good afternoon everybody

so we are in the last class of coordination compounds where we are talking about the complexes and how we can explain their different physical behavior as well as the property and in terms of valence bond theory as well as the crystal field theory we are trying to figure out the electronic configuration

so we all know that how we can have the corresponding electronic configuration and that the changed electronic configuration in say crystal field where we see that a metal ion is considered as a positively charged point center and the ligand is slightly bigger negatively charged species and this particular interaction when they are forming a coordinate bond we are considering them as the interaction what we can find in the crystal of the salts like say sodium chloride and how the different orbitals particularly the d electron configuration

so we are looking at the corresponding d electron configurations in the changed condition with regard to the corresponding geometries which is very important how we can have a metal complex whether we have a ml4 complex or ml6 complex what are the corresponding geometries we should all know and those geometries will also tell us that how many number of unpaired electrons will be there in that particular molecule or the coordination complex because these number of unpaired electrons which we should have some importance related to their reactivity catalysis and all these thing which we do not see very much in the corresponding organic chemistry but the coercion chemistry and the inorganic chemistry of the transition metal ions are largely dominated by the number of unpaired electrons

so those unpaired electrons have some important role to play and how we can determine based on this crystal field theory how we can determine the new n values that means the number of n values which will be directly related to the corresponding magnetic moment values

so what we see now that we have five d levels or the d orbitals and we know that in presence of say six ligands their overall energy is elevated and after that from this value which we consider as the e which is before the splitting

so we require something which we consider as the crystal field speeding

so the splitting will be there and that splitting will give rise to a doublet state and a triplet state and these two doublet states and triplet states are separated by say a magnitude of x and the magnitude of y

so if all of them that means the available capacity of all the five d orbitals that means we can have the ten electrons

so before splitting the energy will be 10 e and after spreading we see that these are the two levels which can occupy four electrons

so it will be four into e plus x

so this will be 4 into e plus x plus 6 into e minus y 6 into e minus y

so that basically give rise to 2 x is equivalent to three y

so what is the gap basically we are looking at this gap from the level e what is this gap x and what is that gap y

so this will give you some relationship which is two x is equal to three y after splitting

so on the left hand side we have the before speeding condition and on the right hand side after speeding and these two we all know that this is the crystal field speeding

so this particular crystal field speeding in octahedral geometry which will be delta o

so that delta o will be this and therefore we get the magnitude of x as and the magnitude of y as three fifth of delta o and two fifth of delta o and if this is also equal to sometime we also write that is equivalent to 10 dqo

so will be equal to 6 dqo and will be equal to 4 these are the magnitude of these separations

so what we see that we know that this is the t2g level and this is the eg level

so this t2g level is therefore stabilized by minus four d q o this is the magnitude the y the magnitude of y and the e g level e g level will therefore be destabilized by plus six dqo with respect to the unsplit very centers with respect to this e level

so with respect to this how this splitting can take place that we can find it out now now that the change condition what we find that we have a new electronic configuration

so instead of saying that we have a dn electron configuration that means the number of d electrons in the different levels it can be three d it can be four d or it can be five d levels but now we just try to write in this fashion in an octahedral geometry what are the number in the t two g level and what are the numbers in the e g level

so we will designate over here the number of electrons in the t2g level that means the corresponding level which has a three fold degeneracy and as i told you that g is the corresponding term related to grad a which is equivalent to even and this two is coming from a typical c two operation because all the d orbitals why it is even because all the d orbitals what we see they are corresponding orbitals retain or they keep their sign of their wave function same with respect to the operation inversion

so that is the thing with respect to the inversion which is at the middle and center

so that is also important that how the metal ion is there in the octahedral symmetry

so symmetry is octahedral

so all the orbitals whatever orbitals we are talking about they all follow the thing that they remain ah the inverted form and the sign of those orbitals are maintained and they are of even category or grade category

so these particular information will give rise to some other information to us but we get that the crystal field speeding which can account for magnetic properties in terms of high spin and low spin complexes

so these high spin and low spin complexes what we see here is related to the corresponding occupancy of the level t2g and eg and now if we just define how we can just go to that particular stage that some of the ligands will categorize them as weak field ligands and others are high spin

so weak field ligands are therefore giving rise to the corresponding high spin paramagnetic species that means ligands are not changing the corresponding pairing of the levels with respect to the corresponding crystal field spitting

so we see compared to that we can have another category of ligands which are strong field ligands which will be responsible for low spin or rather diamagnetic systems

so these low spin or diaminetic systems are very important because sometime we find that the medallion electronic configuration is not immediately giving a low spin configuration of zero magnetic moment is typically diamante situation but through oxidation such as cobalt two plus

so cobalt two plus in whatever coordination geometry whether it is a tetrahedral one or a octahedral one is not diamagnetic but once the octahedral species is oxidized for one electron giving rise to the corresponding trivalent cobalt center we get a diamagnetic situation where the cobalt complexes would be diamagnetic

