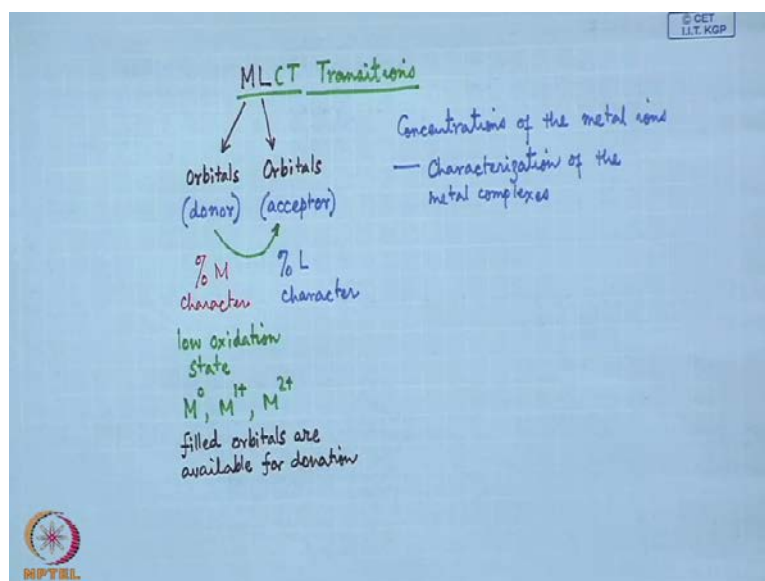


Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 26
MLCT Transitions

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Good evening everybody, so today we will see about the other part of the charge transfer transitions if it originates from the metal center. So, what we have seen so far that during this all these transitions several orbitals are involved which can either be based on the metal or based on the ligand. So, these orbitals, which are based on the metal and ligand they are very important to play in this charge transfer transition, because they are highly filled transitions, because there is no such restriction for the corresponding electronic charge transfer.

So, if this particular one that means the metal orbitals if they can function as a donor orbital, and the ligand can function as an acceptor orbital. Then what we expect? We expect that there should be corresponding charge transfer from the low line metal orbital which is the donor orbital to the acceptor orbitals which are higher in energy. And as a result, we get the corresponding metal to ligand charge transfer transitions. And there are several examples of such transitions, which are very much useful in determining not only

the corresponding concentrations the unknown concentrations of the metal ions, but sometime the corresponding characterization of the metal complexes.

So, these things we should have in our mind and where we will find that since the metal is behaving as a donor orbital when we move from the corresponding ligand field theory to typical molecule orbital theory. We find that we are not talking everything in terms of the corresponding crystal field splitting where we do not accept that metal orbital's are overlapping with the ligand orbitals. But in typical molecular orbital picture, what we see there that some of these metal orbitals do overlap with the ligand orbitals. And we can have certain orbitals which are mainly of metal corrector that means of certain percentage corrector, which is of metal corrector percentage of metal corrector. And in some other cases, where we talk about corresponding mainly ligand orbitals say they have certain percentage of ligand corrector.

So, these are the things basically important to know the amount of charge transfer which is taking from these particular centers from one point to the other. So, what we see that when the metal center is responsible for donation of electron that means metals should be highly reducing in nature that means it has some access electronic charge that means they are in low oxidation state. So, this species will be in low oxidation state and these low oxidation states are there we have certain metal ions. And those metal ions can be in the zero oxidation state also or M 1 plus or M 2 plus oxidation states. And in all this case most of this corresponding orbitals which are available for the free ion are all filled that means some of these orbitals which are available to them are filled that means filled orbitals are available for donation.


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MLCT Transitions

The transition of an electron from the t_{2g} (π) and the e_g (σ^*) to the t_{1u} (π^*/σ^*). These transitions arise from π acceptor ligands and metals that are willing to donate electrons into the orbitals of Ligand character.

They are less frequent- metals commonly accept electrons rather than donate them.

Examples of π accepting ligands are as follows: CO, NO, CN⁻, N₂, bpy, o-phen, RNC, C₃H₃⁻, C=C bonded groups, C≡C bonded groups.

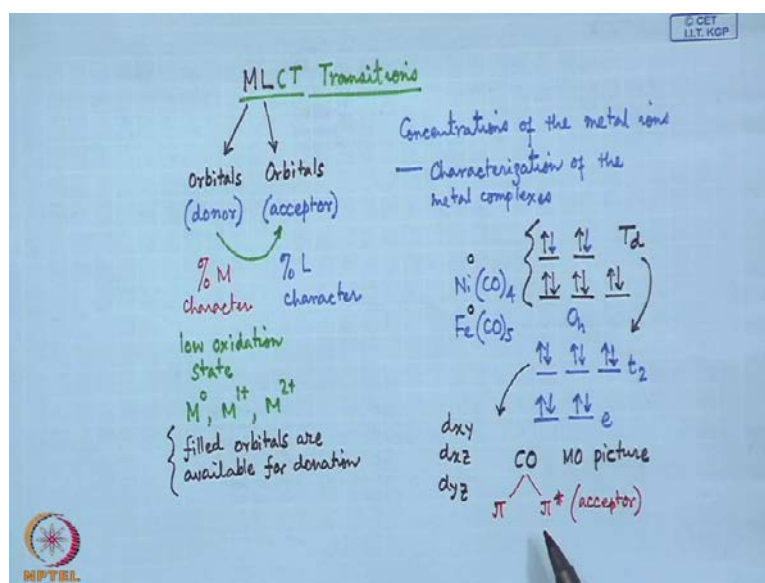


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So, this filled orbitals will basically be there which can donate the electro density to the ligand orbitals. So, we will see how particular transitions can help us in understanding corresponding metal complexes. So, we have the MLCT type of transitions and already we have discussed the other one the complementary where the ligand orbitals are the donor orbitals. And there we have seen that the particular ligand to metal charge transitions which we see typically for certain systems.

And we have seen that some of π and σ electron densities are responsible. And the donation is taking place from some of the orbitals which are having metal corrector to orbitals of ligand corrector. So, next what we will see that there are certain of this metal center present which commonly accept electrons other then denote them. So, examples of such π accepting ligands are therefore, which can stabilized the corresponding metal complexes in low oxidation state that means what we see if we have the carbon monoxide as the ligand.

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What happens to that is if we have the nickel which can form very nicely the corresponding carbonyl nickel zero compound or iron which can also form the corresponding penta carbonyl iron zero compound. So, they are having all the levels which were available for corresponding metal center is in zero oxidation state. So, they have large number of such field orbital available for donation to certain orbitals which are of ligand corrector.

So, if these orbitals are available and we see that in case of nickel we have the corresponding electron density is t_2 g 6 and E g 2. So, the required number of electrons what we can have? We have 2 unpaired electron densities in d_{z^2} and $d_{x^2-y^2}$ orbitals. And this orbitals are basically of sigma corrector, because they are directly facing the corresponding ligands which are in a tetrahedral geometry, but if we consider them as the corresponding orbitals which are present for T_d geometry. The situation is completely different from that of our distribution for the octahedral geometry, because this particular arrangement is for O_h symmetry. But for T_d symmetry, we have the 3 orbitals over here and we have the e set and t_2 set. So, we have 1 2 3 4 5 6 7 and 8 electrons for nickel in plus 2 oxidation state. And apart from that when we just consider this is zero oxidation state, we have two more electrons if it is in octahedral geometry and if it is in tetrahedral geometry we have a situation like this.

