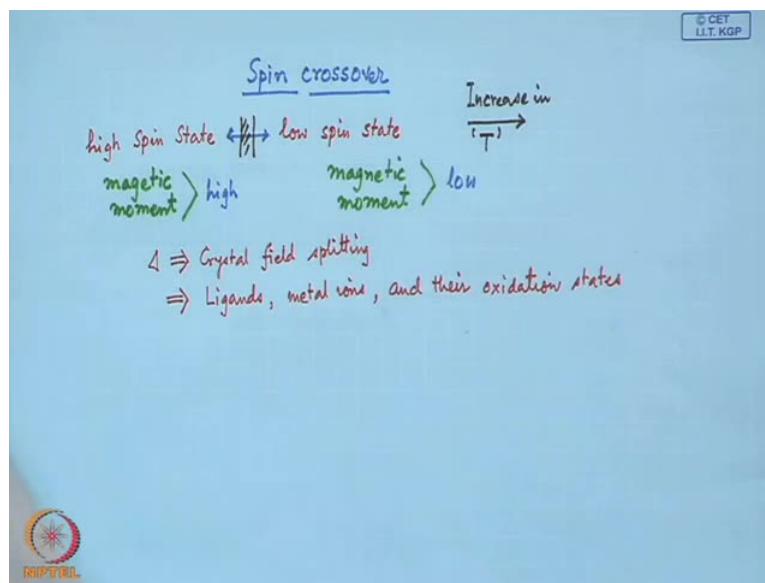


Coordination Chemistry
Prof. Debashis Ray
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Lecture - 20
Spin Crossover and Colour

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Good evening. So, today we will talk about the spin crossover, but we have started our discussion also... So, we have seen that crystal field theory predicts that some of the complexes can be in the high spin state and some more are in low spin state. So, if we try to find out the corresponding magnetic moment, we will see that in this particular case the magnetic moment would be different compared to the low spin state. Here also you can compare the magnetic moment with that of the high spin molecules.

So, high spin states are characterized mostly by large number of free spins, so the determined magnetic moment, what we can determine experimentally would be high also, and in case of low spin state this would be low. So, this particular thing we will interested to know where this particular crossover is taking place, it can be dependent on the crystal field splitting, and also the corresponding different nature of the ligands, that means the ligands as well as the metal ions and their oxidations states.

They all play some important role and do contribute to the system where, we find that at particular region, say in this particular region we do observe the corresponding change

over from a high spin state to a low spin state as we increase the temperature, with the increase in temperature therefore, increase in T value. We will find that the, corresponding spin state will be changing from one particular position to the other and at the same time we will be using the corresponding magnetic moment values for the characterization. So, these compounds when we consider them as the corresponding complexes they are also known as spin crossover complexes or SCO complexes in coordination chemistry or transition metal chemistry.

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Spin Crossover Complexes

Many techniques are available that can be used to detect the SCO phenomena in metal complexes.

X-ray crystal structures can be used to measure the bond distances between the metal and the ligands, which give insight into the spin state of the complex.