so that will see how it can be applied to a situation where we see that both of them are trivalent cobalt center in the left hand side what we see that the

fluoride ligand
so fluoride ligands which is hexa fluoro covalent three species and on the right hand side hexa cyano cobalt tree species one both of them having charge on the ligands and the both of the complexes are anionic but the situation is such that on the left hand side our compounds are corresponding compounds are paramagnetic because if you have if you have six electrons to distribute for cobalt three plus and this is the t2g set and the upper two are the eg set and since the delta is small
so this is the fluoride ligand we can categorize this fluoride ligand as a weak field ligand
so this fluoride ligand will be a weak field ligand and in terms of the corresponding previous definition for the val from the valence bond fixture what we have seen that co f6 three minus having four unpaired electron in the 3d6 configuration that means all the 6 electrons will be paired up and this can be defined from sp 3 d 2 hybridization
so this s p 3 d 2 type of hybridization will give rise to high spin complexes whereas for c o c n whole six three minus or unpaired electron is zero which is still three d six electronic configuration and the hybridization is d two s v three and is low spin
so these two levels what we are now bringing is not due to the valence bond picture but is due to the crystal field picture because in both these two cases what we have seen that it is three d six and it is also three d six and antenna unless we divide these two into the corresponding t two g set and the e g set we cannot explain the different number of unpaired electrons for these two cases
so that will see here in the case of this high spin and the low spin complexes for the different delta values
so for the left what we see here is the corresponding value for is is less
so the fluoride ligands are weak field ligands
so that give rise to a very small value of delta whereas the cyanide ligands giving rise to the strong field for the metal ion and which having some delta value which is pretty high
so simply just comparing these delta values the magnitude of these delta values after crystal field speeding due to the presence of this ligand we see that the cyanide c n minus will be a stronger ligand or a strong field ligand compared to fluoride
so if we take these two examples like that what we have seen in case of the nickel that water molecules the ammonia molecules and ethylene diamine simply we can talk in terms of the corresponding delta values and these are deltas o that means the delta for the octahedral symmetry
so we can have some leveling for these thing and we just simply write now that instead of 3d six electronic configuration for cobalt three plus in an octahedral field if we have a configuration like this how we can measure the corresponding stabilization due to crystal field speeding which we consider it as the crystal field splitting energy
so we will have number of electrons in the t2g level and some other number of electrons in the eg level and that will now give rise to the corresponding electronic configuration in terms of the crystal field picture
so the net energy of the configuration related to the average energy of the orbital is what we have just now calculated is that minus point four x plus point four six y this we are just calculating it out by two ah two fifth of delta o and three fifth of delta o in respect to the delta zero
so that will give rise to the delta o is ten d q and therefore what we see a situation beyond d 3 because d 1 d 2 d 3 3 electrons will initially be fed into the t 2g level

so there is no such competition for occupying the other level but when we move to the default situation
so the configuration is d4
so when the configuration is d4 in the weak field condition
so this is the statement that means in the weak field condition our delta value is less than p p is nothing but our pairing energy whether this fourth electron when we go beyond d3 whether the fourth electron will come to the t2g level or it will go to the eg level
so there will be a choice
so that choice will be dictated by the amount of splitting whether your delta g zero delta o is applicable compared to p if it is higher than p this electron will come to the lower level otherwise it will be in the easy level
so the weak field situation will give rise to something where we have four number of electrons in these levels three t2g level and one eg level
so all of them will be unpaired
so we get some a situation which is a high spin situation but for the strong field ligand which we just now seen for the cyanide ligand the cyanide group which is binding to the cobalt tree center your delta o is greater than p is greater than the pairing energy
so this delta 0 will be higher
so that is why the fourth electron will come to the t2g level which is t2 g4
so simply this particular information can give rise to some info information related to the electronic configuration
so if we have a d four electronic configuration
so that d four electronic configuration now we can write what we are just telling that it will be t two g three e g one and another one will be t two g four only
so this will be high spin and the other will be low spin and terms in terms of the crystal field stabilization energy if we add up all these things related to the corresponding stabilization of the one level as minus four dq or the ah the corresponding one is two fifth of delta zero this will be minus 3 fifth delta o but in this particular case the e value will be equal to minus 8 by 5 delta o plus t we have to consider this one pairing energy because in the t two g level we have three things
so this the third electron is going on all of them are unpaired but when the fourth electron is coming it will be paired up in the t2g level
so we should consider this particular p value for this energy difference
so these are the two energy differences for the high spin and the low spin configuration and we will see what are the corresponding contributory factors which can dictate us that whether we should have a low spin complex or a high spin complex depending upon the nature of the corresponding ligand available to us
so p is therefore the corresponding pairing energy and when we consider the pairing energy together with the crystal field speeding what we find that it increases as the ligand varies in some order just now what we have seen that c n minus is greater than f minus and previously in case of nickel also we have seen some order
so if we put these ligands these three we have seen this h2o nh3 and en we have seen in case of nickel 2 plus and in terms of the corresponding equilibrium the coordination equilibria we have seen that we can have some order when the nickel is hexaco complex if we add ammonia ammonia molecules will be replacing the water molecules and afterwards if we put ethylene diamine that ethylene diamond will also be able to replace the nh3 groups
so that we have seen in terms of the corresponding coordination equilibria and

