Advanced Transition Metal Chemistry – Inorganic Reaction Mechanisms
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Lecture – 46
Inorganic Reaction Mechanisms – Square Planar Complexes

Hello everyone. It is a pleasure to welcome you all once again to MSB lecture series on transition metal chemistry. Since my last lecture that is in my 45th lecture, I started the topic inorganic reaction mechanisms with brief introduction, I also initiated discussion on substitution reactions in square planar complexes. So, let me continue from where I had stopped.

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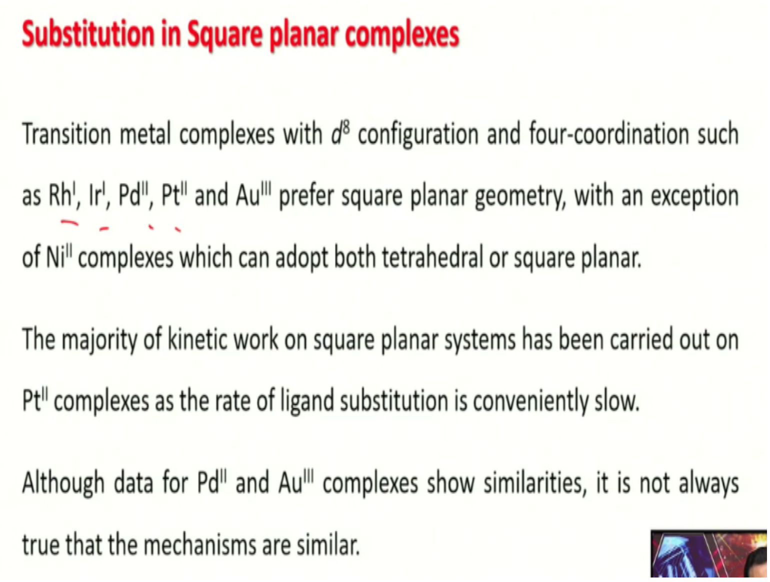

Substitution in Square planar complexes

Transition metal complexes with d^8 configuration and four-coordination such as Rh^{I}, Ir^{I}, Pd^{II}, Pt^{II} and Au^{III} prefer square planar geometry, with an exception of Ni^{II} complexes which can adopt both tetrahedral or square planar.

The majority of kinetic work on square planar systems has been carried out on Pt^{II} complexes as the rate of ligand substitution is conveniently slow.

Although data for Pd^{II} and Au^{III} complexes show similarities, it is not always true that the mechanisms are similar.

So, transition metal complexes having d^8 electronic configuration, we can consider rhodium, iridium, palladium and platinum in +2 state, rhodium and iridium in +1 state and also gold in +3 state, so they all prefer square planar geometry with an exception of nickel(II) complexes. They have a tendency to adopt both tetrahedral and square planar geometries even with sometimes, strong field ligands.

However, majority of kinetic work on square planar systems has been carried out on platinum(II) complexes because the rate of ligand substitution is conveniently slow so that the mechanism can be established with much easily without going to very fancy fast reaction rates systems and other things. Although substitution reaction data is available for palladium(II) as well as gold(III) complexes which also show similarities, they not always follow the same mechanism that is followed by these metals such as rhodium, iridium or platinum.

So, let us look into those differences as we progress with this topic. The extensive mechanistic studies on platinum(II) complexes and observed negative values of ΔS and ΔV suggest that the nucleophilic substitution reactions in square planar complexes proceed by associative mechanisms. Once again, I tell you the extensive data we have on mechanistic studies on substitution reactions in platinum(II) complexes.

And also observe negative values of ΔS and ΔV suggest that most of the nucleophilic substitution reactions that we perform on square planar complexes proceed by associative mechanism.

