Advanced Transition Metal Chemistry – Periodic Table

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Lecture – 10
Early Bonding Concepts

Welcome you all to MSB lecture series on advanced transition metal chemistry. This is the 10th lecture in the series. In my previous lecture, I was discussing about the coordination concept brought out by very systematic and meticulous experiments with critical and analytical evaluation of his own work, Alfred Werner and how nicely he postulated coordination theory.

When a time there was no methodology or any instrumental facilities or any spectroscope means that was available for him to convincingly understand the features of coordination compounds. Nevertheless, whatever the postulations he made by emphasizing for quantitative understanding was proved to be precisely correct, later with the experimental and spectroscopic evidences.

Once coordination chemistry started evolving, people started looking into various bonding concepts to explain how to characterize compounds and how to explain the bonding that happens between metal ions or metal atoms and ligands. In that context, let us look into early bonding concepts.

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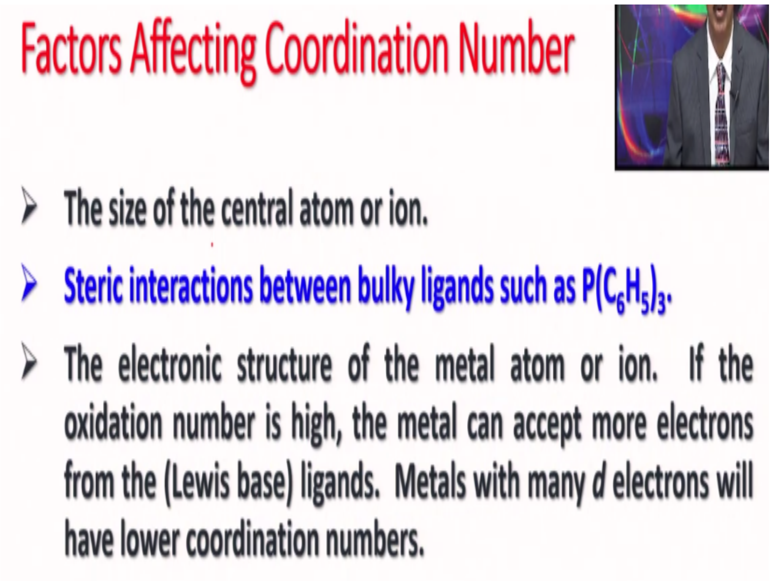

Factors Affecting Coordination Number

- The size of the central atom or ion.
- Steric interactions between bulky ligands such as $P(C_6H_5)_3$.
- The electronic structure of the metal atom or ion. If the oxidation number is high, the metal can accept more electrons from the (Lewis base) ligands. Metals with many *d* electrons will have lower coordination numbers.

Before that, let us look into few points about what are the factors that affect coordination number. The size of the central atom or ion has an influence on coordination number because if the size is larger, it can accommodate more ligands surrounding it. As a result, coordination number can be more. Steric interactions between bulky ligands are also quite important, despite the size of the metal, is appropriate to have four or six ligands.

If the ligand size is much bigger, like triphenylphosphine, it is very difficult to accommodate four ligands. In that context, steric interactions are very important and stearic bulk of the ligand plays a major role in deciding the coordination number of a metal ion. The electronic structure of the metal atom or ion is also equally important. If the oxidation number is high, the metal can accept more electrons from the ligands, that is Lewis bases, because it has more empty orbitals.

Metals with many *d*-electrons will have lower coordination number, that is the reason, when we go towards the late transition metals after d^6-electronic configuration, the coordination number, the tendency to have less coordination number will be more pronounced compared to early metals, which have a tendency to have a larger number of ligands surrounding it. So, now, let us look into some methodologies development to explain bonding.

By the time coordination chemistry was evolving after systematic understanding from Werner's coordination theory, people began looking into bonding concepts. As we see, by the time main group chemistry had very interesting concepts such as VSEPR theory, valence bond theory to explain the structure and bonding among main group elements and same strategy was attempted to expand or extend to coordination compounds. In that context, electron neutrality principle developed by Pauling is very important.