So, if we consider that all the 10 electrons which are coming for donation to the ligand orbitals are all filled. So, this t_{2g} set is the d_{xy} , d_{xz} and d_{yz} set and they are in between the corresponding Cartesian axis which are present for the octahedral geometry, but which can be close to the corresponding tetrahedral orientation of the corresponding ligand system. So, if they can donate the electron density from there to some of these orbitals where we have the carbon monoxide molecular orbitals. If we see the corresponding molecular orbitals picture of the carbon monoxide, it tells us that it can have the corresponding pi electron density which is originating from the corresponding pi 1 between the carbon and oxygen as well it is as the corresponding anti bonding orbital which is pi star. So, if pi star orbital is available for its corresponding acceptance that means if they are behaving as the corresponding acceptor orbital. Then certain amount of charge from these orbitals which are mainly metal center can be pushed to the corresponding ligand acceptor orbital that why since it is accepting the corresponding electron density, it is behaving as a corresponding pi acids.


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MLCT Transitions

The transition of an electron from the t_{2g} (pi) and the e_g (sigma*) to the t_{1u} (pi*/sigma*). These transitions arise from pi acceptor ligands and metals that are willing to donate electrons into the orbitals of Ligand character.

They are less frequent- metals commonly accept electrons rather than donate them.

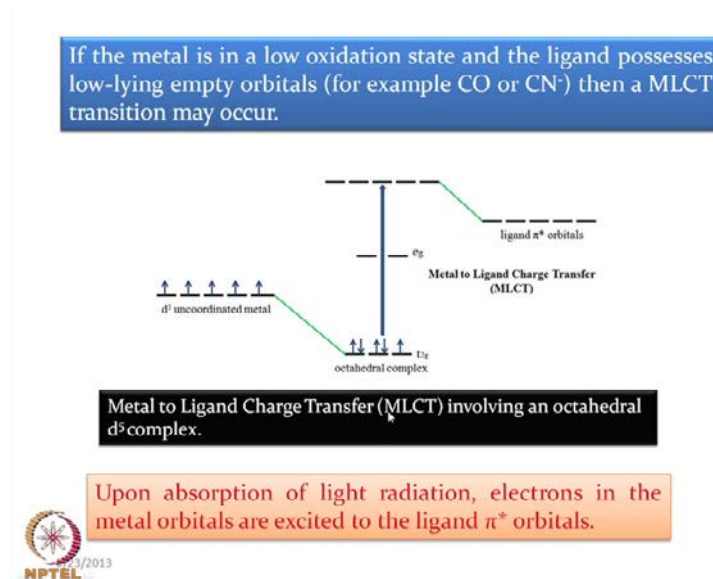
Examples of pi accepting ligands are as follows: CO, NO, CN⁻, N₂, bpy, o-phen, RNC, C₃H₃⁻, C=C bonded groups, C≡C bonded groups.


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So, these orbitals which are there which can give functioning as corresponding pi accepting ligands. So, typical example of this carbon monoxide same is true for nitric oxide C N minus cyanide nitrogen bipyridine and ortho phenantroline. So, like this if we have the corresponding nitrogen center bidentate ligands like bipyridine and ortho-phenantroline, we will find it as also, me pi electron cloud. And those pi electron clouds are there for the corresponding bonding pattern and for anti bonding state we have also

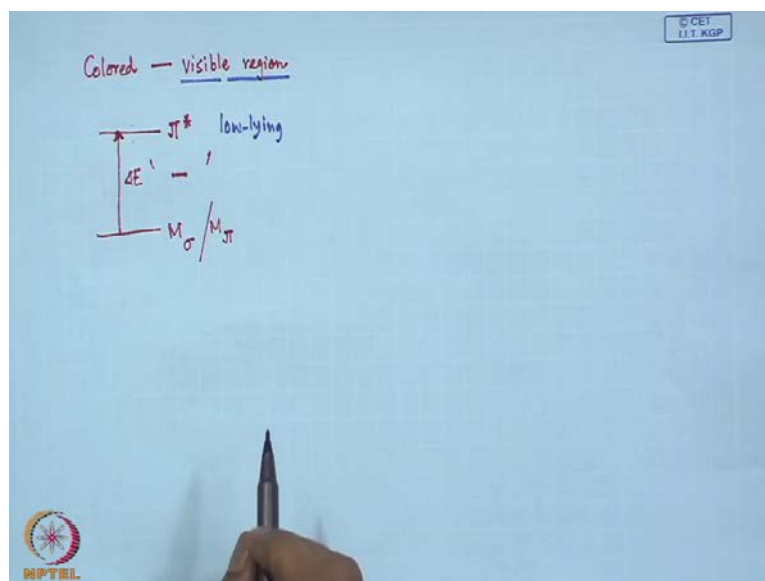
the corresponding pi star level. So, isocyanide then cyclopentadienyl and the double bonded carbon system or triple bonded carbon systems all are having multiple bonds between the atoms whether it is carbon, carbon or carbon nitrogen system. So, whenever we have a sigma bond as well as pi bond, it can definitely have the corresponding pi star antibonding level.

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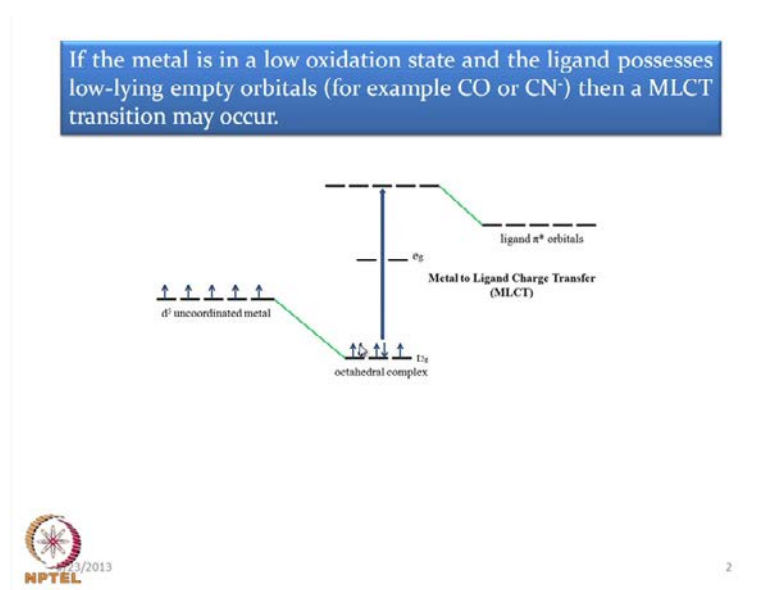
So, all these pi star antibonding levels when they are utilized for acceptance of electron density from the metal center, we have the possibility of getting the corresponding charge transfer transition which can be considered as their characteristic metal to ligand charge transfer transitions. So, if the metal leading you have seen that the metal can be in the low oxidation state and the ligand possesses low lying empty orbital what is called this low lying. Because the energy of this orbitals should be accessible for the transition, if it is in a very high energy region we definitely not get corresponding transitions in the visible region atleast .