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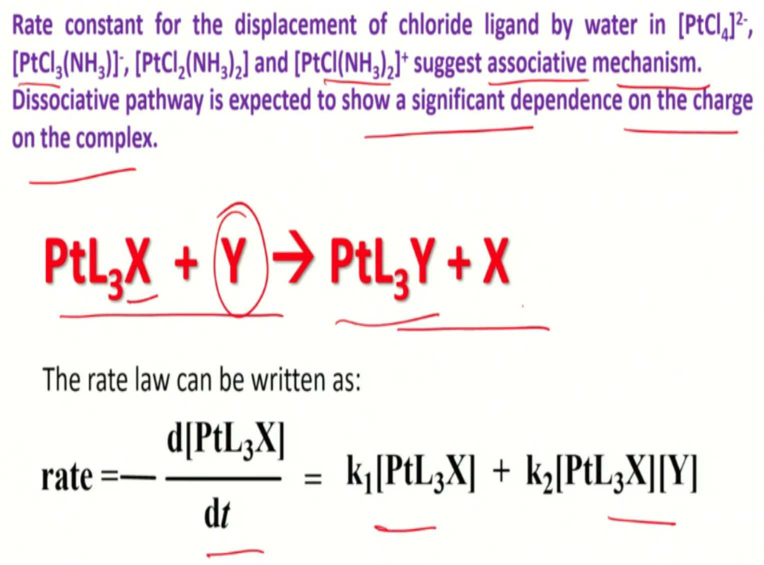

Rate constant for the displacement of chloride ligand by water in $[PtCl_4]^{2-}$, $[PtCl_3(NH_3)]^-$, $[PtCl_2(NH_3)_2]$ and $[PtCl(NH_3)_2]^+$ suggest associative mechanism. Dissociative pathway is expected to show a significant dependence on the charge on the complex.

$$PtL_3X + Y \rightarrow PtL_3Y + X$$

The rate law can be written as:

$$\text{rate} = -\frac{d[PtL_3X]}{dt} = k_1[PtL_3X] + k_2[PtL_3X][Y]$$

For example, if you look into the rate constant for the displacement of chloride ligand by water in tetrachloroplatinate or you can consider here Cl_3 and NH_3 having anionic charge or you have diamino dichloro or having something like this. If you consider any of these four complexes for substitution of chloride by water, they suggest associative mechanism. The dissociative pathways expected to show a significant dependence on the charge on the complex.

Nevertheless, there are ways to explain substitution reaction in case of platinum complexes or d^8 system or square planar complexes using dissociative pathway by looking into some donor solvent interaction which make weak interactions on the axial position to have a tetragonal geometry. So, let us look into those things later. Now, let us consider a typical reaction here square planar complex of platinum(II) that undergoes substitution.

Here again X is the leaving group and Y is the entering group and we have this one and it is forming here. So, the rate law can be written this one in this format where we are considering two terms here k_1 and k_2.

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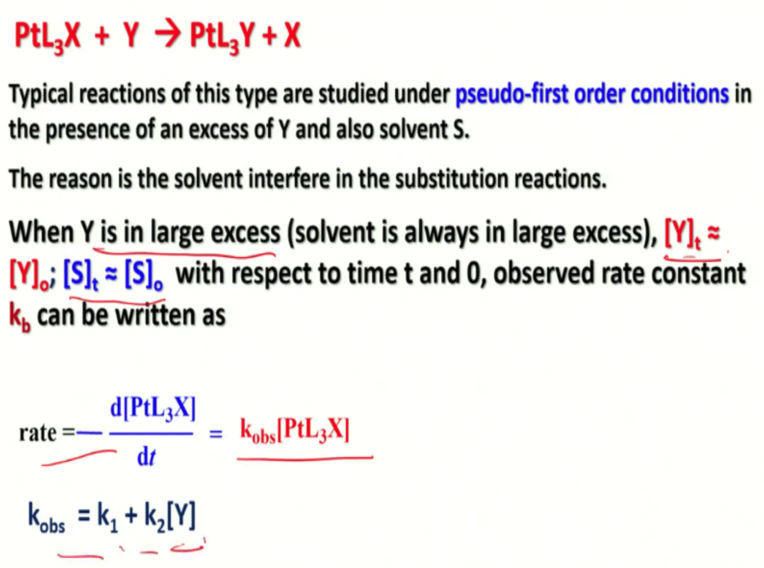

$PtL_3X + Y \rightarrow PtL_3Y + X$

Typical reactions of this type are studied under pseudo-first order conditions in the presence of an excess of Y and also solvent S.

The reason is the solvent interfere in the substitution reactions.

When Y is in large excess (solvent is always in large excess), $[Y]_t \approx [Y]_o$; $[S]_t \approx [S]_o$ with respect to time t and 0, observed rate constant k_b can be written as

$$\text{rate} = -\frac{d[PtL_3X]}{dt} = k_{obs}[PtL_3X]$$

$$k_{obs} = k_1 + k_2[Y]$$

So, the typical reactions of this type are studied under pseudo-first order conditions in the presence of an excess of Y and also solvent S. The two terms are there, you should recall. So, the reason is the solvent interference in the substitution reactions. For example, if Y is in large excess, of course solvent is always in large excess, the change of concentration of Y with the time is almost 0.