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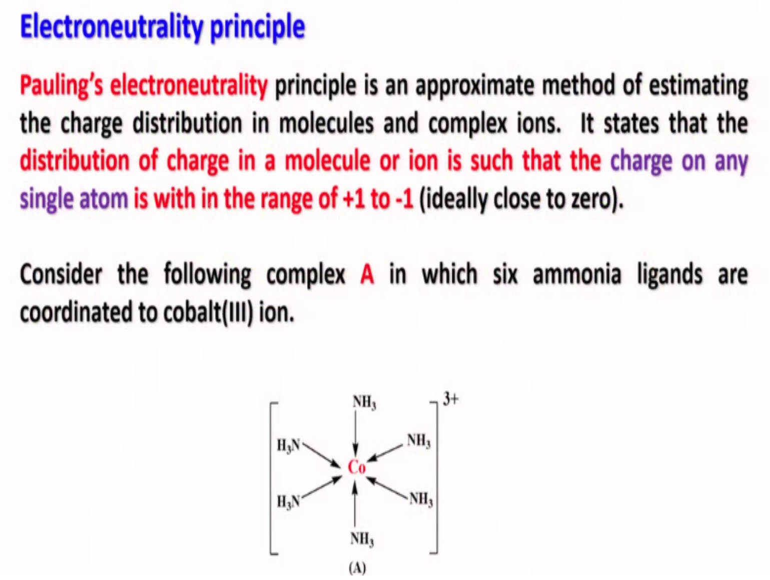

Electroneutrality principle

Pauling's electroneutrality principle is an approximate method of estimating the charge distribution in molecules and complex ions. It states that the distribution of charge in a molecule or ion is such that the charge on any single atom is with in the range of +1 to -1 (ideally close to zero).

Consider the following complex A in which six ammonia ligands are coordinated to cobalt(III) ion.

Pauling's electroneutrality principle is an approximate method of estimating the charge distribution in molecules and complex ions. What it states is: the distribution of charge in a molecule or ion is such that that charge on any single atom is within the range of +1 to –1, ideally close to zero. So, that means in a metal complex all species involved should have a charge between +1 and –1, ideally close to zero. This is what the definition of electroneutrality principle. To test this principle, let us consider one well known example hexammine cobalt 3+ ion.

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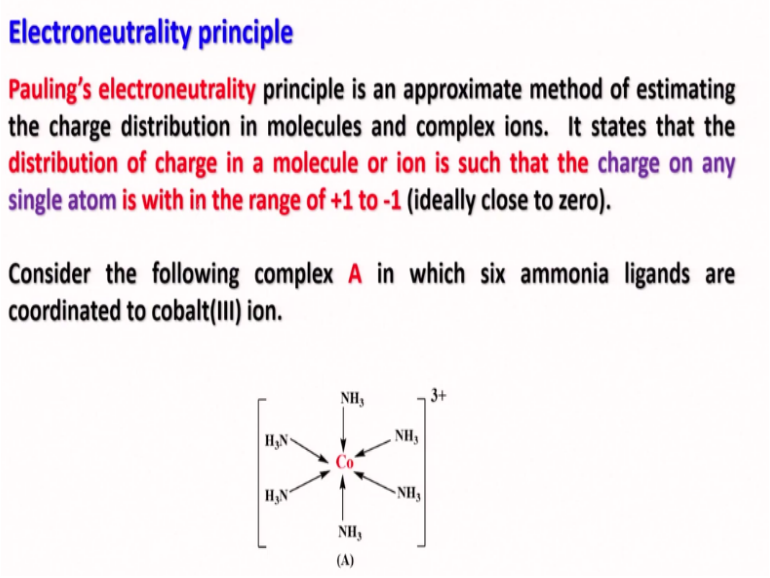

Electroneutrality principle

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Consider the following complex A in which six ammonia ligands are coordinated to cobalt(III) ion.

So, considering hexamine cobalt 3+ let us look into first covalent method. If you consider covalent method, we have 9 electrons in the valence shell that is $3d^7 4s^2$ and assume that 6 electrons are used for covalent bonding leaving 3 charge on cobalt. That means out of 9 electrons from the valence orbitals of cobalt, utilizes 6 for making covalent bonds with ammine or ammonia ligands so that 3 electrons will be left and that should be considered as 3^- charge on cobalt.

This is the first assumption using covalent model. So, this is simply unrealistic as cobalt cannot be negatively charged owing to its electropositive nature. We all know that, in this one, since it is positively charged, it is not very appropriate to assume as negatively charged. So, owing to this this, covalent model was ruled out. So, this is how the covalent model was depicted.

Out of 9 electrons, 6 are utilized for making the bond with ammonia and leaving 3 excess considered as negative charges so that now we have a charge distribution like this, this is simply unrealistic. So, let us look into ionic model. So, +3 charge remains localized. We have 3+ charges. So, Cobalt is in +3 charge. So, ionic model assumes that +3 charge remains localized on cobalt and 6 ammonia ligands remain neutral.

Again, this is flawed because the experimental evidence shows that the complex ion remains intact in solution or retains its identity in solution. That means a complex ion is not a double salt, that fact we know because, here primary valency, secondary valency everything is clearly spelled out and the electrostatic interactions implied by the ionic model are unlikely to be enough to all these things to happen.