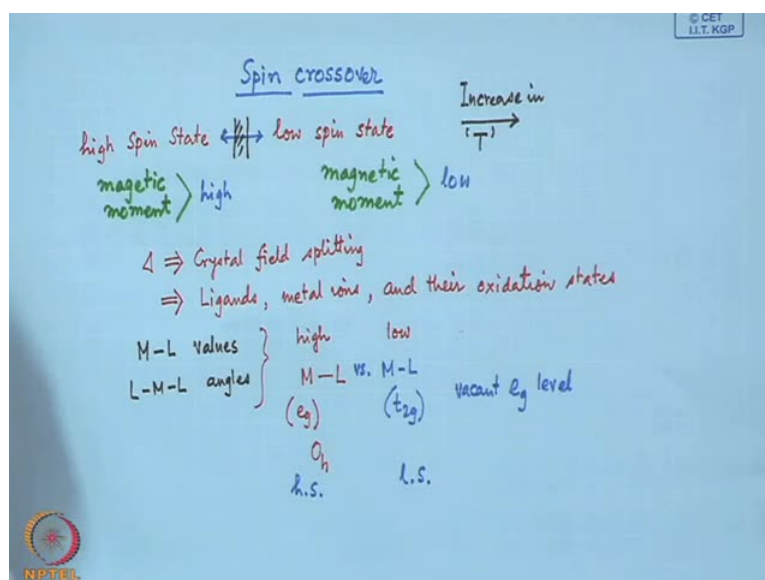
So, we will just little bit, we will just go through some of these techniques, because the basic reason behind the formation of these types of complexes we have discussed. So, what are the techniques basically available which can be useful to detect this particular phenomenon in different transition metal complexes where we have unpaired spins? So, manipulation of the number of unpaired spins for a complex which we designate as the high spin as well as for the complex, where we can designate it as the low spin, how we can detect nicely using some of the physical techniques?

And one such technique is definitely the crystal structure determination because in crystal structure determination, we find that this x-ray crystallographic data, the single crystal x-ray crystallographic data can be useful to find the corresponding bond distances between metal and the Ligands. The spin the M L distances we can find, we can find the

corresponding bond angles as well as other metric parameters related to the corresponding metal complex.

So, once we determine the metal ligand. Distances, it gives insight into the spin state of the complex, that means when we find out precisely the M L values and also the L M L angle from the X-ray crystallographic data, we will see that in some cases these values are high and in some cases they are low. That means when metal ligand distances are high, definitely we have the corresponding metals centre with easy electron configuration.

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The electrons in the easy level can give rise to longer M L bond distance because those orbital's containing the metal ion having the easy electronic configuration, directly facing the ligands along the corresponding cartesian axis in a octahedral geometry say. So, the basic example what we see there that there is a corresponding electronic configuration in octahedral symmetry that, these M L distance should be high similarly, when if it is low the M L bond distance is low. When this, when we compare so they are comparable. So, only we have the electrons in the t 2 g level and vacant e g level. So, the vacant e g level will contract the M L distance and that basically gives rise to the corresponding sort of M L distance, in case of the situation where we get the only electron in the t 2 g level.

So, the electronic configuration in easy level is for the high spin complex and this is for the low spin complex as we all know. So, the access structural data nicely explain the two situation, where we can have the spin compound as well as the low spin compound. So, we can determine the spin state here and the interest for this type of complex is in recent years also because the phenomenon is known for say 60 to 70 years, when first discover. But the recent interest for this spin crossover phenomenon also leads to advanced technological applications such as different types of spin based switches, data storage and optical displays.

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The rapid interest in the SCO phenomenon also leads to advanced technological applications such as switches, data storage and optical displays.

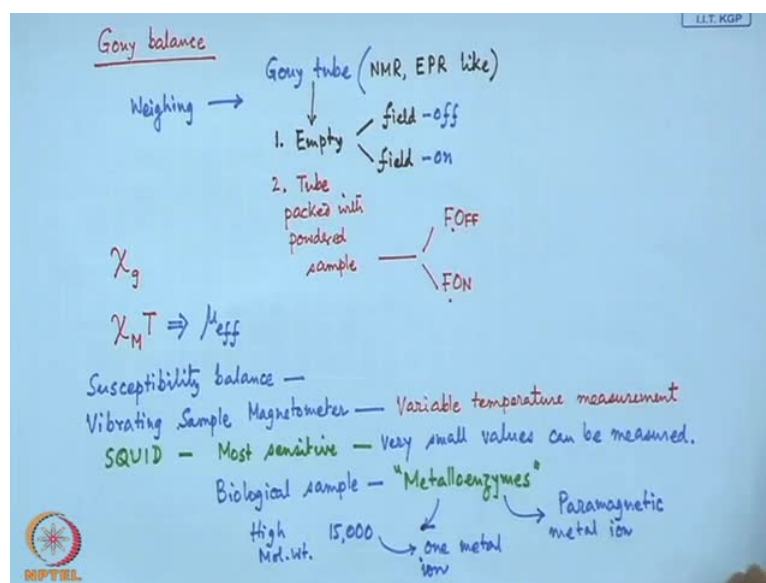
Measurement of the magnetic susceptibility as a function of temperature, (χT), is the principal technique used to characterize the SCO complexes.