So that means after a certain time, the Y concentration does not change. Similarly, solvent concentration also does not change with time because the minimum change in the solvent can be ignored, so it more or less remains the same. So that means with respect to time, the change observed is 0 and then what happens the observed rate constant can be simply written as in this format that means otherwise $k_{obs} = k_1 + k_2 \times [Y]$.

So, k_1 and k_2 can be evaluated by carrying out a series of reactions with various concentrations of Y. I showed you two terms k_1 and k_2, they can be evaluated by carrying out a series of reactions with various concentrations of Y.

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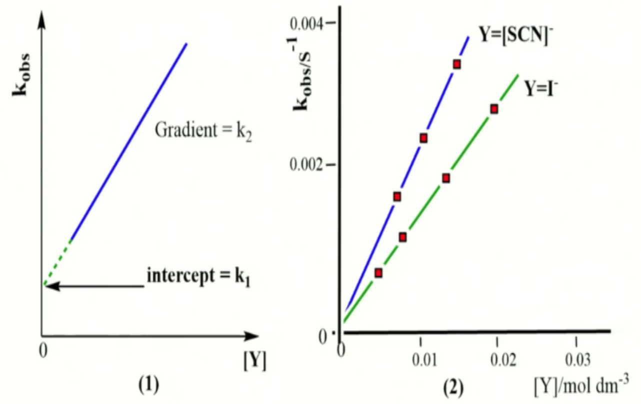

(1) Determination of the k_1 and k_2 rate constants from the observed rate data for ligand substitution in a square planar complex; Y is the entering ligand. The dotted part of the line represents an extrapolation. (2) Plots of k_{obs} against [Y] for the reactions of trans-$[PtCl_2py_2]$ with $[SCN]^-$ or with I^-; both reactions were carried out in MeOH and so there is a common intercept. [Data from: U. Belluco et al. (1965) J. Am. Chem. Soc., vol. 87, p. 241.], Inorganic Chemistry C E Housecroft and A. G. Sharpe 2nd edition.

For example, let us look into these plots here.

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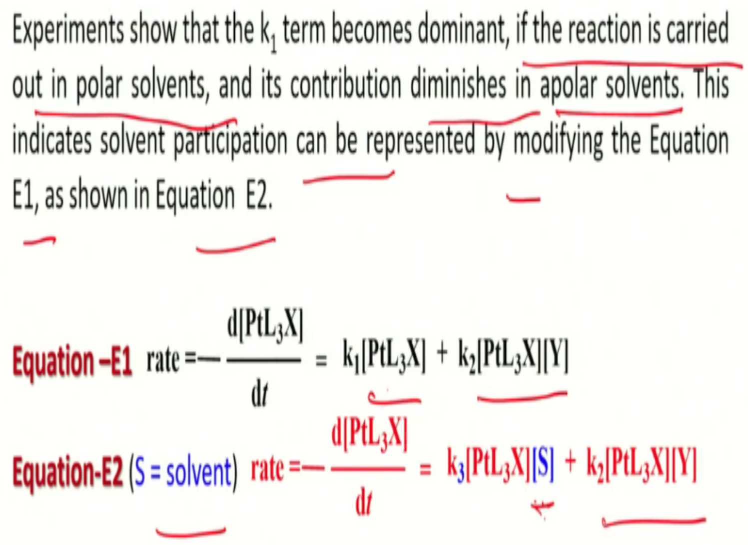

Experiments show that the k_1 term becomes dominant, if the reaction is carried out in polar solvents, and its contribution diminishes in apolar solvents. This indicates solvent participation can be represented by modifying the Equation E1, as shown in Equation E2.

Equation –E1 $\text{rate} = -\dfrac{d[PtL_3X]}{dt} = k_1[PtL_3X] + k_2[PtL_3X][Y]$

Equation-E2 (S = solvent) $\text{rate} = -\dfrac{d[PtL_3X]}{dt} = k_3[PtL_3X][S] + k_2[PtL_3X][Y]$

Experiment shows that the term k_1 becomes dominant if the reaction is carried out in polar solvents and its contribution diminishes in apolar solvents. So, this indicates solvent participation can be represented by modifying the equation in this form. You can see here in this form, so you can see that experiment shows that the term k_1 becomes dominant if the reaction is carried out in polar solvents and its contribution diminishes in apolar solvents, you should remember that.