So, that means if you just consider that cobalt 3+ remains as an entity in that case what happens? If you put into solution that disintegrate, so that is not going to happen, as a result ionic model was also overruled. So, this is how the ionic model was assumed. Obviously, it appears like a double salt and in solution it will disintegrate. Since that is not the case, this is also overruled. Then came electronneutrality model.

What it says is: we know the net charge on the metal centre should be zero or between +1 and –1 close to zero. So, that is cobalt 3+ ion may accept a total of only 3 electrons from 6 ligands giving the charge distribution shown here, I am going to show you. The electronneutrality principle results in a bonding description for the complex having 50% ionic character and 50% covalent character. So, this is what the electroneutrality principle means. That means if you see the charge distribution on all entities is well within +1 to –1 and cobalt being zero here.

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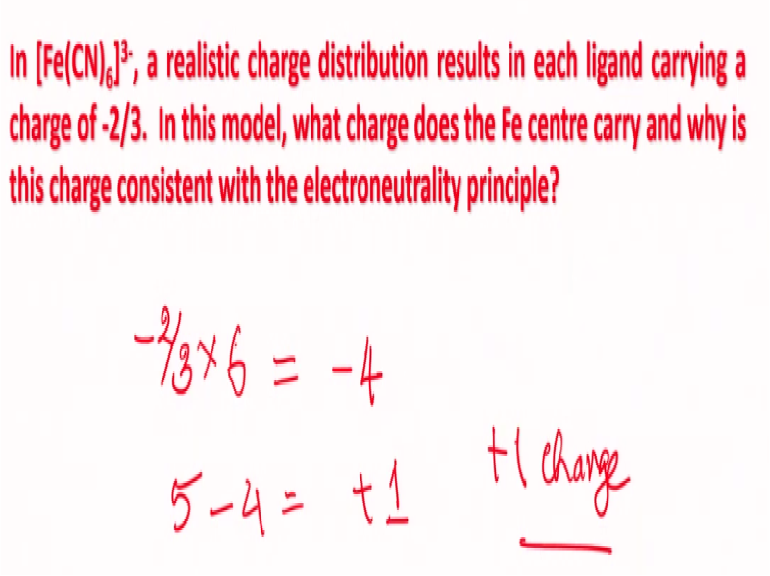

In $[Fe(CN)_6]^{3-}$, a realistic charge distribution results in each ligand carrying a charge of -2/3. In this model, what charge does the Fe centre carry and why is this charge consistent with the electroneutrality principle?

$-2/3 \times 6 = -4$

$5 - 4 = +1$ +1 charge

Using this method, let us try to understand one more problem. So, let us consider hexacyanoferrate, a realistic charge distribution results in each ligand carrying a charge of –2/3. In this model, what charge does the Fe centre carry, and why is this charge consistent with the electroneutrality principle? That means whatever example we saw from hexammine cobalt 3+, let us try to the extent same analogy to this one in which ligands carrying a charge of –2/3.

So, that means here each cyanide is carrying a charge of –2/3 and that means we have now 6 cyanate ligands. So, this will be –4. If it is –4, now if you consider Fe 3+ we have 5 electrons, 5 – 4 = +1. So, in this one Fe carries +1 charge. So, according to electroneutrality principle, the charge carried by iron centre is +1.

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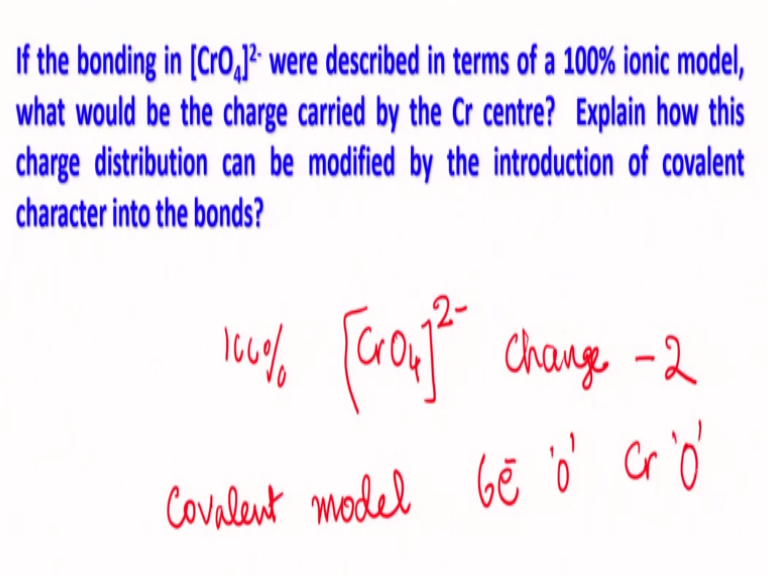

If the bonding in $[CrO_4]^{2-}$ were described in terms of a 100% ionic model, what would be the charge carried by the Cr centre? Explain how this charge distribution can be modified by the introduction of covalent character into the bonds?