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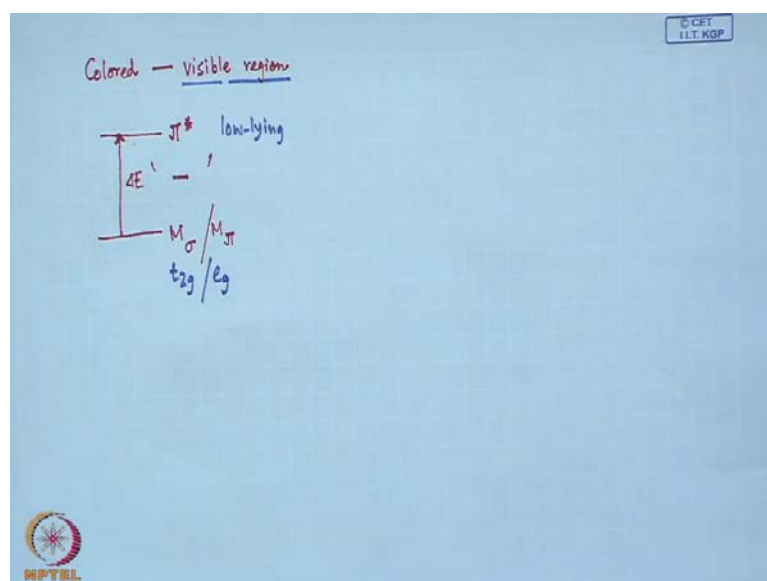


So, the system will not be colored, so to get a corresponding colors system we should have the corresponding transition in the visible region. So, the corresponding level which is pi star levels and this is basically metal sigma orbitals or the corresponding metal based pi orbitals are there. And if these energy gap which is important which is delta E, it spans for the corresponding range basically in the visible region then only we expect certain transition. And which can characterized as the corresponding metal to ligand charge transfer transition and which can be seen as the corresponding color solution for the visible region transition. So, we have the corresponding level which can consider as low lying empty orbital which is acceptor in nature.

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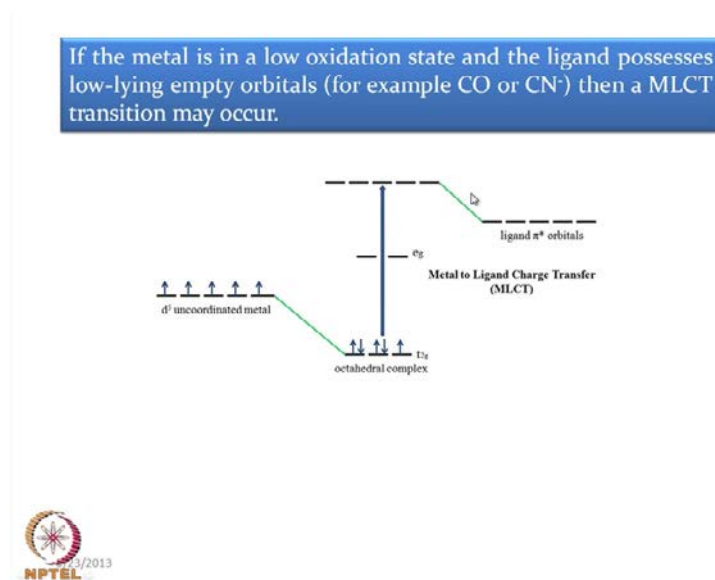
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So, for carbon monoxide as well as for cyanide ion we have the corresponding transitions such as when it is bound to nickel center or it is bound to the iron center. Similarly, for ferrocyanide and ferricyanide system iron is bound the cyanide ions and then an MLCT transition can occur. So, all these MLCT transitions may take place when we have the situation belonging to this ligands like this or the other set of ligands what we are seen just now. So, this is one pictorial representation a very simple pictorial representation what we have seen just now for the level that means what are the corresponding levels for these M_σ or M_π type. What we can see that if we have this particular sigma

type of orbital for octahedral case, we have the t_{2g} type of orbitals or the E_g type of orbitals, which are available for the corresponding octahedral complex.

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So, if we have a d^5 uncoordinated metal centers like Fe^{3+} which is a $3d^5$ systems. So, iron if it is there and particularly when it is forming certain complexes with the ligand, it is forming the corresponding low spin compound. So, low spin iron compound is forming over there and in octahedral geometry, it will have the corresponding electronic configuration of t_{2g}^5 and that t_{2g}^5 electrons will be there. And we have the corresponding other metal orbitals which are e_g level is also available over there. And we have the ligand π^* orbitals which are of ligand corrector. So, these orbitals are of metal corrector mostly they are having some certain percentage of metal corrector. And if we find them there is a mixing of the metal and the ligand corrector here the corresponding metal corrector, we can find it out form some calculations.

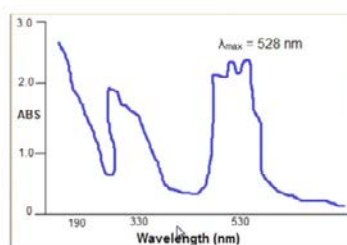
Now a days for some certain amount of sophisticated calculations like density functional theory based on calculations where we find the percentage of the corrector of this orbitals. And when we push the electron density from this level to the upper level and where we have the corresponding ligand π^* level. And the transition is mostly provable for the corresponding range where the t_{2g} level of electron density is giving the corresponding charge density to the ligand π^* orbitals which are highly allowed transition.

Because it can have some transitions to the E g level also which will be for the corresponding d d transitions which are not allowed transitions. But due to some vibronic coupling some other relaxation of the rules the laporte selection rule, we can have certain amount of transitions which can be consider as the d d transitions. So, apart from this d d transitions, we can have highly intense charge transitions charge transfer transitions to the corresponding ligand acceptable levels. And if it happens we have the corresponding lambda max values also if it is colored, it can be in the visible region. We see the color in the visible region as also the corresponding epsilon max values which are accessible 1000 say 50000 or so M whole inverse in centimeter inverse unit.

So, this particular charge basically giving us certain amount of this values, so for d 5 complex, we can have the corresponding metal to ligand charge transfer in an octahedral complex. So, in an octahedral complex the corresponding energy diagram for the transition would be like this when we have the corresponding absorption of radiation. So, when the complex is radiated with light of certain wave length which can be absorbed in the electrons in the metal orbitals or the metal based orbital which are certain percentage say 80 percent or 70 percent of metal corrector are excited to the ligand pi star orbitals. So, this is the main mechanism, so we can ask ourselves that what is, is the corresponding mechanism for typical MLCT transitions. So, what we have seen in other case where we have the different type of mechanism for MLCT transitions. Now, we have completely opposite type of transition for the metal to ligand charge transfer.

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KMnO_4 dissolved in water gives intense CT bands. The two absorptions below result from LMCT.