that equilibria will tell us that ethylene diamine is a stronger ligand with respect to both water as well as ammonia now we see the magnitudes a little bit we are now quantifying the magnitude of the delta the amount of crystal field speeding

so that energy is basically changing from left to right and we are getting all halides basically four halides if we put then the fluoride is stronger within that particular series of this halide

so iodide bromide chloride and fluoride

so these things are always be there and we will find out somewhere that this particular one will also be considering when we talk about a particular oxidation state of the metal ion if the metal ion center is oxidizing and if we try to bind with the iodide one the iodide ligand and we should also consider the corresponding ability of these centers to remain as the individual form or they are getting oxidized if the metal center is oxidizing

so there will be a tendency to oxidize iodide ions to iodine chloride ions to chlorine

so that will also lead us the elimination of iodine bromine or chlorine instead of typical coordination but when we see that the fluoride is there and definitely the fluoride is little bit stronger within this particular series and the fluorine will not be there that means the any metal ion which are forming the corresponding complexes with fluoride will not be able to oxidize the fluoride ion

so we see that this particular series

so we can put more and more number of uh ligand centers even in your cbse book a huge list of those ligands are there which are commonly encountered by us what we commonly use basically because already we know this the halide groups also these three we have known these are known to us with respect to the binding to the nickel two plus center and just now we have seen the corresponding efficacy of this cyanide with respect to the fluoride ion when we talk about their coordination to the trivalent cobalt center

so this particular series or any extended series is known as spectrochemical series

so from the left to right the ligand strength is increasing because that will lead us to some greater amount of splitting with respect to the delta values for these ligands covering this particular metal ions

so on the left hand side the ligands will have the smaller delta values and the right hand side will have the bigger large delta values

so the left hand ligands are weak field ligands and right hand ligands are strong field ligands

so just now the way we have seen how we place those electrons in the different d orbitals

so after d4 we have a situation where we get 85 situation

so d5 situation the drawing will tell us you see now how we draw this just now we have seen that the delta value is less we get the high spin situation and when the delta values is high we have a low spin situation

so just changing this particular number of electrons

so this is a high spin situation for a d5 electronic configuration

so immediately we should know also that what d5 electronic configuration we know for the corresponding metal ions whether it is chromium or manganese or iron in a particular oxidation state

so whether that particular compound will give rise to a corresponding complex which has a very high magnetic moment or a very low magnetic moment having one unpaired electron only then we have the situation just now what we have seen in case of the cobalt center

so the cobalt which is trivalent cobalt and the trivalent cobalt will therefore definitely be considering in terms of these two situation unlike the d5 situation the d5 situation is that one unpaired electron and five unpaired electron and in case of d6 it is zero one pair electron and four unpaired electrons

so four electron paramagnetism versus a diamagnetic situation

so that is the typical drastic condition change that if we are able to make some compound where we get that means the cobalt we make from a cobalt two salt by adding ammonia and oxidizing it by hydrogen peroxide bar by air giving rise to corresponding hexamine cobalt three complex and that hexamine cobalt three complex is a diamagnetic complex

so just looking at the corresponding magnetic property we see that the splitting is such that it only prefers the corresponding low spin situation where all the six electrons will fulfilling the three t two g level giving rise to a corresponding electronic configuration which will be t two g six then next the d5 7 situation which is also true for cobalt does ion the cobalt two plus ion

so cobalt two plus ion will also have a three electron paramagnetism for the wick field ligand and for the strong field ligand we have one electron paramagnetism

so this is the situation what we basically encounter for making a compound which is initially cobalt two plus like any cobalt two salt like cobalt as chloride or cobalt as nitrate if we take in presence of ammonia is basically getting oxidized by the o2 of air or hydrogen peroxide or any other mild oxidizing engines we do not need any strong oxidizing agent to oxidize that and this unpaired electron which is there if the cobalt center is in the by valence state which will be removed from the system and the system will be oxidized and this typical stabilization and the diamagnetic compound is getting stabilized in that way next is the d8 situation which is very common for bivalent nickel

so in the nickel two plus situation what we find that we do not have any condition where we get that thing that in the on the left also if we even if we go for these two conditions we cannot change the number of unpaired electrons on the left as well as on the right

so this is a situation where we cannot have any condition that we can put that is a low spin condition or the high spin condition