100% $[CrO_4]^{2-}$ Charge -2

Covalent model $6\bar{e}$ '0' Cr '0'

Let us look into another problem here. If the bonding in $[CrO_4]^{2-}$ were described in terms of 100% ionic model, what would be the charge carried by the chromium centre and explain how the charge distribution can be modified by introduction of covalent character into the bonds. That means we have to examine this example $[CrO_4]^{2-}$ using both 100% ionic model and also a covalent model.

If you just look into 100% ionic model, the $[CrO_4]^{2-}$ here charge will be -2. In this case the charge will be -2 here, but if you consider covalent model, so 6 electrons are there and these 6 electrons are utilized in making 6 metal to ligand bonds. According to the electroneutrality principle in that case what happens? Number of electrons left and chromium will be zero so that here the charge on chromium will be zero.

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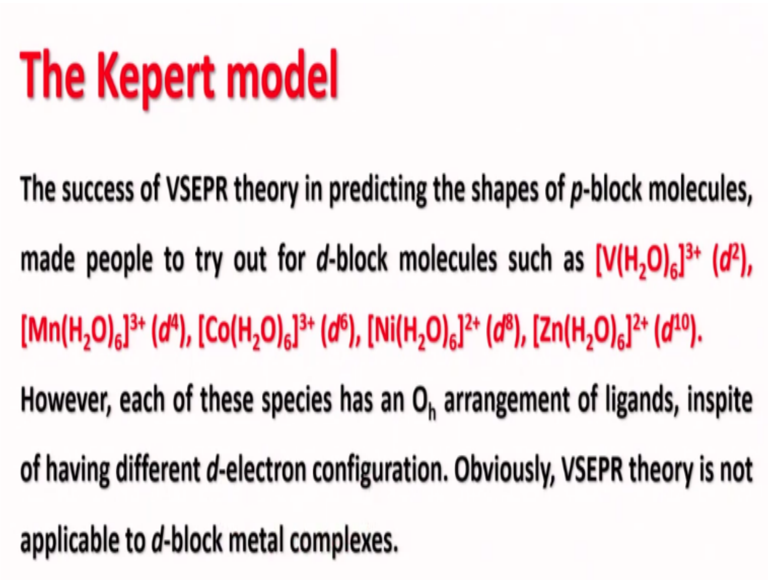

The Kepert model

The success of VSEPR theory in predicting the shapes of *p*-block molecules, made people to try out for *d*-block molecules such as $[V(H_2O)_6]^{3+}$ (d^2), $[Mn(H_2O)_6]^{3+}$ (d^4), $[Co(H_2O)_6]^{3+}$ (d^6), $[Ni(H_2O)_6]^{2+}$ (d^8), $[Zn(H_2O)_6]^{2+}$ (d^{10}). However, each of these species has an O_h arrangement of ligands, inspite of having different *d*-electron configuration. Obviously, VSEPR theory is not applicable to *d*-block metal complexes.

Next after successfully applying VSEPR theory to explain bonding among main group compounds, attempts were made by Kepert to utilize VSEPR theory to explain bonding in transition metal complexes. So, for this one, following examples were considered and here like all six coordinated compounds, but having different valence shell electronic configuration were considered.

For example, vanadium 3+ has 2*d* electrons and manganese 3+ has 4 electrons and then cobalt 3+ has 6 electrons and then hexaaqua nickel 2+ has d^8, eight electrons and zinc hexaaqua zinc here we have $3d^{10}4s^2$, so 10 electrons are there. That means we are considering examples of vanadium, manganese, cobalt, nickel and zinc having octahedral geometry, homoleptic hexaaqua compounds but having different electrons left in their *d*-orbitals that means the d^2, d^4, d^6, d^8 and d^{10}.

However, each of these species has an octahedral arrangement of ligands that we know in spite of having different electron configuration. So, obviously if you go by VSEPR theory to count all electrons, VSEPR theory cannot explain the bonding among *d*-block metal complexes.

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Assumption: Metal lies at the centre of a sphere and the ligands are free to move over the surface of the sphere.

Ligands are considered to repel one another similar to those in VSEPR model, but unlike VSEPR model, Kepert model ignores non-bonding electrons and assumes Coordination Geometry of a *d*-block species is independent of ground state electronic configuration of the metal centre.

