH 3 and BCl 3 reacts in liquid ammonia to form B NH 2 3 times, whereas BF 3 simply forms an adduct. The preparation of alkyl boron and aryl boron compounds is essentially starting from the corresponding boron halides. For example, BF 3 on treatment with methyl magnesium iodide can give trimethyl boron, of course plus you get magnesium halides such as. So, MgI F. And similarly one can also treat BF 3 with methyl lithium; methyl lithium is tetramer so one can write like this: it gives so one can write either Me or one can also write CH 3.

So, boron halides containing boron boron bonds also have been prepared. The best known of these compounds are essentially B 2 X 4.

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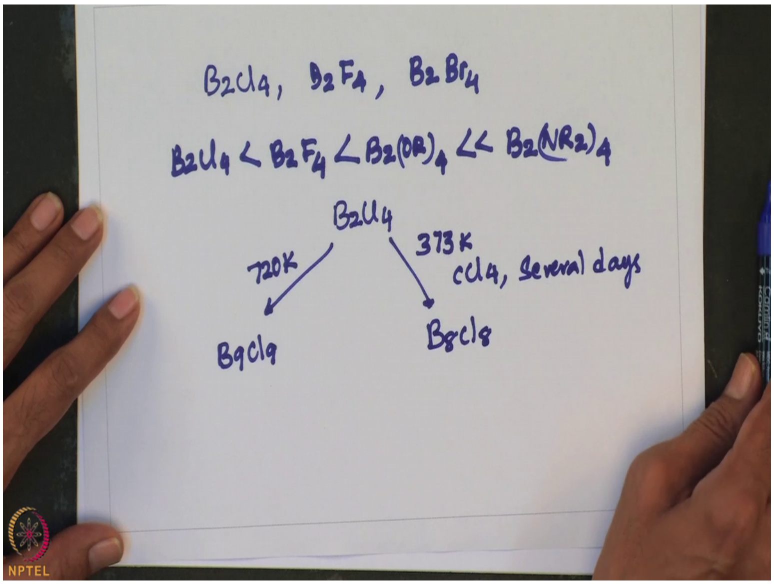

B_2Cl_4, B_2F_4, B_2Br_4

$B_2Cl_4 < B_2F_4 < B_2(OR)_4 << B_2(NR_2)_4$

$$\begin{tikzcd} & B_2Cl_4 \arrow[dl, "720K"'] \arrow[dr, "{373K \; CCl_4, \text{ several days}}"] & \\ B_9Cl_9 & & B_8Cl_8 \end{tikzcd}$$

So for example: B 2 Cl 4. So, this is essentially a planar molecule one can also make similarly B 2 F 4 as well or B 2 Br 4. So, here we can see in solid state B 2 F 4 and B 2 Cl 4 are planar molecules. You can see here.

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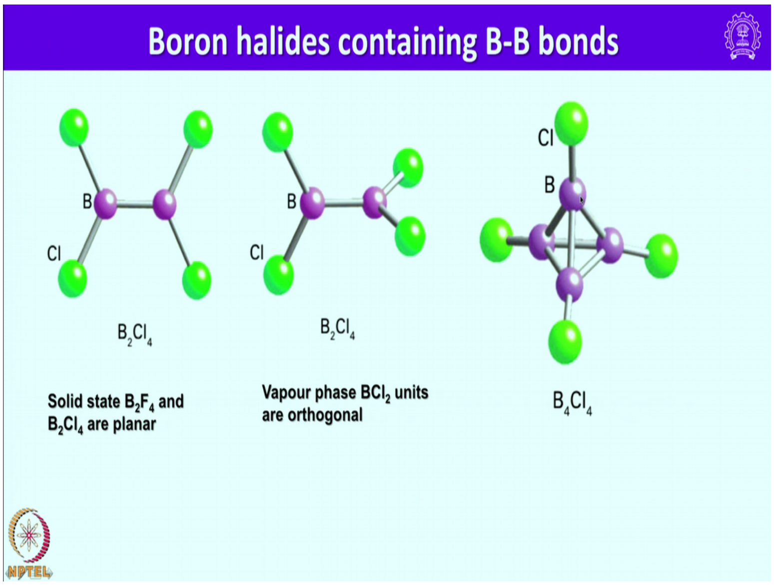