so irrespective of the crystal field will have two unpaired electron for the bivalent nickel

so these two situations are typically different for d5 d6 and d7 but the di d8 system is completely different we cannot distinguish between the high spin and the low spin complexes then we go to the other field which is a typical tetrahedral field

so as we have seen and we just jotted down all these informations for the octahedral field now we know how we draw a particular tetrahedral field within a cube

so this particular tetrahedral field when we draw we have seen that a particular octahedral field or a octahedral crystal field we have to place six ligands around the metal center

so if at the center the red dot is the metal ion we can have the ligands on the six faces of the cube this is one from the front face and this is another one the back face

so we have this particular octahedral complex but what about the tetrahedron one

so tetrahedron one we have to draw again within a cube and we place the same metal ion center at the center of the cube but now we have the ligands

so ligands will be there four ligands will be there at the alternate corners of the cube

so if we just recall back the shape of the different d orbitals we now face that in this particular case the five d orbitals are giving the sets the t two g level and the e g level but the corresponding interaction for these for the tetrahedral field will be different where the e g level will be stabilized and this will be leveled as e and the t2 level will be the destabilized one

so we will have two low energy levels and three high energy levels and g is dropped because this has no center of symmetry or center of inversion with respect to the corresponding crystal field

so this will be the corresponding crystal field splitting when instead of octahedral field when we have a corresponding tetrahedral field ok

so this we see here for the placement of all the orbitals

so these two will be stabilized because these are not facing now directly these green dots are the ligand dots but in this particular case they are more interacting with those orbitals

so this t two set which is d y j d z x and d x y these three will be destabilized

so t two will be higher in energy compared to the e two e set

so this is the situation you see now these the black circles are the alternate corners of the cube and if we consider all the d orbitals available and how they are interacting with each other and more simplistic arrangement is that this is the metal on center and x y z if we consider and these are the approach of the four ligands on the four corners

so this will be the crystal field speeding with respect to the corresponding spherical environment when all the four ligands are coming to split these five levels

so this will be the corresponding levels and likewise our delta o level we have the delta t level for the separation is the total separation is delta t which will be in the reverse order

so it will be stabilized by three fifth delta t and which will be destabilized by two fifth of delta t which is reverse of that of our octahedral geometry

so again we have can have the corresponding electronic configurations from d one to d nine when we place the number of d electrons in these two levels the number of electrons in the e level and the number of electrons in the t two level

so we get the corresponding electronic configuration with respect to the crystal field splitting now the how this magnitude of delta and particularly the more examples we consider for the corresponding delta for the octahedral field how it is dependent on the other factors the first thing what we have just considered is the corresponding nature of the corresponding ligand we have compared that the fluoride as well as the cyanide

so the cyanide ion cn minus is the stronger ligand compared to fluoride

so the electronically how we consider that thing when we encounter two of the compounds where we can have two different oxidation states of the same metal ion

so the middle ion will also change the corresponding magnitude of this delta

so this delta value which we experimentally we can determine by measuring the corresponding electronic spectra because now we have two levels as we i told you that if we have two levels e one and e two for electronic transition and if we move the electron from the lower level to the other level we can experimentally determine the magnitude of that separation between u1 and e2 the same thing we can have with respect to the corresponding hexagon lutheranium two plus

so ruthenium in the by valence state is giving rise to a nineteen thousand eight hundred centimeter inverse separation with respect to the corresponding ah

called ah wavelength that means that it can measure it in terms of the corresponding lambda value in nanometer but if we move it for its corresponding trivalent state you see is changing from nineteen thousand eight hundred to twenty eight thousand six hundred centimeter inverse

so for the same ligand system that means the same hexa echo species our separation is changing with respect to the corresponding oxidation state

so even if you have this and if this is not stabilized this particular species is not stabilized with respect to this ligand then once it is going for the corresponding oxidation you can change this oxidation ah environment oxidized environment by other ligands as i told you in case of cobalt

so covald initially has the hexaco cobalt two plus and which is ultimately oxidized to corresponding cobalt in the trivalent state which is the hexa amine cobalt

so the number of ligands and the geometry as we just see that in octahedral case we have 6 number of ligands and the corresponding geometry is octahedral and in case of tetrahedron the number of ligands surrounding the central metal ion is less

so the corresponding splitting that means delta t will be less than delta o that will be there and is roughly if we consider for same type of ligands for the same metal ions in the same oxidation state we will see that the delta t

so delta t is about 4 9 of the delta o values

so these are very weak

so most of these cases when we see that this corresponding fluoride chloride bromide and iodide species they are coordinating to the metal ion centers they are basically giving rise to the corresponding tetrahedral complexes where there is no such extra stabilization due to the corresponding gain in the cfse values