As a result ions of type $[ML_n]^{m+}$ and $[ML_n]^{m-}$ have the same geom

As a result, some assumptions were made in VSEPR theory to accommodate the explanation of bonding in *d*-block element complexes. So, what is the assumption that was made? Metal lies at the centre of a sphere and the ligands are free to move around the surface of the sphere. So, that means metals assume as a sphere and the ligands are free to move about the surface of the sphere and occupy positions as far away from each other as possible to minimize repulsion between the ligands.

The ligands are considered to repel one another similar to those in VSEPR model where we were using steric numbers, but unlike VSEPR model Kepert model ignores nonbonding electrons and assumes coordination geometry if a d-block species is independent of ground state electronic configuration of the metal centre. So, this is assumption. According to their convenience, they postulated this assumption to imply VSEPR model to explain bonding in coordination complexes.

So, as a result what happens ions of the type [ML$_n$]$^{m+}$ or [ML$_n$]$^{m-}$, irrespective of they are cationic in nature or anionic in nature, if the number of ligands are the same, they are bound to have the same geometry. Again, we know that this cannot be used due to various reasons because most of the complexes, if you look into geometry, reactivity, properties and everything depends on the electronic configuration, the oxidation state and many other factors. As a result, this initially made early method, called Kepert model to imply VSEPR theory did not work well.

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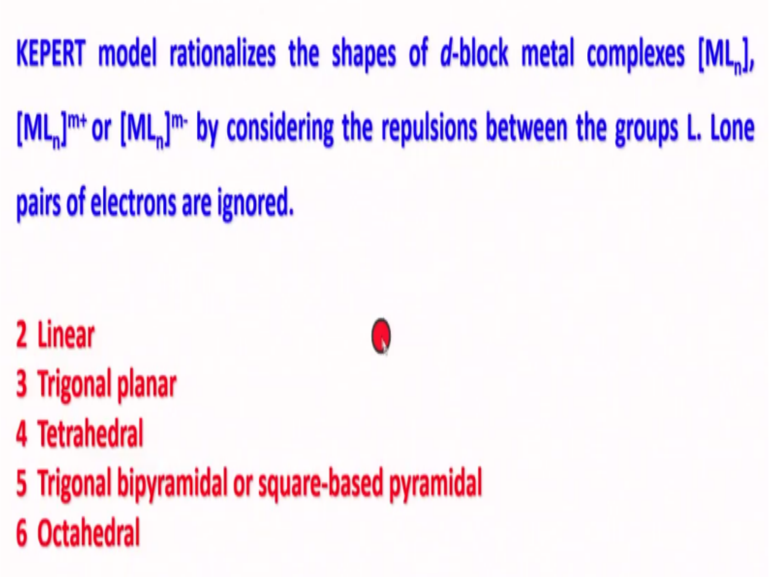

KEPERT model rationalizes the shapes of *d*-block metal complexes [ML$_n$], [ML$_n$]$^{m+}$ or [ML$_n$]$^{m-}$ by considering the repulsions between the groups L. Lone pairs of electrons are ignored.

2 Linear
3 Trigonal planar
4 Tetrahedral
5 Trigonal bipyramidal or square-based pyramidal
6 Octahedral

Kepert model rationalizes the shapes of d-block metal complexes and by considering the repulsion between the groups L, lone pairs of electrons are totally ignored. And here also if two ligands are there, they propose linear geometry. If three ligands are there, they propose trigonal planar geometry. If four ligands are there, they are considered tetrahedral geometry and five are there square pyramidal or trigonal bipyramidal geometry and for six octahedral geometry.

So, what they did was the number of ligands surrounding the metal ion was considered as steric number ignoring the electrons present, nonbonding electrons present in the orbital. Then it is bound to show results very similar to main group elements, but certainly it does not explain and then when we have different type of ligands it can further deviate. As a result, it was concluded that Kepert model is not a suitable model and VSEPR theory is not a suitable theory to explain bonding in coordination compounds.

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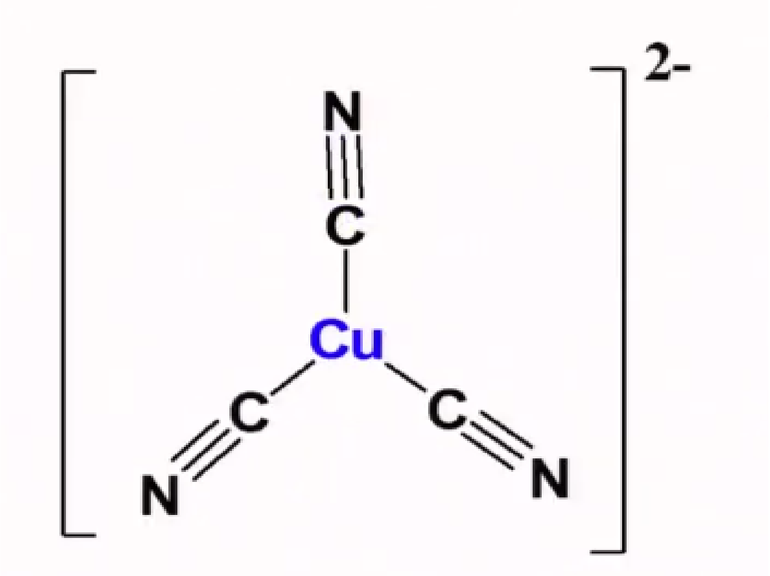