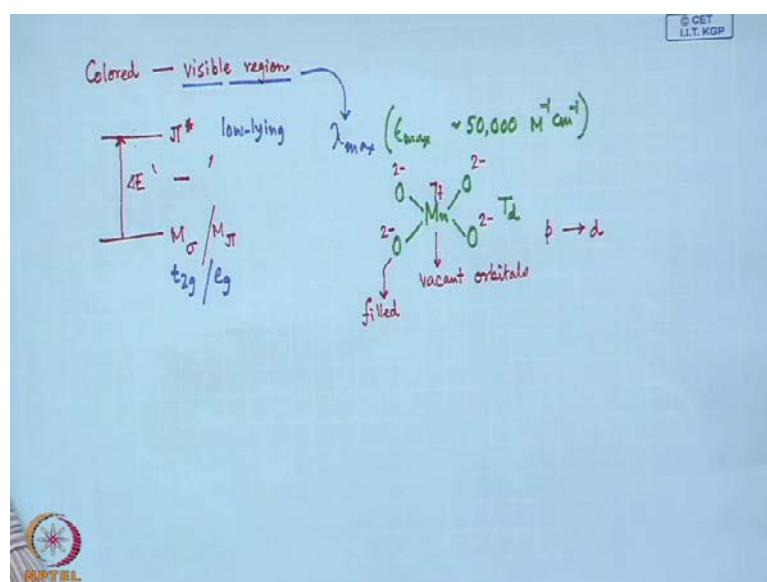


The band at 528 nm gives rise to the deep purple color of the solution. An electron from a 'oxygen lone pair' character orbital is transferred to a low lying Mn orbital.

So, this sort of charge transfer play some important conclusions to us like that what we have seen the ligand to metal charge transfers. This is we have seen, we have already discussed this thing for $KMnO_4$ when you dissolve it in water it gives intense charge transfer band. And to absorptions below what we see now that what type of transition we can have when we record with in a corresponding spectra photo meter it results the basically corresponding transition like this. So, when one particular band which is structured is around 528 nanometer. So, if we measure this particular one in corresponding spectrum is giving the corresponding band at 528 nanometer, which is due to the corresponding pink coloration of this. And some other transitions are also there which are of corresponding less intense which is in the low region of the wave length which is around or less than 320 nanometer or so.

So, this intense charge transfer band which say corresponding dilution at the 10 to the power of minus 5 molar, we have an absorbance value of say 2,5 or so. So, we can get this in the corresponding spectrum. So, this 528 nanometer band gives rise to the deep purple color, it is the color due to the solution an electron from an oxygen lone pair. So, oxygen, all the 4 oxygen atoms in $KMnO_4$ what we have seen, that we can consider this as the corresponding field level.

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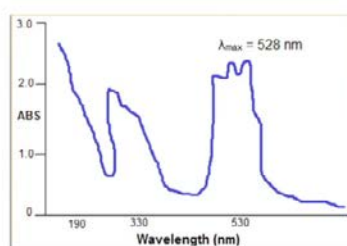
So, whenever we have in a tetrahedral geometry of this MNO_4 and in the terms of the corresponding hybrid digestion scheme what we know like that of our methane molecule

we have a $s p^3$ hybrid digestion scheme. Similarly, for this one we can have the corresponding $s d^3$ type of that means the d orbitals are involved for the corresponding tetrahedral geometry. So involvement of this d orbitals for the corresponding tetrahedral geometry tells us that this has zero electron density for the 7 plus oxidation state and all the oxygen atoms are 2 minus 2 minus 2 minus.

So, they are all filled, so we have the generated vacant orbitals. So, all the metal ion orbitals are vacant, now it can accept the electron density from the filled ligand orbitals which are filled on the oxygen. So, oxygen orbitals basically the corresponding s and p orbitals. So, other the p orbitals basically are available for donation to the metal centers. So, the transition is basically if it is completely p centers to d of the metal ion. So, it is highly favored transitions. So, we have a huge intensity for this transition from the oxygen to the manganese center.

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$KMnO_4$ dissolved in water gives intense CT bands. The two absorptions below result from LMCT.

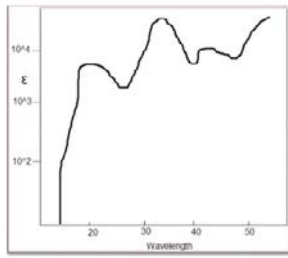
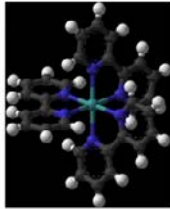


The band at 528 nm gives rise to the deep purple color of the solution. An electron from a 'oxygen lone pair' character orbital is transferred to a low lying Mn orbital.


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Tris(bipyridine)ruthenium(II) dichloride is a coordination compound of formula $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$.

$[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ is dissolved in water and a CT band is observed.



A d-electron from the ruthenium atom is excited to a bipyridine anti-bonding orbital. The very broad absorption band is due to the excitation of the electron to various vibrationally excited states of the π^* electronic state.

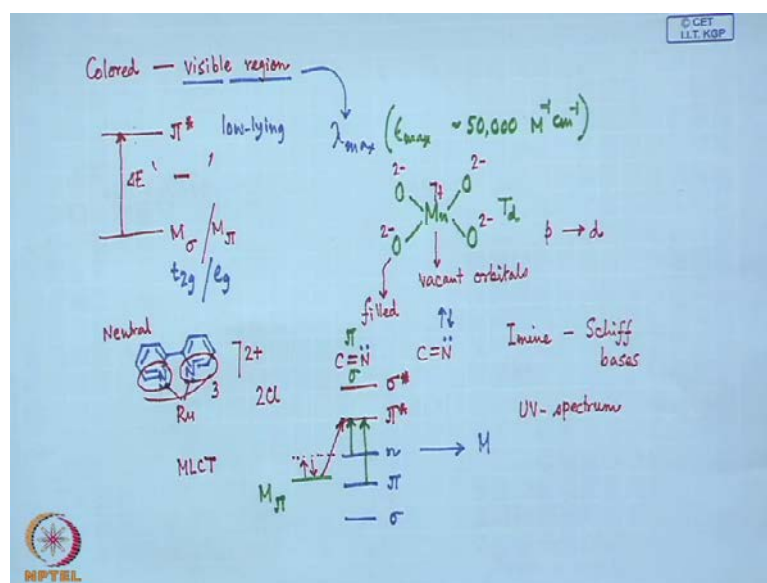


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So, now we have in this particular case what we have discussed also earlier that in this particular case we have low lying manganese orbital. But in case of what we have discussing today for the metal to ligand charge transfer transition, we should have certain other type of orientation where the metal orbital giving us the corresponding low lying orbital. So, one such example is the tris, bipyridine ruthenium compound, ruthenium complex. So, ruthenium is plus 2 state, it can also be same for iron compound, but this in intensity is very good and the corresponding band for this charge transfer is very much characteristic for this compound. So, whenever we make this compound, because it has some good catalytic, catalytic properties to show for this tris bipyridyl ruthenium 2 chloride compound.