so the nature of the ligand as i told you that you can expand the corresponding number of ah ligands more and this has been taken from your cbse book of chapter of quartz and compounds where we put iodide bromide chloride and fluoride and in between we are bringing thyroinate as well as sulphide groups also

so the thyroid when binding to the metal center through nitrogen will come in between bromide and chloride and the sulphide which is coordinating through sulphur only which is bigger one and which is little bit soft also which is ah having some strength which is less than fluoride but greater than chloride then we occasionally encountered the all the oxygen donors oxygen donors you see that water is having some greater stabilizing due to the splitting

so the delta value for water will be higher than that of our hydroxide and though we consider that it has charge similarly for the oxalate ion it has charge but the charge is not considering these are the experimental quantities related to the corresponding delta values

so the dipoles the dipole of water molecules will interact and give the corresponding ligand field which will be stronger than oxalate ion and the hydroxide ion and this we already seen that the corresponding one for water ammonia and ethylenediamine edta will be in between and lastly these two things will consider now that why we can place these as the cyanide and the carbonyl complexes that mean the carbon monoxide can also bind to the metal ion in low oxidation state that will see very quickly

so this give rise to the corresponding color thing that means we see that how the crystal field spitting can also explain the color this table is there in your book and how we can read these values also that when we have this compound that the pentamine chloro compound of cobalt two plus

so is a bivalent cobalt

so the wavelength which is absorbed as five thirty five nanometer which is in the range of yellow

so we should remember that the vivjor thing and the vivjor will the color wheel we should remember and we can put the ranges for the corresponding range for the violet indigo blue red etcetera

so this is the color which is absorbed but we see the color of the solution

so the complex color will be violet

so this is the complementary color what we see for the corresponding compound for this complex similarly if we change the chloride ion by water molecule and the oxidation state is also in the trivalent state our value for this absorption is going to a lower energy value that means immediately you can know that one is absorbing at 535 nanometer and the other is absorbing as 500 nanometer what does it mean it is moving to the lower ah values of the wavelength that means is high energy value that means the separation is bigger now the delta value is bigger

so when the delta value is bigger it will absorb in the blue green region and the corresponding color of the compound would be red

so definitely this will be the red and if you go further that means all of them are substituted by ammonia no chance of cl

so cl is weak that's why you can also get the information that cl is weak and force with respect to cl is water is stronger and with respect to water your ammonia is stronger

so now we quantify whatever we have seen earlier that we can replace those

so if we get that if we just have some idea that we can also be able to replace this chloride ion by water and water by the ammonia but it is not

so true for compound where we have something where two different types of ligands and pleasure and more complications are there but simply looking at the molecular formula of these compounds what we see that the energy is changing towards the high energy values that means the lower wavelength values that means your delta values are changing

so it is going to the range where the absorption of the color is blue and we get the corresponding yellow orange compound and the solid compound is also nicely orange in color yellow is orange in color for this compound which is nicely crystalline solid we can get similarly when we compare the fluoride as well as this compound we have compare compared this is a cyano compound

so hexacyno compound which is absorbing you see very close to the corresponding if that is the uv range

so it is 350 is basically the starting point of our visible range

so it is absorbing at 310 nanometer

so this particular splitting is pretty high and that splitting is basically is giving rise to the corresponding range which is uv range that we all know we are just knowing the hydrogen spectrum we are knowing in other chapter the hydrogen spectrum and the separation between the one s orbital and two s orbital of hydrogen is also false in this particular range which is u v range but what about the corresponding delta o values of the octahedral complexes we see most of them are coming in the visible range and this visible range is comparable to the series what we see in case of the hydrogen spectrum is the bomber syringe where we know that the bummer siege all the electrons transitions are taking place from the higher cells to the second cells

so the bomber series energy is comparable to the corresponding crystal field energy for these 3d elements

so this and which is a very paleo almost colorless in case of the copper case we have the corresponding ah this tetrahedral complexes we can also get the octahedral complexes which is absorbing at some longer wavelength

so which is red in color

so again for in respect to copper these water molecules are giving rise to a wick filled environment which is red and the compound is blue and for the

hexagon titanium it is 495 nanometer and which is violet in color and which is also characteristic we can measure this 498 nanometer experimentally that we just see

so a light of wavelength we have to measure with respect to the transition from the e1 to e2 and that transition if we just apply how this transition can take place with respect to corresponding hexa echo titanium compound which is trivalent

so just now what we have seen from your book is telling us that it will have some absorption as 598 nanometer

so a range of light which is in the 500 nanometer which is easy to remember that the 500 nanometer energy is sufficient to promote the electron from one level to the other which is the ground level to the excited level for one electron which is in the t2g level to the eg level

so this transition can take place due to the light absorption of 500 nanometer and we can also measure the corresponding delta value for that transition

so how it looks like we basically measure in one axis it is the corresponding centimeter inverse we have plotted but experimentally in a spectrometer we ah measure in the nanometer scale