Boron halides containing B-B bonds

B_2Cl_4

Solid state B_2F_4 and B_2Cl_4 are planar

B_2Cl_4

Vapour phase BCl_2 units are orthogonal

B_4Cl_4

Whereas vapour phase B Cl 2 units are orthogonal to each other. So, one of the B Cl 2 becomes orthogonal or it will be perpendicular to another B Cl unit. And of course, B four Cl 4 has a structure like this where 4 boron atoms are disposed to 4 corners of tetrahedron and here these are all chlorine atoms. And metathesis reaction can be used to make these B 2 X 4 derivatives, and the thermal stability of this derivatives increases with increasing tendency of the X group to form pi bonds with boron.

So, one can write the stability in this order: B 2 Cl 4, B 2 F 4, B 2 OR 4. And this B 2 Cl 4 at high temperature can give higher analogs of boron halides. For example, B 2 Cl 4 when it is heated to 720 Kelvin within few minutes it forms B 9 Cl 9. Or on heating this one to 373 Kelvin in presence of CCl 4 more several days it gives B 8 Cl 8. And B 2 Br 4 adopts a staggered conformation in the vapour liquid and solid phase. Of course, the preference of this one is not clearly understood; B 2 Br 4 unlike B 2 Cr 4 or B 2 F 4 adopts a staggered conformation in the vapour phase as well as in liquid as well as solid phase, these preferences are not readily understood or can be explained.

Probably, one can anticipate that because of the largest size when their planar probably that leads to the bromine bromine interaction to prevent that one instead of like this instead of something like this, it becomes something like this. So, if you assume this is boron B boron and another one instead of like this it becomes like this so that bromine atoms can move away from each other giving a staggered conformation, ok

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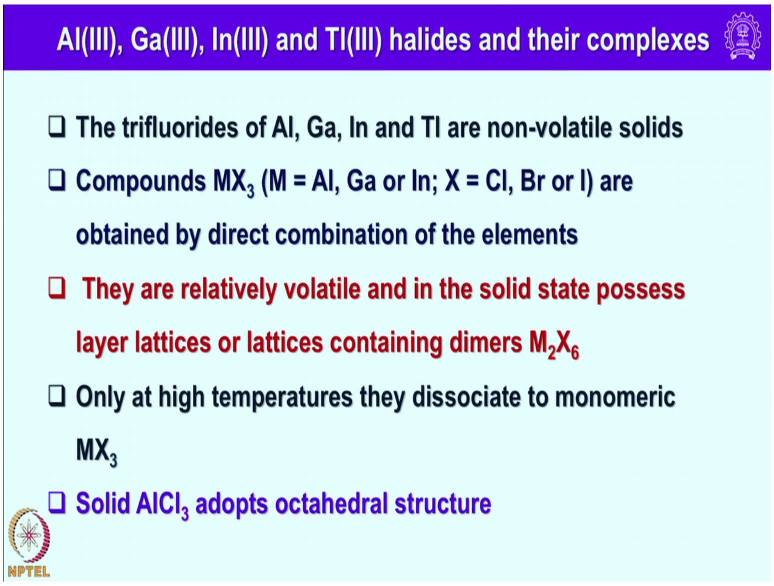

Al(III), Ga(III), In(III) and Tl(III) halides and their complexes

- The trifluorides of Al, Ga, In and Tl are non-volatile solids
- Compounds MX_3 (M = Al, Ga or In; X = Cl, Br or I) are obtained by direct combination of the elements
- They are relatively volatile and in the solid state possess layer lattices or lattices containing dimers M_2X_6
- Only at high temperatures they dissociate to monomeric MX_3
- Solid $AlCl_3$ adopts octahedral structure