This indicates solvent participation can be represented by modifying the equation E1, E2. You can see here. So, for example here we are taking k_1 into PtL_3X concentration of this one and then concentration of this one also, whereas in this case when the solvent is there you can also add the term solvent here in this case. So, this is how the influence of solvent can also be added to the rate equation.

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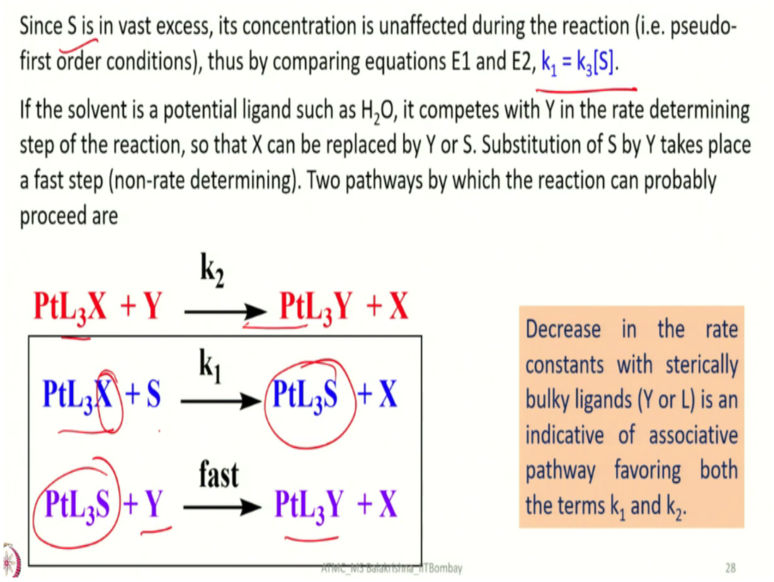

Since S is in vast excess, its concentration is unaffected during the reaction (i.e. pseudo-first order conditions), thus by comparing equations E1 and E2, $k_1 = k_3[S]$.

If the solvent is a potential ligand such as H_2O, it competes with Y in the rate determining step of the reaction, so that X can be replaced by Y or S. Substitution of S by Y takes place a fast step (non-rate determining). Two pathways by which the reaction can probably proceed are

$$PtL_3X + Y \xrightarrow{k_2} PtL_3Y + X$$

$$PtL_3X + S \xrightarrow{k_1} PtL_3S + X$$

$$PtL_3S + Y \xrightarrow{fast} PtL_3Y + X$$

Decrease in the rate constants with sterically bulky ligands (Y or L) is an indicative of associative pathway favoring both the terms k_1 and k_2.

Since S is in vast excess, that means solvent, S is solvent, is in large excess its concentration is unaffected during the reaction, literally there is no change and hence it can be considered pseudo-first order condition, by comparing the equations 1 and 2 what we can get is this is the one. Simply by comparing we get $k_1 = k_3 \times [S]$. If the solvent is a potential ligand such as water, it competes with Y, the entering group in the rate determining step of the reaction so that X can be replaced by Y or S to begin with, X is the leaving group.

Substitution of S by Y takes place in a fast step that is non-rate determining step. So, therefore two pathways by which the reaction probably proceed are represented in this one. For example, this is a typical reaction here so that we can see first initially before X is leaving, S comes here and then it establishes this intermediate and then this intermediate would react with Y to give the product in the fast step.

That means that decrease in the rate constants with sterically bulky ligands Y or L is an indicative of associative pathway favouring both the terms k_1 and k_2. So, that means the steric factors when we are considering, we have to consider the ligands already present on the metal such as L and also the stearic bulk of the entering ligand Y, both have to be considered to understand about the nature of the pathways.

But here very clearly one can tell about the decrease in the rate constant with sterically bulky ligands indicates the associative pathway. That means, when associate pathway is there that favours both the terms k_1 and k_2. In majority of substitution reactions of square planar platinum(II) complexes, stereochemistry is retained. You should remember in majority of substitution reactions of square planar complexes stereochemistry is retained.

The entering group occupies the leaving group position and associative or A mechanism involves a five coordinate intermediate or transition state and since the energy difference between the five coordinate geometry is small, one would expect rearrangement of five coordinated species to be facile unless for example it is sterically hindered that means here I_a or its lifetime is too short like I_a you have to be considered.