so this is the wavelength axis and this is the absorbance axis

so that basically gives rise to the corresponding maximum absorption with respect to 498 nanometer and that 498 nanometer is equivalent to 20 300 centimeter inverse is due to the transition from the corresponding level which we see that the transition is at excite

so it is upper level is the eg

so easy to t2g energy gap or you can consider it as the transition when you move when you promote this electron to the other

so the transition is when we after sometime it will come down

so you can write this transition as also and during absorption what is happens is the absorption spectroscopy optical absorption we are talking

so the during absorption the transition is taking from t to g to a g but after sometime it relaxes from eg to t2g an energy gap in terms of the wavelength which is 498 nanometer in terms of centimeter inverse and in terms of kilojoule per mole also we can have which is 243 kilojoule per mole

so this particular information that when we have a metal ion in solution we see the color and we see the transitions very nicely

so what about the thing which we see for the color of some gemstones which is also there a part a one page basically in your book and you should read it nicely there that when a particular light of visible range can ah strike a particular material which is the precious gemstone it will absorb some color like your solution the solution is absorbing one part of the color and its eliminating or giving rise to the corresponding color which is complementary in nature

so what is ruby

so ruby has a very fine color which is red in color and it absorbs all other wavelengths from the white light spectrum only it is reflecting the red that means it is the complementary color which is coming out from that is red

so that is why ruby is red in color and ruby is nothing but is a gem quality corundum quantum is nothing but our crystalline alumina al2o3 but the color is due to some impurity which we call as the doping

so one percent or less than one percent point five to one percent doping of the chromium three plus on the corundum can give rise to the chromium three plus electronic spectra for the corresponding color what happens now in the solid state all the oxides are your new ligands

so in the solid state we can consider these o2 minus as our new ligands instead

of water or hydroxide ion
so these o2 minus will be now placing around the chromium 3 plus and will just distort the octahedral arrangement which was originally present for the alumina structure because the chromium size is different from the aluminum size
so doping is basically bringing some information to the system and it will slightly alter the corresponding absorption which we do not get for the corresponding hexa ako chromium 3 complex
so the new position of the o2 minus in the distorted form will be responsible for a typical coloration for this ruby gem another one is also sapphire and is the chemical composition of both of them are corundum but they exhibit different colors this is due to the placement of the corresponding one which we get that the composition is different
so primary chemical composition may be same but the corresponding impurities are different
so what is purple in color the sapphire one is purple where we get instead of chromium in ruby we have vanadium and it can come from different shades depending upon the corresponding distortion and sometime you can have some iron also present in this particular thing and you can have the paleolithic green in color
so if both titanium and iron impurities are present together and a correct valence state but what is the oxidation state of the titanium center and what is the corresponding oxidation state of the iron center we will be able to get a deep blue color
so synthetically also in the laboratory we can make nowadays the synthetic gem materials or the gemstones by knowing the corresponding metal ion which we can impregnate and we get the corresponding coloration for all these things
so beryl is another example for emerald is a colorless pure mineral if it is pure only but when chromium impurity like ruby is there it will have a different color
so it manganese is added instead of chromium burial becomes pink and name will be morganite but if iron is present this will be a different color and becomes an aquamarine
so it is blue is in color
so all these things are basically related to the formation of this beryllium in the aluminum cyclosilicate
so what we talk now like your corundum here also we have aluminum at the side but is not in oxide lattice but is a silicate lattice cycle cyclic silicate lattice we have and we try to replace this aluminum by chromium this aluminum by manganese and this aluminum by iron because all are 3d elements
so 3d elements can be useful to substitute this aluminum which is in the octahedral field having comparable size
so the supplier that replacement this mrn will give you a green coloration for this when we have trace amount of chromium and sometime we can have the vanadium also
so this impurity on all these gems will give rise to something which can give rise to the corresponding compounds
so like your valence bond theory the crystal field theory also have some limitation but it can explain many more things which we cannot explain in case of the corresponding valence bond theory
so here we the very basic assumption what we take that we are considering these as point charges but all these ligands whatever ligands we can have that cannot be the point charges
so whatever is this we are talking here in this environment these ligands which we are talking as point charges but is not that if we have a bigger ligand say