So, whether these metal complexes can be useful for all these devices? The devices, the device making things have been utilized for the use of this interesting class of molecules. So, what we have just seeing that we can determine not only the axis structure, but also we have to determine the corresponding magnetic susceptibility. And these magnetic susceptibility always can be very nicely measured in such thing, where will find in detail also when will study the magnetic properties of all the transition complexes or the coordination compounds in detail.

But right now we can see that this magnetic moment where we just determine the corresponding product, that is been susceptibility and the temperature product is utilized as the principal technique to characterized the SCO complexes. So, the susceptibility what we can determine using some Gouy balance.

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So, the home made Gouy balances are there, that was the oldest technique where people can measure the corresponding magnetic moment values. It is nothing but the weighing of the sample, there are several steps over there. We can have a very small Gouy tube, which is very much similar to the tubes, what we use for NMR measurements and EPR measurements . So, this Gouy tube is initially is empty, so for empty Gouy tube we take two weights. So, it is basically a balance, very sensitive balance and will be taking the weight in presence of magnetic field and in absence of magnetic field. So, when the field is on and the field is off.

So, the empty tube in field off situation and field on situation, then in the second step what we can do? We can do that the corresponding tube will be packed with power samples, so power sample of the compound is back. And then again will take these two that means field off situation and field on situation. So, we will have four weights, four different weights and form the difference of all these weights, we judge basically calculate the corresponding susceptibility value. So, we can calculate the corresponding gram susceptibility, then we can multiply with the molecular weight of the compound giving rise to corresponding molar susceptibility.

And when we multiply it with the temperature of the measurement, this particular product that means χ_{MT} , which can be used for the calculation of the corresponding magnetic moment. So, effective magnetic moment can be determined. So, one such

technique is the Gouy balance technique, then we have the the susceptibility balance little bit sophisticated compared to the Gouy balance, then the susceptibility balance, those balances are available. Then we can have the vibrating sample magneto meter, which are also useful, and they are also useful for variable temperature measurements also, variable temperature measurement.

And the most recent one and is highly sophisticated one is the squid magneto meter, which is super conducting quantum interference device. So, the superconducting quantum interference device is the most sensitive one, which can measure nicely the various small magnetic moment values. So, very small values can be measured. Even these technique is so sensitive that we can handle the biological samples, particularly this transition metal bearing or Metalloenzymes, so these Metalloenzymes. So certain of these Metalloenzymes, which can have at the centre the paramagnetic metal ion if paramagnetic metal ion we can have, and that so its corresponding magnetism.

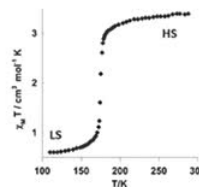
So, how to detect the paramagnetism because this metalloenzymes have several thousand, say 15,000 molecular weight, so 7 kilo Dalton molecular weight it can have, so have high molecular weight with say one metal ion, which is paramagnetic. So, the presence of this one metal ion within this particular huge molecule, huge biological molecule is definitely a difficult task to use as its corresponding measurement for its susceptibility. So, squid squid is well suited for measuring that particular magnetic moment, which is available through some Metalloenzymes.

So, these are the different techniques what we can use for these magnetic moment measurements, so the measurement for this magnetic susceptibility for characterization of spin crossover complex is the most useful one and if we just plot the $\chi M T$ values, which is centimeter square mole inverse k against temperature in Kelvin.