So, let us look into now aluminium, gallium, indium and thallium halides. These trifluorides are non-volatile solids and compounds are obtained by direct combination of the elements. Again treating aluminium, gallium or indium with the corresponding halogens one can make this trihalides. And they are relatively volatile in the solid state poses layer lattice or lattice containing dimers of the type M 2 X 6, only at high temperature they dissociate to monomeric MX 3. And solid AlCl 3 adopts octahedral structure; I will show you that structure. Before I show the structures of all this halides let me show the methods of preparation of these halides.

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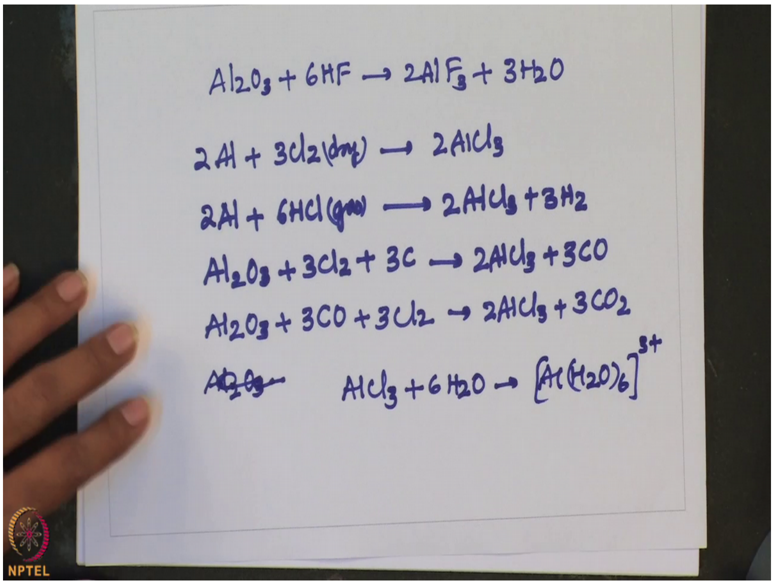

$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O$

$2Al + 3Cl_2(dry) \rightarrow 2AlCl_3$

$2Al + 6HCl(gas) \rightarrow 2AlCl_3 + 3H_2$

$Al_2O_3 + 3Cl_2 + 3C \rightarrow 2AlCl_3 + 3CO$

$Al_2O_3 + 3CO + 3Cl_2 \rightarrow 2AlCl_3 + 3CO_2$

~~Al_2O_3~~ $AlCl_3 + 6H_2O \rightarrow [Al(H_2O)_6]^{3+}$

Al 2 O 3 on treatment with 6 HF it gives Al F 3 plus 3 H 2 O.

So, the preparation of anhydrous aluminium chloride can be planned using one of the following methods I am going to write. For example, you can treat directly aluminium with dry chlorine gas should be very dry to get anhydrous aluminium trichloride. Of course, if it is hydrated or it is wet one can also sublime aluminium trichloride to get anhydrous aluminium trichloride. And repeated sublimation can give you ultra pure very dry aluminium trichloride.

One can also use aluminium oxide and chlorine in presence of carbon as reducing agent. One can use carbon or carbon monoxide. So, when we use carbon monoxide you get carbon dioxide. And aluminium trichloride reacts towards moisture; for example, it can form aluminium oxide. Let me show you the structures now.