if you have a iodide iodide is also not a point charge and if you have a very bigger organic molecule or organic moiety over there
so this will not be a point charge
so this particular problem comes to us when we talk about the corresponding ligand as the carbon monoxide carbon monoxide is a well known ligand and long back it was discovered that we can make some compound during the purification of nickel the solid nickel which is in the atomic state that means the nickel zero when the gas valve contains nickel and the gas cylinder contains carbon monoxide it is getting corroded due to the formation of tetracarbonyl nickel zero compound
so this is the corresponding deposition on the gas cylinder with that valve and that valve will tell us this can form and then in the zero oxidation state
so this is one aspect that how we can tackle a corresponding compound where the nickel is in zero oxidation state another one is the corresponding ligand which is not a point charge
so if we do not consider that point charge
so the typical interaction what we are discussing
so far about the corresponding charges for the positively charged metal ion and the negatively charged ligand that the interaction we are considering as the corresponding interaction is purely electrostatic that means the electrostatic interaction what we see in the rock salt like sodium chloride but that electrostatic interaction is not present what we see here that if we have some ah molecule like carbon monoxide or c n minus another example is also c n minus
so it will have some orbitals
so those orbitals will have some ah lone pair of electrons and this metal ion will also have some orbitals which are having some vacancy or field
so there will be something where we can overlap of the orbitals from the metal ion and the orbitals of the ligand
so this particular picture of the electrostatic interaction only picture is now slowly fading away
so we have to consider some amount of covalent interaction
so that amount of covalent interaction how we can modify in case of a typical complex which is like m l six
so what is that covalent interaction covalent interaction is nothing but the molecular orbital formation what we have seen like that of the same formation of carbon monoxide molecule how a carbon monoxide molecule can form out of that corresponding configuration like this lewis dot structure for the carbon monoxide molecule from the atomic orbitals of carbon and the from the atomic orbitals of oxygen
so what we get at the end we get the corresponding molecular orbitals of m of carbon monoxide now the donor levels or the acceptor levels whatever we have on the ligand now it is your ligand
so this ligand will have certain number of molecular orbitals and those molecular orbitals will now slowly interact with the atomic orbitals of this metal ion but when we have this is also a picture what we will get like the formation of carbon monoxide if m on the left hand side and l on the right hand side
so we can also draw ah some levels which will be your molecular orbital levels like this one will be stabilized and there will be destabilized molecular orbital level for the m l six
so that is the more improved version of the crystal field theory for bonding picture
so we will not be able to consider this as the corresponding point charges for the dipole only case and which does not take into account of the overlap of the

ligand and the metal orbitals
so consequence is that why we can say that the carbon monoxide is the stronger ligand then cyanide we will unable to explain that antenna unless we consider that carbon monoxide is having some interaction with the metal center as in covalent nature
so we go for a ligand field theory where we introduce the concept of molecular orbital picture for this and the valence orbitals will be considered by involving the middle ion orbitals and the ligand orbitals are symmetry adapted linear combination salc is nothing but you remain within the symmetry picture that symmetry adapted linear combinations of those orbital will give rise to the several molecular orbitals and those molecular orbitals will give rise to types of bonding which can be sigma bonding and which can also be pi bonding
so we can where we have the ligand as a single valence orbital directed towards the central of the metal ion and the pi bonding when the ligand has the field orbital of the pi symmetry around the metal ligand axis whether middle is can give you the function as a donor or the ligand can also function as a donor
so this we see for a very good example that the corresponding molecular orbital detail molecular orbital picture which is there in any common book that what we see that these are the levels and instead of writing this that is the carbon which is having higher energy for this two s and two p level compared to this oxygen
so when we have the total number of ten electrons on carbon monoxide we will having the placement of this as the three sigma electron and two pi electrons
so the sigma electrons on ah having some character which is close to the carbon character which will give rise to the corresponding sigma donation
so the homo will have this particular picture and this blue orbital which is on the carbon side this is carbon and this is oxygen
so this will be the donor orbital similarly the lumo basically we can have two lumo two of them are of the pi character
so these two pi character of this
so the lumo of this will be there
so on the ah carbon monoxide side we can have this loma also will be there and available for bonding to the metal ion center or the corresponding metal in the zero oxidation state
so this is typically the sigma donation and that sigma donation will basically give rise to something where the carbon side of this will be bound to the corresponding metal ion just now what we have seen in case of nickel nickel in the zero oxidation state interacting with the carbon monoxide
so we will have four such bonds will be forming
so the nickel carbon bond will be there
so we can have four nickel carbon bonds in tetra carbonyl nickel zero species and if we consider this nickel is in the zero oxidation state
so we can have all the levels filled
so you can have not a 3d 8 situation we can have a 3d 10 situation
so all the levels are filled still some of the orbitals which are higher in energy or some of the molecular orbitals really speaking some of the molecular orbitals will all be available which are high energy acceptor orbitals
so high energy acceptor orbitals will be there which can accept the electron density the sigma donation if we consider from the carbon monoxide to those level for a typical one direction bonding but at the same time since the all the levels are filled on the nickel zero nickel zero if you have the orbitals whether it is a typical ah atomic orbital but we are not considering atomic orbitals now these are the molecular orbitals on metal centered or molecular orbital