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The rapid interest in the SCO phenomenon also leads to advanced technological applications such as switches, data storage and optical displays.

Measurement of the magnetic susceptibility as a function of temperature, (χT), is the principal technique used to characterize the SCO complexes.



Magnetic susceptibility plot showing a spin transition at 180 K.



Real, Gaspar and Muñoz, *Dalton Trans.*, 2005, 2062.

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So, from 100 to 300 Kelvin, if we plot these susceptibility and temperature product though the product of susceptibility molar susceptibility and temperature this is $\chi M T$, so $\chi M T$ against temperature. So, what we will find that at low temperature this is the axis where magnetic moment can increase, so with rise in temperature the $\chi M T$ values are increasing. So, these are the corresponding data values at particular temperature.

So, as we move from a say 30, 30 or 25 degree Kelvin and as we move upwards, so around 175 k, this value of the magnetic moment is rising very fast and within this particular zone basically. So, it is close to 170 to 180 Kelvin, so 170 to 180 Kelvin the molecule is entirely transforming to a low spin state to a high spin one. So, sudden jump in magnetic moment, say from a value of 1 to 3 is due to the corresponding transformation of the molecule from a low spin state to a high spin state, is clearly seen from this particular plot. It is a very simple plot we can determine even with a use of primitive Guoy balance.

The Gouy balance can be utilized for the determination of the susceptibility parameter and the temperature of the measurement, but only difficulty is that the Gouy balance is cannot be operated nicely at different temperatures. So, at least we should have the corresponding vibrating sample magnetometer, if the squid is not available or any other type of magnetometer which can be utilized for measurement at different temperature

values. So, these different temperature values gives us certain magnetic moment values, relating to the corresponding molar susceptibility at different temperature.

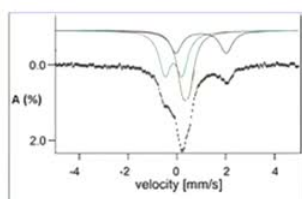
So, as we cross 200 degree Kelvin and after that there is a marginal change in the corresponding moment value, that means the magnetic moment value at the high spin state has been saturated. So, we get these temperature a range basically, is this particular temperature range of 170 to 180 Kelvin is the typical range for the corresponding spin transition. So, this is the corresponding region where we can assume that their spin crossover is taking place between the low spin state and the high spin state. So, this is basically nothing but the magnetic susceptibility plot showing a spin transition and at around 180 k.

So, we have the range that means it is starting from here an ending over here, but the other is this particular point so this particular staircase type for plot is well known for task for the other type of physical measurements, what we find for the (()) symmetric titrations of acid and base and the redox parameter, so we get these type of plots. So, at 180 k, we have the corresponding transition from the low spin to the high spin and this is a very recent work we will have done it in published in Dalton transaction in 2005.

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⁵⁷Fe Mössbauer Spectroscopy

This technique gives the proportion of Fe^{II} and Fe^{III} centers that are in the LS and HS states because the isomer shift and the quadrupole splitting differ significantly for these spin and oxidation states.



Mössbauer spectrum for an iron complex at 300 K. The red, blue and green lines are simulations of contributions of LS Fe^{II}, HS Fe^{II} and LS Fe^{III}, respectively



Dunbar et al. (2007) *J. Am. Chem. Soc.* **129**, 6104.

So, the second technique after the magnetic moment and let us take rather the third technique, will be the Mossbauer spectroscopy. The Mossbauer spectroscopy is very much useful, if we have the corresponding iron compound, that means if we have iron

and whether that particular complex is in the low spin or the high spin, that can be very nicely tackled if we have the monitoring system using the Mossbauer spectrometer. The Mossbauer spectrometer can be utilized for this particular isotope of iron that is ^{57}Fe , which is Mossbauer sensitive and the technique through this measurement gives the proportion of iron 2 and iron 3 centers that are high spin and low spin in states because the isomer shift and the quadrupole splitting differ significantly for these spin, and oxidation states.