So, example they showed this tris or tricyanocuprate, that we can use VSEPR theory ignoring the *d*-electrons to arrive at the geometry, of course here trigonal planar geometry is correct, but citing one or two example, it is not an ideal way to accept the model.

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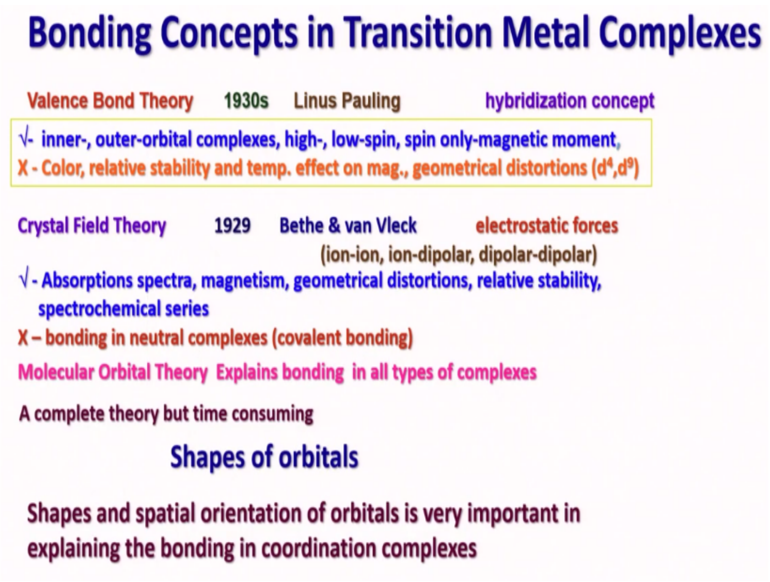

Bonding Concepts in Transition Metal Complexes

Valence Bond Theory 1930s Linus Pauling hybridization concept

√- inner-, outer-orbital complexes, high-, low-spin, spin only-magnetic moment,
X - Color, relative stability and temp. effect on mag., geometrical distortions (d^4,d^9)

Crystal Field Theory 1929 Bethe & van Vleck electrostatic forces
(ion-ion, ion-dipolar, dipolar-dipolar)
√ - Absorptions spectra, magnetism, geometrical distortions, relative stability, spectrochemical series
X – bonding in neutral complexes (covalent bonding)

Molecular Orbital Theory Explains bonding in all types of complexes

A complete theory but time consuming

Shapes of orbitals

Shapes and spatial orientation of orbitals is very important in explaining the bonding in coordination complexes

So, now let us look into the bonding concepts that were later used to explain bonding in transition metal complexes. The first one was valence bond theory. It was proposed in 1930 by Linus Pauling and he brought hybridization concept to explain bonding and also a couple of properties. And using this bonding he could explain inner orbital complex, outer orbital complex, similarly high spin complex and low spin complex and spin only-magnetic moment.

So, in fact, when Linus Pauling wrote his very famous and popular book “Nature of Bonding”, he gave emphasis for his theory and demonstrated giving importance to recognizing magnetic properties of transition metal complexes using valence bond theory, but however it can predict spin only-magnetic moment and beyond that many other properties including colour and the effective magnetic moment, geometrical distortions all those things Linus Pauling’s valence bond theory could not explain.

As a result, people were looking for an alternate, that time crystal field theory was proposed by Bethe and van Vleck mainly based on electrostatic forces. That means if you take a metal ion and when you put a metal ion into the electric field generated or originated from ligands, what happens, the degeneracy of orbitals will be two fold and this is how this work was started.

And then early electrostatic interactions and their utility was mentioned by Becquerel who is known for discovery of radioactivity along with Marie Curie and Pierre Curie for which he got a Nobel Prize in 1903. Crystal field theory looks very ideal and here it explains different types of interactions between metal and the ligand. If the metal is cationic and ligand is anionic then one can talk about ion-ion interaction.

And if the metal is cationic and the ligand is neutral, one can bring ion-dipolar interaction. But, if the metal is neutral and ligands are neutral, like what we see in case of zero valent metal carbonyl compounds such as chromium hexacarbonyl, iron pentacarbonyl where metal is neutral and ligand is also neutral, in that case we have to evoke dipolar-dipolar interaction.