So, once again I tell you in a substitution reaction on square planar complexes the stereochemistry is retained, the entering group occupies the position left by the leaving group and associative mechanism or interchange associative mechanism involves a five-coordinate intermediate or transition state, I_A transition state in A intermediate. Since the energy difference between different five coordinate geometries is small, especially in I_A, one would expect rearrangement of the five coordinate species to be very facile.

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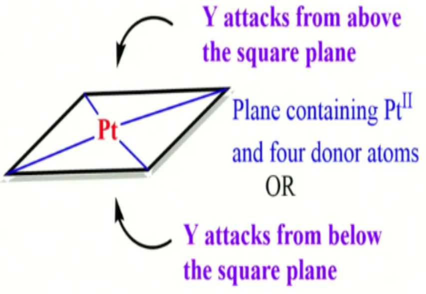
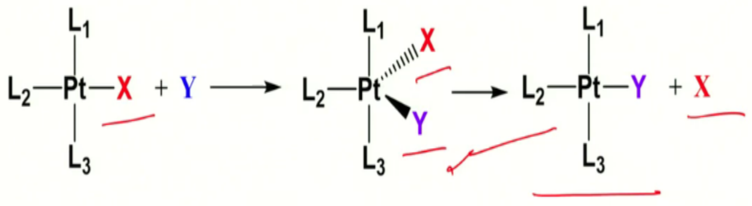


Y attacks from above the square plane

Plane containing Pt^{II} and four donor atoms

OR

Y attacks from below the square plane



For example, this is the one I am telling you, very facile unless for example it is sterically hindered, A or I_A does not matter or its lifetime is too short in that case it is I_A. The stereochemical retention can be envisaged as shown in this figure here, you can see in this figure why does intermediate or transition species have the trigonal bipyramidal geometry.

So, that means now the question is, if associative mechanism is followed exclusively with square planar complexes during their substitution reaction and it increases the coordination number by 1 in the intermediate that is going from 4 to 5, in that case the preferred geometry is trigonal bipyramidal. You can see here, it is added, now it is reverted back to square planar geometry after X leaves, that means here it indicates substitution is completed.

Now, the question is why it adopts trigonal bipyramidal geometry, why not square pyramidal geometry? Square pyramidal geometry, it can come and attack something like this and then this can go on, it can revert back to square planar geometry, so that is the thing. Now, this is the appropriate time to bring the concept called trans-effect. Trans-effect is very important when we talk about the substitution reactions of square planar complexes.

Perhaps you are wondering why I did not bring the term trans effect or why I did not introduce trans-effect prior to the discussion of square planar complexes. Of course, I was waiting for this juncture to introduce trans-effect.

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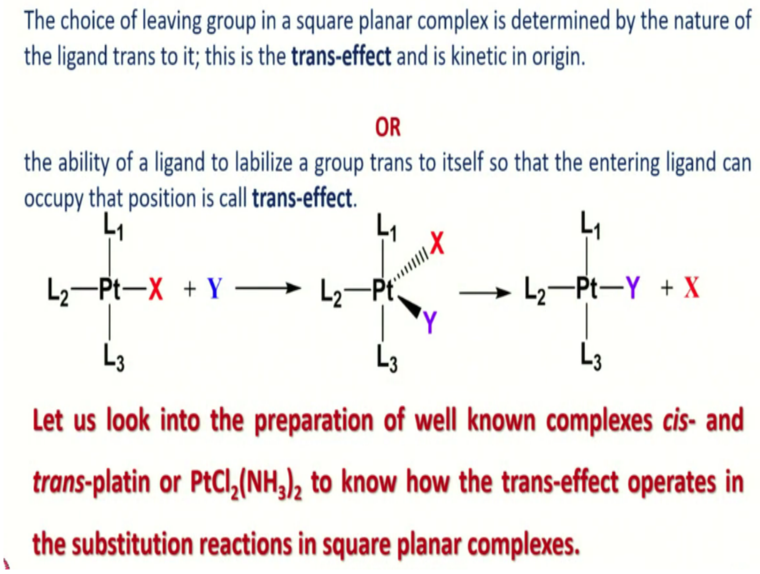

The choice of leaving group in a square planar complex is determined by the nature of the ligand trans to it; this is the **trans-effect** and is kinetic in origin.

OR

the ability of a ligand to labilize a group trans to itself so that the entering ligand can occupy that position is call **trans-effect**.