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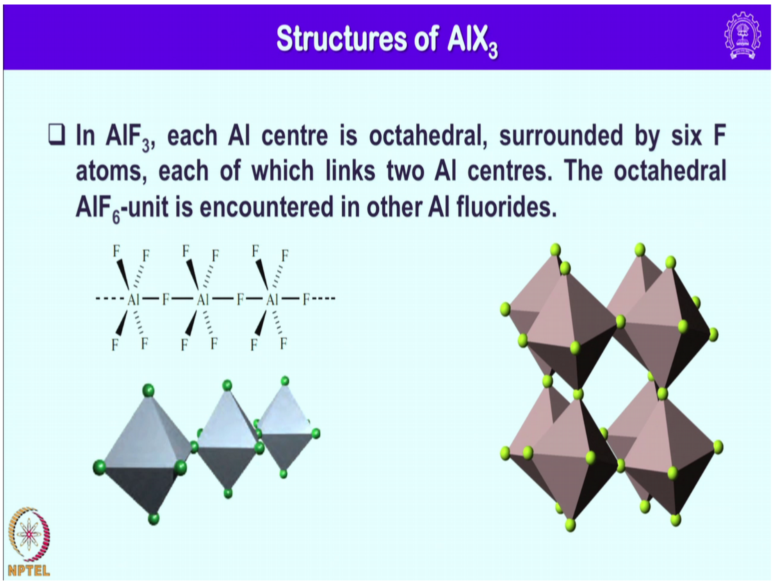

Structures of AlX_3

- In AlF_3, each Al centre is octahedral, surrounded by six F atoms, each of which links two Al centres. The octahedral AlF_6-unit is encountered in other Al fluorides.

So, here in aluminium trifluoride each aluminium centre is octahedral surrounded by 6 fluorine atoms, each of which links to aluminium centres in a linear manner. So, having angle close to 180 the octahedral Al F 6 unit is encountered in other aluminium fluorides. So, if you just look into the monomeric unit it looks in this fashion.

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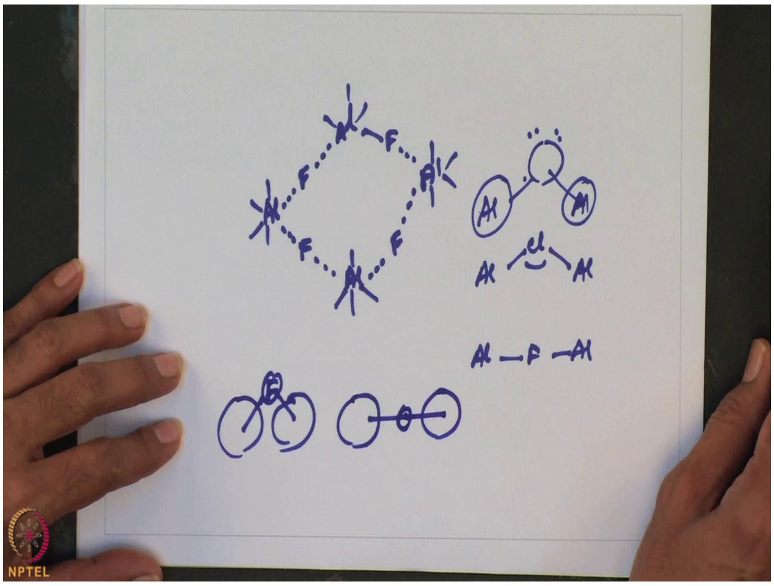

For example if I consider;o, it continues like this each monomeric unit will be having this kind of linear one, of course I can tell you why it is linear. Whereas, in case of chloride is little different you can see here.

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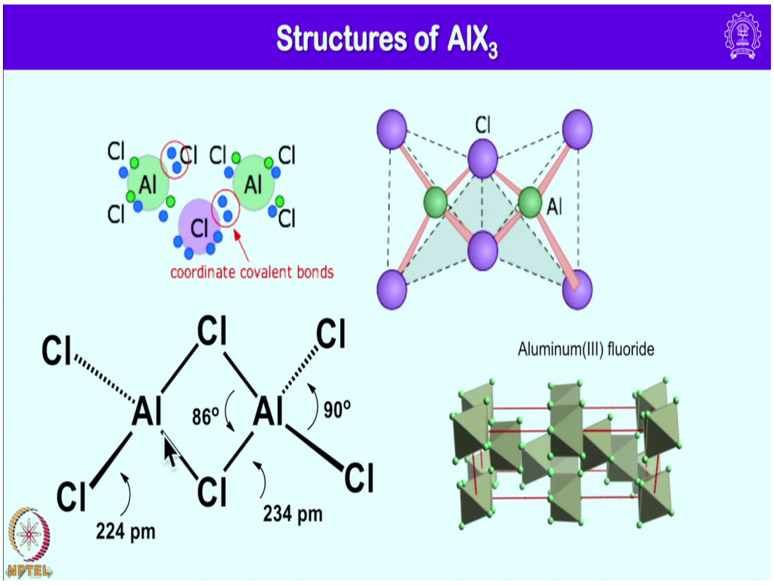