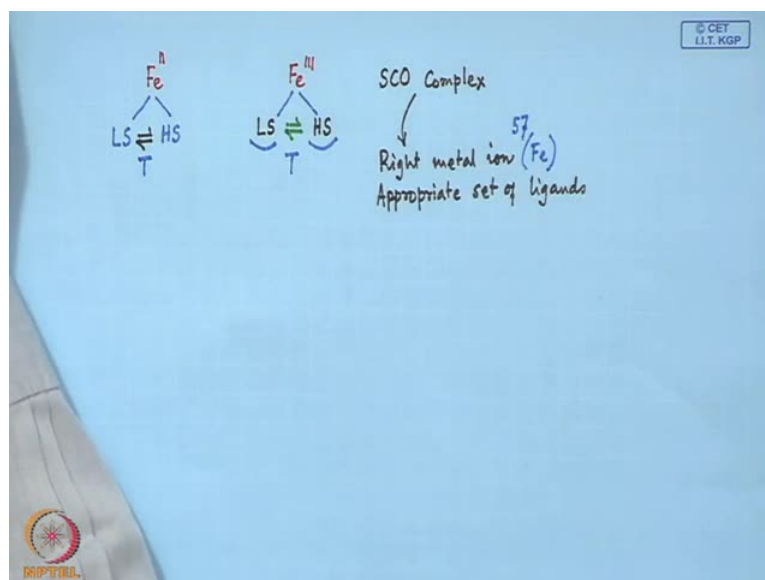
So, both these two oxidation states is a very nice technique, that iron 2 in L S and H S and iron three also in L S and H S can be handled. That means if in a particular compound if we have both iron 2 and iron 3 compound, those two oxidation center as well as the high spin and low spin proportions are present, so we should have the corresponding signature in Mossbauer spectroscopy, that whether all four systems. That means iron 2 low spin or high spin and iron 3 low spin or high spin is present over there. It can be found out because in all four species the corresponding isomer shift and quadrupole splitting, these are the two valuable parameters to judge a particular Mossbauer spectra.

So, these values basically tells us immediately that whether the center is in high spin or the low spin states therefore, this particular spectroscopy is also helpful in identifying the corresponding spin crossover or the spin state equilibrium situation. So, this is the thing where we can get, this is the overall spectrum and these were the corresponding stimulated one. That means we have basically 1, 2, 3 spectra within this particular, overall spectrum. And this is a corresponding Mossbauer spectrum of an iron compound, so this black dotted one and the red and blue and green lines can have the corresponding red, blue and greens these three lines, so we can basically stimulate the entire spectrum for the individual components.

So, one particular component we have the second one this one and the third one also are the simulation of contribution of three species only, not all four species present. So, that means the simulation of the entire spectrum gives us that they spectra what we are getting is basically a mixture of three components and the simulations basically giving us the contributions from low spin iron 2, high spin iron 2 and low spin iron 3, one is missing therefore, that means in this particular case, the high spin iron 3 that means high spin ferric compound is not available.

So, iron compound that particular iron complex at 300 k, which is close to room temperature give rise to the proportions of three different species, that means we cannot control the corresponding oxidation state. That means exclusively we are unable to produce the compound in the ferra state, it can have some ferric component and the ferra state again present in two forms, that means both low spin and high spin, but the ferric form is present only in the low spin form. And this is also another observation in recent years which is published in j of American chemical society in 2007 by Kim Dunbaret and his group. And two other examples, what we can see that right now we see that, the Mossbauer spectra can give rise to the corresponding environment for iron 2 and 3 in both high spin and low spin form.