So, when we dissolve in water and this particular compound basically gives a charge transfer band, it can be dissolve in acetonitrile, it can be dissolve in dichloromethane also, where it gives the corresponding charge transfer transition. So, charge transfer transitions will not take place from metal to this ligand. So, we have 3 bipyridyl ligand, this is one bipyridyl; this is another bipyridyl and this is another bipyridyl ligand we have. So, now we have again certain type of this structure transitions, like what we have seen just now for KMnO_4 . So, we have certain this transitions, so these are so these are 200 300 400 type of these is not 30 40. So, this particular transitions what we see that structure transitions which is mostly centered over here where this particular one around 330 or so.

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The d electron from the ruthenium atom is excited to the byp anti-bonding orbital. So, we have this bipyridine ligand. So, this is the by tented n n donor ligand what we have in our hand and this is attached to one ruthenium, so 3 such ruthenium species is there and these are all neutral. So, from the point of view of any other charge separation during complexes when is not taking place and over all charge of the complex would be 2 plus. So, that why we have 2 counter anions as the chloride anion, so we have C double bond N here particularly if we just focus a retains on this similarly, we have another C double bonded. So, we have large number of that means the 6, such C double bond N bonds are there which is present also present in such a imine bonds when we get these imine bonds from the Schiff bases. So, they also give rise to those imine bonds, so we have the corresponding bonds when they are forming between this carbon and nitrogen basically we have the sigma and the corresponding pi bond. So, whenever forming this particular bonds. So, what we have seen that a typical organic compound that means when we talk in terms of the corresponding isolated bipyridine molecule what we see that we have the sigma bonding level then the pi bonding level.

And if we have certain amount of lone pair of electron, because this nitrogen's, because this nitrogen lone pairs are available over there. So, these nitrogen lone pairs are basically utilized for the donation to the metal center. So, we have the n electrons are non bonding electrons and this n electrons are basically engaged in forming the corresponding bonds. So, if we find that there are 2 such n electron the non bonding

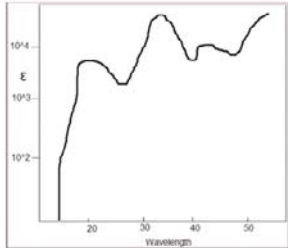
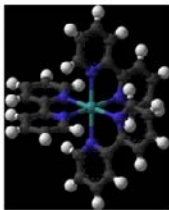
electron. And if they are basically donated, if we have this non bonding electrons on the nitrogen, they are basically donated to the metal center for the corresponding coordinate bond formation. So, we have on the other side in the high energy side, we have the corresponding anti bonding level of pi. So, the pi star will be of low energy since sigma is mostly stabilized. So, if we consider this as the corresponding central part that is the very center, so we have the sigma star level is of here.

So, within the bi pyridine molecular cell we have some ultraviolet spectrum. So, ultraviolet spectrum for the corresponding bi pyridine molecule can show us that we can have certain transitions which one is of low energy transition is the n pi star. And the most provable one is the corresponding pi pi star transitions. Now, this bends are already there and these are basically seen in the visible region U V region sorry. So, there are seen in the U V region. So, they are of high energy now in at certain points if the during the formation of this bonds to the bi pyridine molecules, if the corresponding metal orbital is coming over here. So, this metal sigma or the metal pi level the filled level the metal filled pi level is coming over here. And if these are then responsible for the donation that means these levels are also filled the metal orbitals are also filled. And if they can donate the electron density to the pi star level of this molecule, we will find that this can show us the corresponding metal to ligand charge transfer transition.


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Tris(bipyridine)ruthenium(II) dichloride is a coordination compound of formula $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$.

$[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ is dissolved in water and a CT band is observed.



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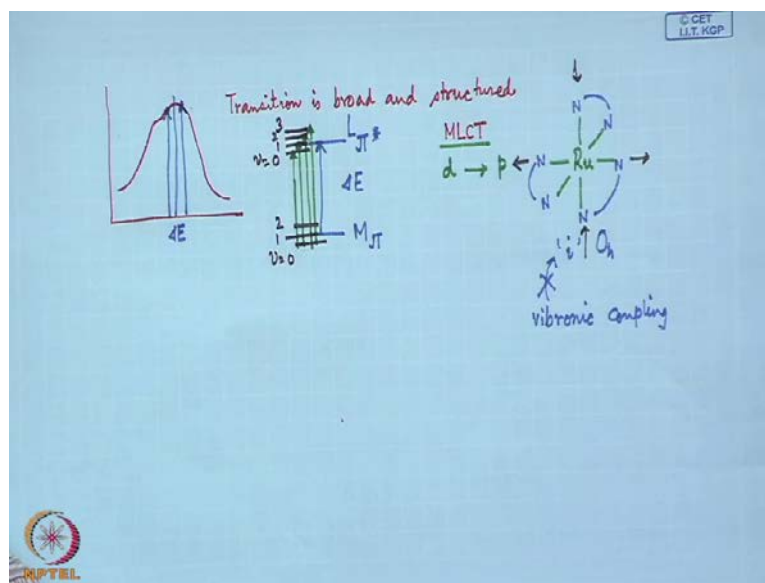


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So, that is the typical mechanism where we see that how and why the ruthenium tris bipyridine compound is showing the corresponding transition. So, we have mostly very broad absorption band. So, several closeness split other levels are also available is due to the excitation of the electron to the various vibrationally excited states of the pi star electronic state.

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Why this particular signal is broad? Because these you can see that whenever we have a particular electronic transition and which is basically structure and broad. So, the transition is broad and structured, why this is so? Because whatever transition we are talking about based on the metal level as well as the pi star level of the ligand. So, it is 1 pi star and say this is M pi sa.

So, 1 pi star and M pi is involving for the corresponding electronic transition and we find it as it is corresponding separation is the corresponding delta E value for the corresponding amount of separation between these 2 levels. Now, we have within this electronic state since we are talking that we have the corresponding d level for this MLCT charge transfer transition, what we find that this particular transition we can consider as the metal d level to the ligand P level, because the P orbitals are involved for the formation of the pi as well as the pi star level. So, this is the situation where it is mostly allowed so highly allowed transition can take place from d to p. And due to these and another also good thing is there since the ruthenium is present in an octahedral

geometry. So, we have 3 bipyridine groups are there. So, these are the 3 bipyridyl ligand attached to the ruthenium center and which is center symmetry that means i is there and which is fully controlled by the corresponding symmetry group which is the octahedral symmetry group. But the change in this particular ruthenium nitrogen bond, because the thermal vibration is always taking place such that we can destroy the corresponding i for the molecule due to vibronic coupling.

So, the molecular vibration is taking place along the ruthenium nitrogen bond axis. And we just basically because some of this bonds are getting stressed and some are squeezed. So, the i is lost is not typical center symmetry and due to that lose in the center symmetry there is the corresponding symmetry requirement for this is relaxed. And we have certain amount of allowed transition due to that so that vibronic coupling is also basically giving us some of the other vibrational levels for this molecule. so, within one particular electronic state. So, we basically get the corresponding levels not only for the metal center, but also for several other vibrational levels where v is equal to 0 1 2 etcetera. similarly, for the excited state is equal to 1 2 and 3. So, we can have along this particular transitions for this electronic transitions we can have several other transitions from $d 0$ to the other levels.