Structures of AlX_3

coordinate covalent bonds

Aluminum(III) fluoride

We have a bend structure here, and in liquid state and gaseous state it exists in the dimeric form.

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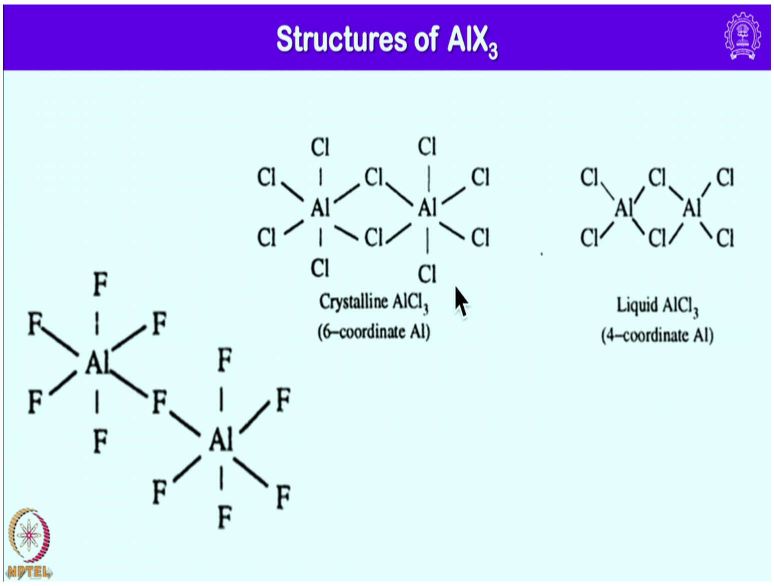

Structures of AlX_3

Crystalline $AlCl_3$
(6–coordinate Al)

Liquid $AlCl_3$
(4–coordinate Al)

Whereas, in solid state it is hexa coordinated in this fashion.

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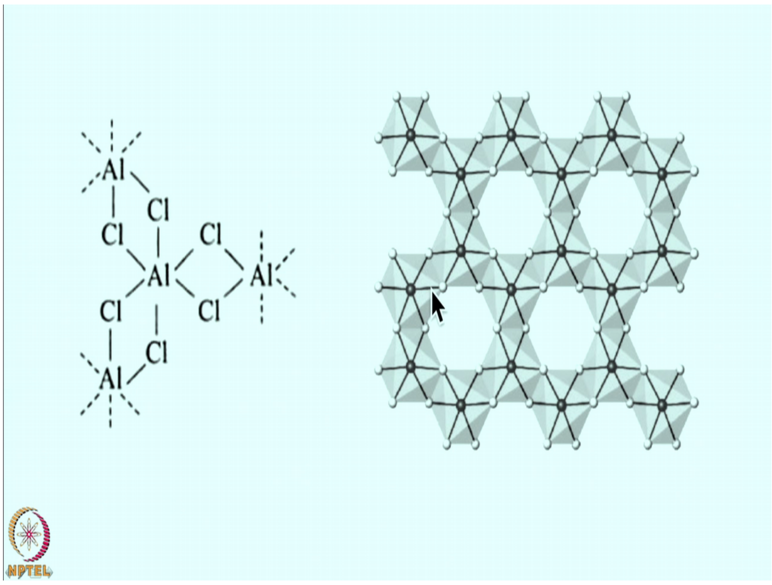

You see this how it is there you have a layered structure something like this, and that can be seen here in this one.