Let us look into the preparation of well known complexes *cis*- and *trans*-platin or $PtCl_2(NH_3)_2$ to know how the trans-effect operates in the substitution reactions in square planar complexes.

The choice of leaving group in a square planar complex is determined by the nature of the ligand trans to it, this is the trans-effect and is kinetic in origin. That means in other words, I can also explain the ability of a ligand to labilize a group trans to itself, so that the entering ligand can occupy that position is called trans-effect. That means, the labilizing effect of a group trans to itself during a substitution reaction to make way for the entering ligand is called trans-effect.

Let us look into the preparation of well-known complexes of cis and trans-platin that means $[PtCl_2(NH_3)_2]$ is a square planar complex, you all know and it shows geometric isomerism cis and trans. So that means how cis and trans complexes can be prepared using trans-effects, so how trans-effect operates in substitution reactions of square planar complexes, we can look into it just with the beginning of understanding of the formation of cis and trans diaminodichloro platinum complexes.

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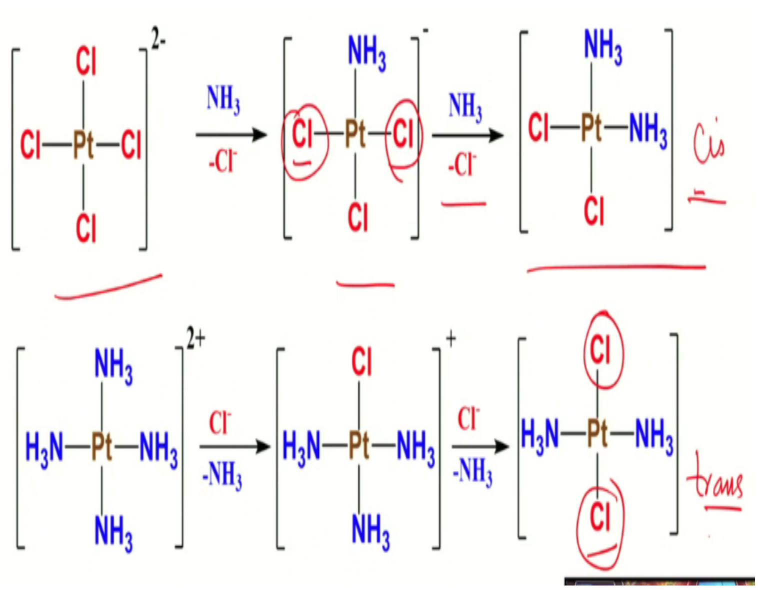

So, look here. We started with here tetrachloroplatinate, here you should remember of course we are adding ammonia and by spectrochemical series also you know that the moment a strong field ligand such as ammonia comes, chloride a relatively weaker ligands, leaves, yes it goes and now we have three chlorides are there and one ammonia is there in this one. And next continue adding another molecule of ammonia, so that replaces another one and then we get cis compound here.

So, that means we are getting a cis compound means either replacing this one or this one, not this one, so we are getting the cis product here. In contrast, we start with tetramineplatinum(II) complex. So, now in order to make a chloroamine complex we have to add Cl^- when we are adding Cl^- obviously one of the ammonia goes, does not matter which one goes, we end up getting three ammonia and chloride comes.

Next when we add NH_3, this NH_3 adds to a position trans to that chloride here so that means that results in the formation of trans compound here. So, trans compound is obtained. That means tetrachloroplatinate if you take and add in the sequential order ammonia that leads to the formation of a cis product here. On the other hand, if you take tetrammineplatinum(II) complex, add chlorides in two steps, that leads to the formation of trans compound.

So, this was the beginning of the reactions that led to the understanding and explanation of trans effect and hence the substitution reactions in square planar complexes. And in case of octahedral complexes, this trans effect may or may not influence the substitution, whereas in case of square planar complexes this trans effect influences a lot and it has tremendous influence on the rate of the reaction and also in understanding the mechanism of the reaction.