So, these transitions can also take place along with these transition which is mainly required for $\Delta \lambda$ values. So, that is why if it is centered for these that means if it is centered for these ΔE value we can have some certain smaller and certain higher transitions. Due to the different transitions what we can have for the different vibrationally excited levels which are available for the excited state which is $L \pi^*$ level. So, due to the possibility of several other vibrational levels which are closely associated with the $L \pi^*$ level, we have a very broad signal for this particular compound for its corresponding MLCT transitions at the π^* electronic state.

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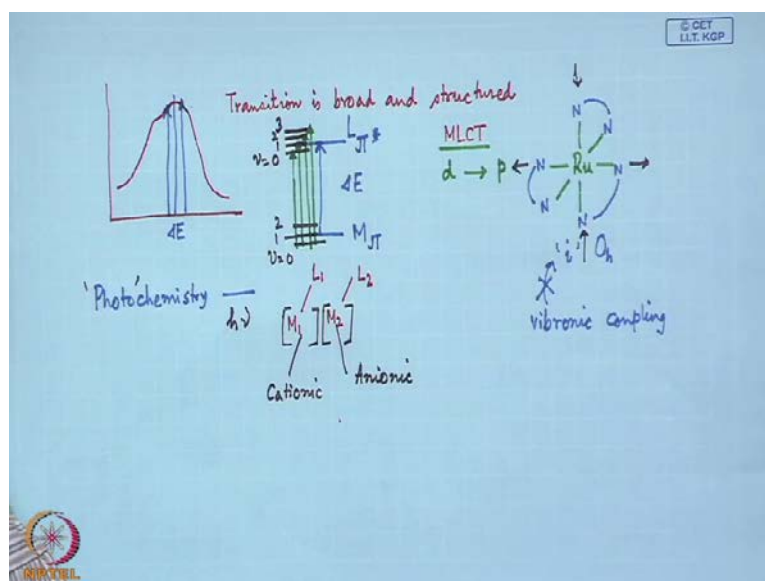
Light-induced reactions which originate from outer sphere (OS) CT excited states have been shown to play an important role in the field of photochemistry of coordination compounds.



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So, we have the light energy which is falling on the system and light induced reactions can originate from outer sphere charge transfer excited states. So, we can have, because for the compound what we can have one particular complex species is there, and on the outer of the coordination sphere we have another species if we can have. So, in certain cases we have these outer sphere charge transfer excited states at the same time. And they can play some important role in the field of photochemistry of coordination compound.

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So, this particular thing is also related to certain amount to the photochemistry, because we are giving certain amount of radiation to excite the system from the ground state to the excited state. So, if the supplied $h\nu$ is such that that means the photons are falling on the metal complex. And we expect that the certain chemical reaction can take place followed by the corresponding absorption of the photon energy. So, if we have the corresponding fissioned transitions for this MLCT type. So, at thus particular wave length we get the basically the corresponding molecule, if we pause this radiation continuously to the molecule. And the entire molecule system can absorb all the radiation which is falling on the molecule. And so, all the molecule are getting excited to its first excited state that means the excited states due to the corresponding charge transfer transition due to metal ligand charge transfer.

So, this particular radiation can excite the molecule from lower level to the higher level. And if we have certain species of two part that means the cationic part and anionic part. So, this is the cationic part and this is the anionic one, and we can have different particular different species that means if where we have a M 1 species. And here we can have M 2 species with certain ligands that means L 1 type of ligand and here also we can have L 2 ligand type of ligand. So, if we can see that one particular system is behaving as a corresponding charge transfer species, the other can be of opposite type then we can see that a complex type of charge transfer transition can take place when we have the corresponding outer sphere excited states.

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Light-induced reactions which originate from outer sphere (OS) CT excited states have been shown to play an important role in the field of photochemistry of coordination compounds.

Aqueous solutions of the ion pairs $[\text{Rh}(\text{bipy})_3]^{3+}[\text{M}(\text{CN})_6]^{4-}$ with $\text{M} = \text{Fe}, \text{Ru},$ and Os display M^{II} to bipy OS MLCT absorptions at $\lambda_{\text{max}} = 480 \text{ nm}$ ($\epsilon = 61$) for $\text{M} = \text{Fe}$, 400 nm for Os , and 379 nm for Ru .

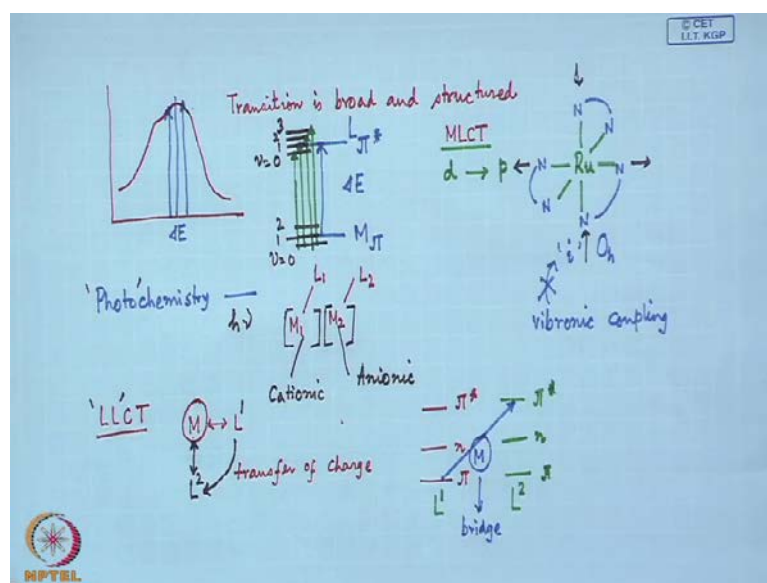
As expected the OS CT bands shift to lower energies in the order of increasing reducing strength of $[\text{M}(\text{CN})_6]^{4-}$ ($E_{1/2} = 0.19 \text{ V}$ for Fe , 0.40 V for Os and 0.70 V vs SCE for Ru).

So, in these cases basically if we can have a compound like this, this is of this particular complex where we have a part which is a cationic part. And we have the corresponding anionic part and they play some important role in the photochemical transformation. Also, if we have this typical compound we are calling this as ion pair, but is a typical corresponding compound recording upon the corresponding amount of this particular species. So, this whole thing can spot the charge balance which is 3 plus and this is 4 minus that means the metal is present in a bivalent state but this is in the trivalent state.

So, this particular for balance, so if you can have like that our Prussian blue type of structure where iron is attaching to that particular ferrocyanide and ferricyanide system. Here we have this is this can be the whole 4 and this can be whole 3 to get the corresponding charge neutral species for this. So, when we dissolve this in water solution we see they basically display first thing that this when M is present as iron ruthenium and osmium. They all display metal to bipyridyl in this particular case is a rhodium one outer sphere MLCT absorption at 480 nanometer for when iron metal is iron 400 nanometer when it is osmium and 39 nanometer when it is ruthenium for a series of iron ruthenium and osmium where this basically are changing. So, this particular one in this case what we have seen just now for the corresponding ruthenium compound for the bipyridyl also. So, when they are bound to this particular case they can show the different types of charge transfer transitions in such 10 complex species also.