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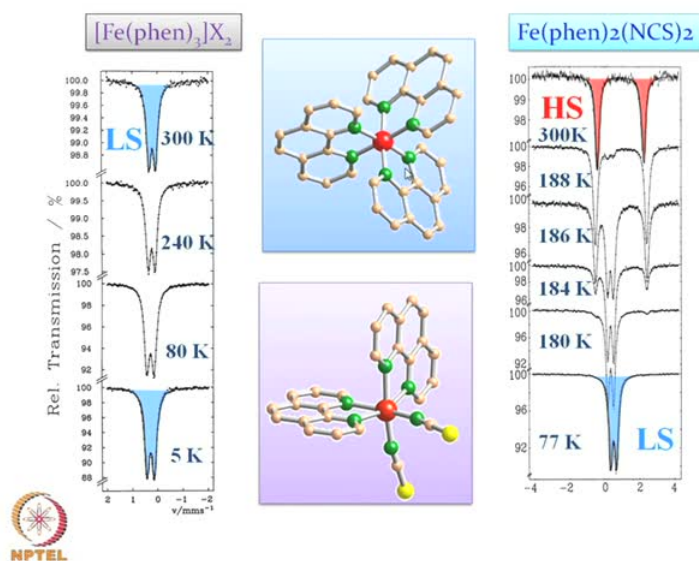


So, this spectroscopy is basically can be utilized to identify these two oxidation states, in several of the compounds and if the spin state equilibrium is present, we will see that some equilibrium is operating between the high spin state and the low spin state. Similarly, for the ferric state also we can have the low spin state and high spin state and these two states can be in equilibrium at the same time. So, the basic proposition what we are dealing with in the original assumptions for the spin crossover complex say, that one particular spin crossover complex we can have, provided we choose the right metal ion and the appropriate set of Ligands of ligands.

These two things basically tells us that, this particular metal ion in these Ligand environment can have the corresponding chance is to provide both high spin and low spin compounds, which is controlled by that corresponding temperature variation. So, the right metal ion luckily when we are talking about the corresponding Mossbauer spectroscopy, we are lucky enough to take the corresponding iron center as its Mossbauer spectra. We will be talking about the 57 iron species. So, 57 iron isotope can give rise to these signatures, for these two different types of splitting for isomer shift and the corresponding quadruple splitting.

So, when we measure that how far it is going from the central position, that basically tells us about the corresponding isomer shift and one particular spectra how the corresponding signature is being spitted into a doublet or so that will give rise to corresponding quadruple splitting.

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So, we just simply take the tris phenanthroline compound, so is a very useful compound we will find this, use this compound in the corresponding optical spectroscopy also. Three phenanthroline ligands when attached to the iron site in the ferric state, we get the compound like this. So, we have the octahedral center and this octahedral center is nicely providing us the corresponding tris chelate and it is in the ferric state, so two of these x groups it can be chloride, it can be bromide or it can be iodide depending upon the compound isolation technique, we will just you can have three different salts from there.

So, is the dicationic compound is obtained as its corresponding salt and these anions have some profound effect due to the crystal field packing for their high spin and low spin states. Similarly, one other compound we can have, where one of the ligand can be replaced by two thianthrene groups, because these thianthrene groups give rise to a different crystal field parameter to the iron site and that the change in this particular thing can be comparable, whether that particular phenanthroline substitution. That means we are substituting one phenanthroline by two thianthrene group, and these orthophenone groups are organic nitrogen bearing groups.

So, these are also nitrogen donors to the iron site and two of these nitrogen sites of the one phenanthroline ring is changed or it substituted by two thianthrene nitrogen, which are purely inorganic in nature. So, the nature of the nitrogen environment compared to the phenanthroline can be compared when I moved to the other compound and we can have the particular type of transition at a different temperature. So, the other molecule will look like this. So, we just have not substitute these two groups. So, these two groups are still there and we are having only the corresponding NCS and NCS binding. So, the environment around iron is still six, this is also six.