So, we have a layer structure where each aluminium has a 6 coordinated. And these chlorine atoms again make bond with the neighbouring aluminium in this fashion and this layer structure continues. And the question is; why in case of aluminium chloride we have a bend structure like this, whereas in case of aluminium fluoride we have a linear. And this has to do something with the size of the halides. If you just see here the size of this one is little bigger something like this, and here it is much more bigger. So, one can expect them to have this kind of overlapping. Here of course, here we have lone pairs.

Whereas, in case of fluorine because of the smaller size if we try to make a bend structure we have to force two aluminium atom come very close I mean your fluorine will sit somewhere here because of the smaller size. And because of this situation what happens these two which start repelling two cations coming very close together will repel as a result it is destabilized. Instead, they prefer to have this kind of. So, here cations are kept away from each other; for this reason most of the fluorides have linear structure. And to have a polymeric structure they have to be the monomers has to be minimum of trimeric, but mostly they prefer tetrameric structure. Whereas, in case of chlorine one can have Lewis anticipate bent angles at chlorine atoms.

Cryolite is essentially Na 3 Al and F 6 that occurs naturally, but can also be synthesized to meet the commercial needs and also in case of electrolysis of aluminium oxide and to get aluminium. So, solid state structure of cryolite is related to the perovskite lattice.

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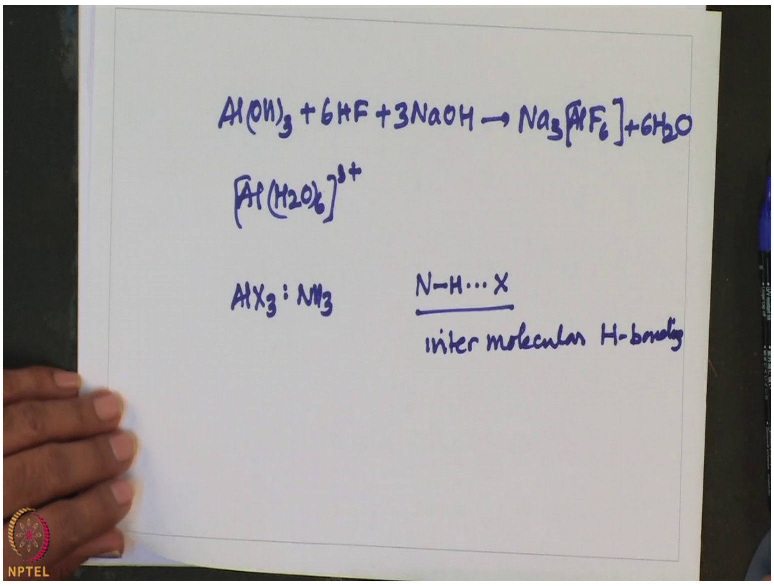

$Al(OH)_3 + 6HF + 3NaOH \rightarrow Na_3[AlF_6] + 6H_2O$

$[Al(H_2O)_6]^{3+}$

$AlX_3 : NH_3$ $\quad \underline{N{-}H\cdots X}$

inter molecular H-bonding

And one can conveniently prepare starting from aluminium hydroxide treating with HF in presence of sodium hydroxide it gives Na 3 Al F 6 H 2 O. So, when water is dripped on to solid aluminium trichloride vigorous hydrolysis occurs, but in dilute aqueous solution it forms 3 plus and with NH 3 aluminium trichloride forms in adduct in the solid state. And of course, in this one there is a intramolecular hydrogen bonding is there that exist as a result of this kind of interactions; some intermolecular hydrogen bonding is anticipated.

So let me stop here, and let me continue in my next lecture more about gallium and indium, trichlorides, tribromides, and also their lower halides.

Thank you very much.