So, this outer sphere charge transfer bands can shift to lower energies in order of increasing reducing strength. So, if this M C N whole 64 minus is present. And they have different half wave potential, if we measure in it by cyclic voltammetry where we will find the corresponding half wave potential values the E half values are varying from point 19 to 0.70 for iron to osmium to ruthenium that means the corresponding reduction potentials. So, more and more, we basically going for positive value as we move from iron to ruthenium. So, these basically gives us a corresponding clue for the corresponding shift in lower energies as we move for complete electron transfer, because the reduction is nothing but the complete electronic charge transfer from one orbital to the other for the species like iron for its reduction osmium when its reduce from and the ruthenium and its reduced form. So, when these are present for iron osmium they are all plus 2 oxidation state. So, when we go for their reduction they will be forming in the plus 1 oxidation state.

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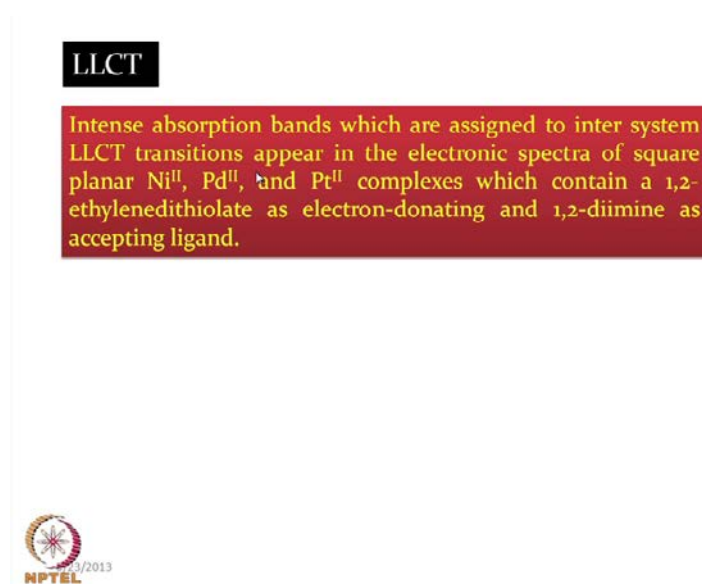
So, next we will just see that other 2 types of categories for this charge transfer transitions where we see that ligand to ligand charge transfer transitions are also important. So, earlier we have seen that metal to ligand charge transfer and ligand to metal charge transfer that means we are basically talking certain systems where we have the metal ligand bonding. And either the metal is transferring the charge to the ligand orbitals or ligand is charging some metal orbital.

But now, we have reached earlier going to discussed one particular situation where both the 2 spots are the ligands that means they are present in the system where it is bond to the metal ion and where we have this ligand also. And if we have L 1 is one type of ligand and L 2 is another type of ligand and they are still bond to the metal center. But one type of ligand is highly oxidizing and another type of ligand is highly reducing so, if this is reducing and this is oxidizing. So, the reducing ligand center can transfer the electronic charge to the oxidizing ligand center.

So, for transfer of charge so they are bond to the metal ion, but the corresponding charge transfer is taking place basically between 2 ligand systems what we have seen earlier for a particular single ligand system, we can have the pi level as well as the pi star level or the N level. So, in that particular case, what we see the pi star level is donating the electron density to pi star level and the N level is donating the electron density to pi star level. Now, the situation is if this is for L 1 and the other one is for L 2. So, this


particular pi star, it may not be of same energy and it has also another pi and it has also another N. So, the L 1 molecular orbital level; the ground state level is the donor level and acceptor level will be on L 2. So, we have the corresponding transfer of charge density from L 1 to L 2 and which is basically going through the metals.

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LLCT

Intense absorption bands which are assigned to inter system LLCT transitions appear in the electronic spectra of square planar Ni^{II}, Pd^{II}, and Pt^{II} complexes which contain a 1,2-ethylenedithiolate as electron-donating and 1,2-diimine as accepting ligand.

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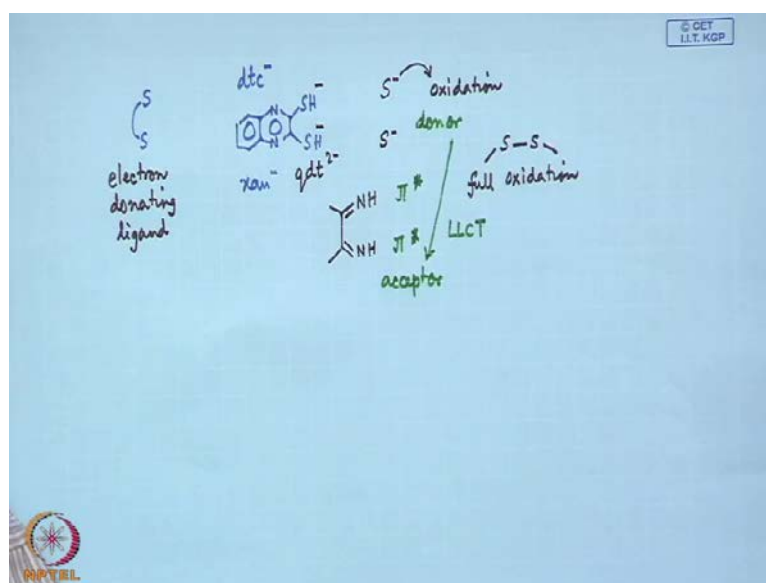
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So, the metal is basically functioning as a bridge for this type of charge transfer. So, we have the LLCT type of charge transfer in this particular case. So, here we get basically intense absorption bands which can assigned to inter system ligand to ligand charge transfer that means the system has 2 different types of ligands if possible, and transitions appear in the electronic spectra of square planar complexes this. So, this particular area is very rich some of the groups around the world they are working on this square planar compounds of nickel palladium. And platinum species which contain a 1 2 ethylenedithiolate type that means the sulfur bearing ligand where the sulfur donor groups can donate their electron density very easily, because sulfur donor atoms are very big in size. And they cannot hold this particular charge to them they donate the electron density very easily to the other system. So, that is why all sulfur bearing compounds are prompt to oxidation that means they can donate the electron density to some other acceptor level.

So, if we have any sulfur sulfur bearing compound what we have earlier seen that it can be dithiocarbamate, or it can be typically coaxialinedithiol which is can be prepared very

nicely S H S H or it can be the xanthate type of ligand. So, whenever we have the sulfur, so we have this higher electronic charge on the sulfur groups. So, this can be donated or we see the corresponding oxidation. So, this is the typical type of ligand system which can function as electron donating ligand for the corresponding ligand to ligand charge transfer transitions. So, other type of ligand what we can have the typical diimine type or diamine type of ligand which can be simple ethylenediamine, or which can be simple bipyridyl type of ligand. Where we seen we have seen that bipyridyl type of ligand can be a very good acceptor ligand for metal to ligand charge transfers what we have seen.