so the field orbital electrons ah the orbitals now push the electron density to the empty molecular orbitals on the carbon monoxide
so highest unoccupied molecular orbitals
so the highest unoccupied molecular orbital the homos are available for accepting the electron density from the corresponding metal centers
so this will give you one corresponding sigma donation and this will consider as the pi acceptance
so that is why the carbon monoxide molecules will be considered as the good pi acceptor ligands we classify them pi acceptor ligands and that pi acceptor ligands will give rise to some multiple bonding between the metal and the carbon center and the interaction is pretty strong and that strong interaction is basically responsible for changing the corresponding splitting between the levels and with the splitting in the terms of the corresponding delta values what we are considering for the crystal field theory
so the separation is very high
so on the spectrochemical series thats why the carbon monoxide is on the extreme right hand side
so in the zero oxidation state we can have several such compounds and these compounds are very good examples for the simple carbon monoxide as the ligand for these compounds
so we have the nickel and this nickel is coordinating to those co which is tetrahedral in nature and this tetrahedral cos are there and this basically another co
so this four co will be giving rise to this now the stabilization
so the stabilization we can consider little bit with respect to the effective atomic number what we use for the main group compounds with respect to the 18 electron rule
so 18 electron rule can also be applied to these species such that initially we should know what is the formula
so this is the carbonyl compound unlike your n i c n whole four two minus where this nickel is plus two
so if we count the total number of electron this will be eight and this is giving rise to four into two
so four plus is a sixteen electron species
so it is not eighteen electron species
so but it has some stabilization in a particular geometry because we all know that in a particular geometry is for this is the square planar geometry
so the square planar geometry in this particular environment it has the stabilization but for the zero oxidation state this nickel will have now 10 electron plus the covald ah sorry carbon monoxide is also providing two electrons
so four into two
so is eighteen electron system
so tetracarbon in nickel is a eighteen electron system
so it has a stabilization if we consider not ten instead of ten if we consider that another eighteen electron from the whole series it will be there for the effective atomic number for this will be 16 in that particular case also
so not only nickel tetracarbonyl you can also consider it for the iron iron is having some electron which is there we know that the eight which is atomic number of twenty six
so twenty six that means eight plus two into five ten
so it is also eighteen electron this is also eighteen electron but the situation is that what you can have for this dimeric compound this ah this is also these two dimeric examples which is the corresponding manganese dimer and

the cobalt dimer what is there in your book also
so this is the last slide what i have taken from your book also and you should also some idea about the stabilization
so these are the five carbonyl compounds these are the good example of your corresponding organometallic compound though they have given as the corresponding carbonyl compound where the carbonyl ligand is in the extreme right hand side of the spectrochemical series
so this is 18 electron configuration this has 18 electron and this has also 18 electron configuration this chromium because the chromium having the 6 electron and the 6 carbon monoxide can give rise to six into two twelve electrons
so this is also an another eighteen electron species but what about these manganese basically manganese when we see that manganese we get
so manganese is zero
so that will give rise to a 7 electron to you and then around 5 that means we are not going for a octahedral situation
so we get 5 for that
so that is there
so we get in this fashion
so 5 of them
so five co
so five co
so five into two
so is equal to ten
so all together we are getting a 17 electron species
so this 17 electron species is not stable
so if it can get something where we can have some bonding with another fragment
so this is one part
so left hand part of this if we go for another part like this m n c o whole five
so due to this manganese manganese bonding we have to consider one electron because it is made up of two electrons
so this manganese manganese bonding can contribute another electron
so this will also be eighteen electron
so that basically gives that to the corresponding stable species which is eighteen electron in nature similarly for the species like c o two c o hole eight
so that will also give rise to the corresponding counting and all the time we should have some idea that how many carbon monoxide are there five will be as monorented and no such as the bridging groups and one as the metal metal bonding similarly for the corresponding cobalt system you can have the bridging carbon monoxide because this can also function as a very good bridging group but considering the number of electrons for this particular one we can also consider the bond
so this will also have a ah cobalt cobalt bonds which will consider that extra electron giving rise to a corresponding 18 electron configuration for that species
so all these compounds whether we have the three mononuclear compound nickel iron and chromium but two dinuclear compound the manganese or the cobalt because in this particular case we have the cobalt cobalt bond further you have the corresponding bridging because the number of cobalt centers are less compared to your manganese compound
so this is bridging because the bo all the center because the left hand cobalt center and the right hand cobalt centers are octahedral in nature
so all these five electrons basically are stable and we can have some idea in

relation to the 18 electron rule
so if is something is not known
so f is unknown and your ligand is also tell us that is the carbon monoxide
so how many co we can accommodate around the metal center is easy to decipher easy to identify from applying this 18 electron rule whether it is nickel or iron or chromium or a dimeric species by looking at the 18 electron configuration with respect to all these species and that stability is basically gained out of that and we can have some idea that is not a simple example and you have to memorize everything the logically you have to think that 18 electron configuration is preserved in all these species and the available number of carbon monoxide is there
so definitely if m is covered your carbon monoxide number is eight ok thank you very much you