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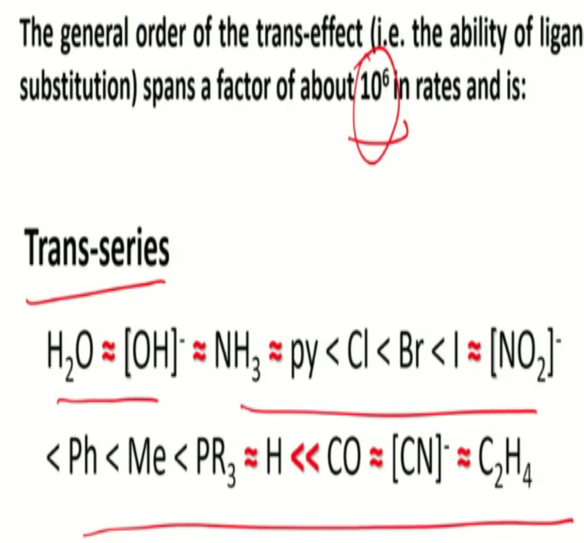

The general order of the trans-effect (i.e. the ability of ligands to direct trans-substitution) spans a factor of about 10^6 in rates and is:

Trans-series

$$H_2O \approx [OH]^- \approx NH_3 \approx py < Cl < Br < I \approx [NO_2]^-$$
$$< Ph < Me < PR_3 \approx H \ll CO \approx [CN]^- \approx C_2H_4$$

So, the general order of the trans effect that means the ability of ligands to direct trans substitution spans a factor of about 10^6 in the rates. That means their influence is remarkable. If you can see to what extent the influence is represented by this order that indicates to what extent this trans effect has an influence on the substitution reactions in square planar complexes. That trans series is given here.

For example, if you just look into this one, you should be able to see how a ligand can be replaced with another ligand, can be clearly seen. So this is the trans series and one can also extend it adding some more, but these are the important ligands we come across when we perform substitution reactions in square planar complexes.

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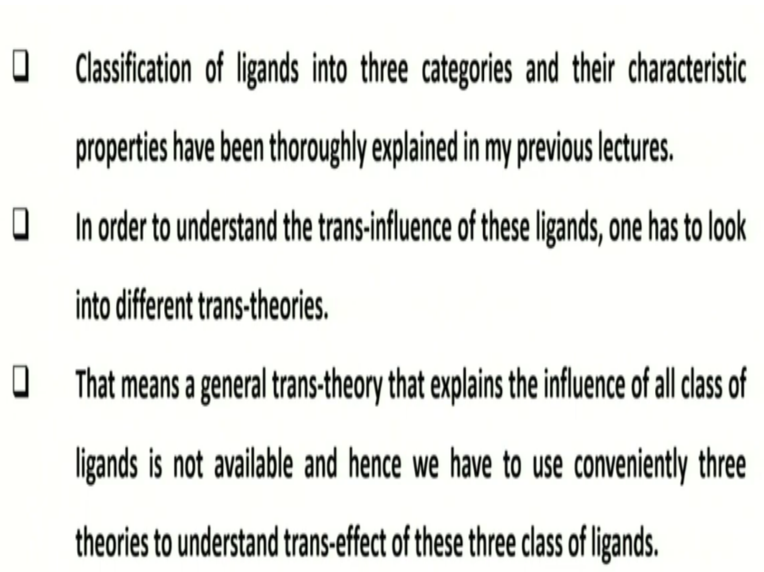

- Classification of ligands into three categories and their characteristic properties have been thoroughly explained in my previous lectures.
- In order to understand the trans-influence of these ligands, one has to look into different trans-theories.
- That means a general trans-theory that explains the influence of all class of ligands is not available and hence we have to use conveniently three theories to understand trans-effect of these three class of ligands.

So, now with this information, let us look into the classification of ligands. In my previous lectures, when I was talking about classification of ligands by donor atoms, so I tried to convince you about the type of ligands we have and also how they can be classified. That means classification of ligands; one can classify into three categories and their characteristic properties have been thoroughly explained in my previous lectures.

So, in order to understand the trans influence of these ligands, one has to look into different trans theories. That means the three class of ligands I classified and told you are the (i) sigma donor ligands and (ii) sigma donor and pi donor ligands, and (iii) sigma donor and pi acceptor ligands. That means we do not have a very general trans theory to explain the influence of these ligands on substitution reactions, but we have to go for different theories depending upon the nature of the ligands we are using.

That means since we have three categories of ligands, we also should have three categories of trans theories. That means we cannot have a general theory that can explain the influence of all class of ligands. So, we have to have conveniently three theories to understand the trans effect of these three classes of ligands. What I will do is in my next lecture, I shall elaborate on trans-effects.

And what are the trans theories we have at our disposal and what kind of ligands should follow which theory all those things I shall tell you in more detail. So, until then have excellent time reading chemistry. Thank you for your kind attention.