Unfortunately, crystal field theory does not explain the bonding arising out of dipolar-dipolar interaction when the metal is neutral and ligands are neutral. That was the one limitation and later to accommodate this dipolar-dipolar interaction, the covalency was included and accommodated in crystal field theory and that become ligand field theory and ligand field theory is a beautiful theory. It is a very nice combination of molecular orbital theory, crystal field theory and also to an extent valence bond theory.

The advantage of crystal field theory is: it can explain absorption spectra, that means colour of complexes and it can explain magnetism and also it can explain geometrical distortions and also relate to stability, because it brings a spectrochemical series and gives definite position in the spectrochemical series for ligand to say whether it is a strong field ligand or a weak field ligand. And bonding in neutral complexes was also brought through ligand field theory.

And overall, molecular orbital theory explained bonding in all types of complexes, whatever the bonding molecular orbital theory presently we are using is nothing but ligand field theory having good parts of all these theories, valence bond theory and molecular orbital concept, and also crystal field theory; very nicely developed by Bethe and van Vleck and it is a very complete theory.

It may appear like time consuming, but nevertheless it can give you literally all information that is needed to understand the reactivity or the application in various aspects. So, before we start digging deep into these bonding concepts, it is better to understand the shapes of the orbitals and the relative orientation in space.

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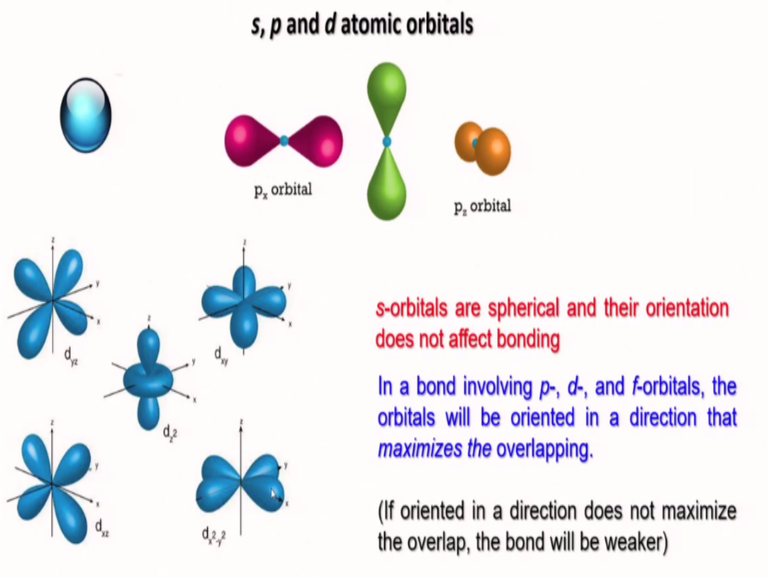

s, *p* and *d* atomic orbitals

s-orbitals are spherical and their orientation does not affect bonding

In a bond involving *p*-, *d*-, and *f*-orbitals, the orbitals will be oriented in a direction that *maximizes the* overlapping.

(If oriented in a direction does not maximize the overlap, the bond will be weaker)

So, we know that *s* is spherically symmetrical and we have p_x orbital dumbbell shaped, the p_y and p_z. They are orthogonal to each other. And then we have d_{xz}, d_{yz}, and $d_z{}^2$ and d_{x2-y2} and d_{xy}. So, these five *d*-orbitals are there. So, s orbitals are spherically symmetrical and their orientation does not affect bonding, but in a bond involving p orbitals, d orbitals, and f orbitals, the orbitals will be oriented in a direction that maximizes the overlapping. So, that means, their orientation matters. If oriented in a direction does not maximize overlap, the bond will be weaker.

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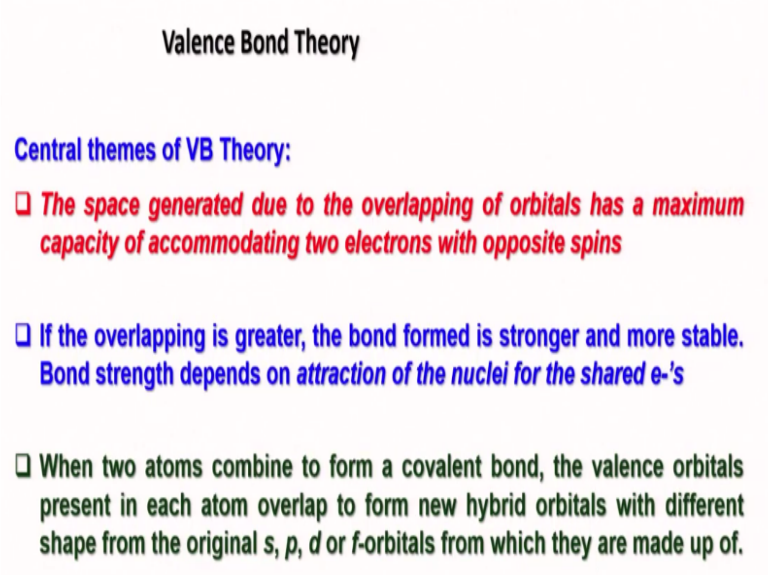