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So, this is one simple drawing basically for that we can have. So, many types of sulfur sulfur for bearing ligand if it is for ethylenedithiolate. So, ethylene backbone will be there which is typically a rigid one which is present also over that q d t 2 minus, because two of them can go for deprotonation giving 2 charges on this 2 sulfur. So, it is coaxialine dithiol type of group. So, we have a rigid backbone, so this backbone is typically rigid. So, the rigid backbone is also required for their corresponding donation and we can have at certain point that if we have the typical oxidation then we can get the corresponding sulfur sulfide coupling.

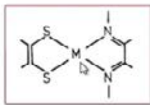
So is for full oxidation of the ligand system on the thioal type of ligand, basically we will end up with sulfur sulfur bridge species. So, which is full oxidation and full transfer of electron charge 2 electron oxidation for this sulfur sulfur bridge? So, we have this sulfur

sulfur backbone and then we can certain diamine type of ligands. So, diamine is very easy to visualize that means easy to consider. So, one such diamine type of ligands, we can have the glyoxal then simple N H can be there. So, glyoxal plus ammonia give rise to some diamine type of ligands system. So, where the carbon nitrogen double bond is there and that carbon nitrogen double bond can have what we have discussed just now that we can have certain orbitals which can be the corresponding acceptor orbital. So, they have the pi star orbitals on this groups. So, they can be very good acceptor so, we have the donor level on this sulfur bearing group and the acceptor on this carbon nitrogen groups. So, we have from the donor to these acceptor we have the corresponding LLCT charge transfer.


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LLCT

Intense absorption bands which are assigned to inter system LLCT transitions appear in the electronic spectra of square planar Ni^{II} , Pd^{II} , and Pt^{II} complexes which contain a 1,2-ethylenedithiolate as electron-donating and 1,2-diamine as accepting ligand.



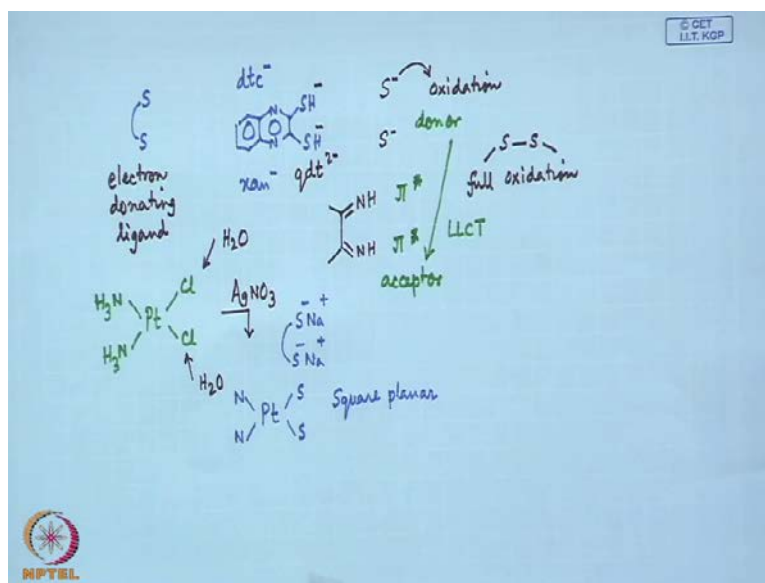
The energy of this transition is almost independent of the metal M^{II} .



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So, we have this particular backbone where basically that what type of ligand we have. So, we say typically it is not always very easy to make this compound of nickel palladium and platinum, because in most of these cases we have the corresponding homiletic species that means both the sulfur ligand bearing molecule, we can have or both the nitrogen bearing molecule we can have. But to make this heterolytic compound that means one dithiol and diamine type of ligand is very difficult to make sometimes. So, some experimental manipulation is there some procedure is always there where we can make this molecules in A.

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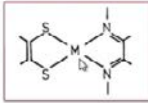
Typical way that means first we can make the corresponding dichloro compound the way we make it for the platinum having two ammonia groups and its chloro derivative. So, this is basically double known molecule what we talk about the corresponding drug also, for anticancer is a cisplatin this molecule. If we go for that and if we are able to get, because they go and go inside the cell this platinum chlorine bond are getting hydrolyzed and they are basically go in the corresponding replacement for water molecules.

So, in this particular case so certain basic background we can have for this type of synthesis that if we use simple silver nitrate to take out this ligands from the platinum center we have the corresponding diaco compound and then any of these ligands basically we can use this S S. And it is corresponding sodium salt to other S minus N a plus S minus N a plus. Then we will end up with a compound like this where we have nitrogen nitrogen and sulfur sulfur environment around the platinum center. So, we have the mixed or the heteroleptic species based on the platinum compound which is square planar. So, this geometry is also important that it should be square planar for this side of electronic transitions.


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LLCT

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The energy of this transition is almost independent of the metal M^{II}.



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So, energy of this transitions is almost independent of the metal ion in the bivalent oxidation state. So, whether we are making a nickel compound or a palladium compound or a platinum compound the corresponding transition energy, or the lambda max what we get for this LLCT transitions is of close energy that means the metal orbitals are not involved in this ligand to ligand charge transfer transitions. So, which is a very important clue that how we can identify that a particular charge transfer transition is not of MLCT type or LMCT type, but it would be of LLCT type.

So, if it is metal independent nature that means if we have 3 different types of complexes of the same metal ions, metal sides then we measure the corresponding lambda max values. And those values can immediately can tell us that if they are of same energy or close to same energy, we can tell them they are originating from the corresponding ligand to ligand charge transfer transitions.


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MMCT

Cationic Co^{II} amine complexes are well suited as electron acceptors. When they are combined with the reducing anions $[\text{Fe}(\text{CN})_6]^{4-}$ or $[\text{Ru}(\text{CN})_6]^{4-}$ ion pairs are formed which are characterized by OS MMCT absorption bands.

The rather short wavelength of these absorptions is certainly due to the large reorganizational energy which is associated with the reduction of low-spin Co^{III} .

Since an electron is accepted into an antibonding eg orbital (in Oh symmetry) the MMCT transition requires a large extension of the cobalt-ligand bond distance.

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So, we have the last category is the MMCT type, where we have the cationic cobalt amine complexes, which we can find for the two form that means the hexacyano iron 4 minus that means the corresponding ferrocyanide species and the corresponding ruthenium analog. And if they form basically in pairs which are characterized by corresponding outer sphere MMCT transitions. So, cationic cobalt compound is present an anionic this particular part is there, then only the metal orbitals are responsible for the corresponding transitions.

So, short wavelength of this absorption are due to the large reorganization energy which is associated with the reduction of the low spin cobalt 3 compound. That means the cobalt 3 compound is there, and cobalt orbitals are really available for the corresponding acceptance of the charge density. And since an electron is accepted into an antibonding E g orbital the MMCT transition require large extension of the cobalt ligand bond distance.

So, this cobalt amine compounds are therefore, basically responsible for accepting the electron density. And the corresponding metal orbitals on this hexacyano derivatives are there which are basically donating the electron density. So, that gives rise to the last type of, or the 4th type of corresponding charge transfer transitions where two metal orbitals are involved. And we get the corresponding metal to metal charge transfer transition.

Thank you very much.