Valence Bond Theory

Central themes of VB Theory:

- ❑ *The space generated due to the overlapping of orbitals has a maximum capacity of accommodating two electrons with opposite spins*
- ❑ If the overlapping is greater, the bond formed is stronger and more stable. Bond strength depends on *attraction of the nuclei for the shared* e-'s
- ❑ When two atoms combine to form a covalent bond, the valence orbitals present in each atom overlap to form new hybrid orbitals with different shape from the original *s*, *p*, *d* or *f*-orbitals from which they are made up of.

Let us start looking into valence bond theory. Let me tell you about the central theme of valence bond theory. I am sure most of you are familiar with valence bond theory. The space generated due to the overlapping of orbitals has a maximum capacity of accommodating two electrons with opposite spins. That means when you overlap orbitals from two atoms that can accommodate two electrons with opposite spins, that means between two orbitals essentially the electrons are localized.

That is the first concept. If the overlapping is greater, the bond formed is stronger and more stable. Bond strength depends on attraction of the nuclei for the shared electrons. That means if the overlapping is greater, that means if the electronegativity is comparable and the size of the orbitals are comparable, then these two nuclei can come very close to each other and establish a bond. In that case what happens, the bonds will be much stronger.

When two atoms combined to form a covalent bond, the valence orbitals present in each atom overlap to form new hybrid orbitals with the different shapes from the original s, p, d or f orbitals from which they are made up of. That means before two atoms combine to form a covalent bond, the valence orbitals in each atom overlap to form a new set of orbitals called hybrid orbitals that carries properties of all the orbitals involved in that hybridization.

For example, if you consider the *sp* hybridization, in that one, one s and one p involved so that the *sp* hybrid orbital would have 50% s-character and 50% p-character and this is how it goes. And in sp^2 what happens? We have one-third s-character and two-third p-character whereas in case of sp^3 hybrid orbitals, we have one-fourth s-character and three-fourth p character. That means 25% s-character and 75% p-character.

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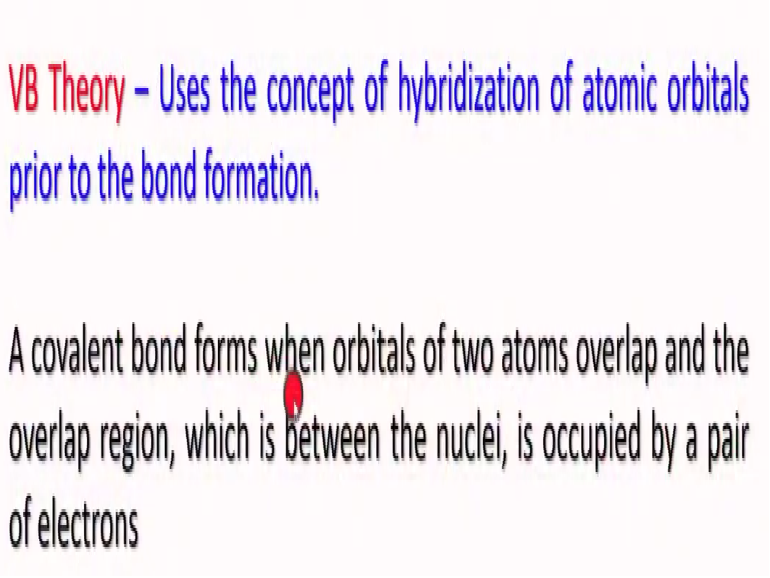

VB Theory – Uses the concept of hybridization of atomic orbitals prior to the bond formation.

A covalent bond forms when orbitals of two atoms overlap and the overlap region, which is between the nuclei, is occupied by a pair of electrons

That means valence bond theory uses the concept of hybridization of atomic orbitals prior to the bond formation. A covalent bond forms when orbitals of two atoms overlap and overlap region which is between the nuclei is occupied by a pair of electrons. This is an important concept that was proposed by valence bond theory. One is hybridization concept and the second one is concentration of electrons with opposite spin between the two atoms that are combined, two nuclei. That means it gives emphasis for localization of electrons between the two atoms. Let me stop at this stage and continue in my next lecture, more discussion and with more examples on valence bond theory.