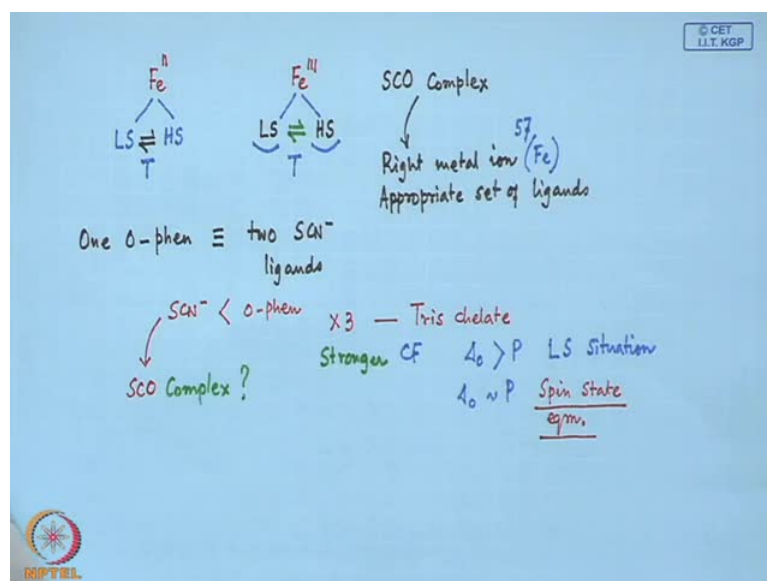
What already we have seen from the spectrochemical series, that the position of the thianthrene groups are different compared to the phenanthroline, because the phenanthroline ligands are stronger compared to the thianthrene ligand, so we are providing some little bit weaker crystal field parameter around this particular iron again in the ferric state. So, what basically we will see that in case of the trisacetyl, we have the corresponding Mossbauer parameters or the Mossbauer splitting, in their corresponding spectroscopy.

We find that as we move from 5 Kelvin to 300 Kelvin, we do not see that the values are changing the relative transmission is changing, but the corresponding splitting is not changing much, it is almost same. That this with change in temperature, we are not getting any kind of transition from 5 K to 300 K for this particular compound. So, whatever environment we can have provided by the phenanthroline ligands, the three such phenanthroline ligands are providing a strong crystal field. So, a strong crystal field is being provided to iron center and that center is therefore, low spin in nature.

So, the crystal field strain that means the Δ value the Δ_0 is basically dictating the corresponding spin state, and we are not close to the corresponding equilibrium situation

or the crossover region, where we expect that with rise in temperature our spin state can change from one spin state to other spin state and it remains in the low spin state only. So, what about the corresponding thycanet species? We will find that here the expected thing is operating, that as we reduced the corresponding crystal field strength by substituting the corresponding phenanthrolin.

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So, orthrophenanthrolin, one orthrophenanthrolin is being changed with two SCN minus ligand . s and in the spectro chemical series we all know that SCN minus is less than orthrophenonthrolin in spectro chemical series. So, this will exert stronger crystal field compared to thycanet. So, to get this spin crossover complex our original idea is that, how we get the corresponding spin crossover complex? How to get that?

So, when the ligand is strong enough such as phenonthrolin and when we are providing three in that tris chelate, so incase of tris chelate we have three orthrophenon together. That means we have the corresponding stronger crystal field. So, we have the stronger crystal field and in this stronger crystal field we have the corresponding delta octahedral, which is greater than P and will end up with low spin situation. But when we go for the thrycanate compound we are compromising that means, we are trying to reduce the corresponding crystal field strength and as we reduce the corresponding crystal field strength, our expectations should be there also with two substitutions of the fascinate by one phenonthroline, that our delta octahedral would be comparable to P.

So, that is the expected condition, expected situation where we can have the corresponding spin state equilibrium. So, once we get this spin state equilibrium for this particular situation, so once we know that definitely only the low spin compounds are forming so we can go on reducing the corresponding strength of the corresponding crystal field, such that we at one point have high spin compound. So, at 77 k which is liquid nitrogen temperature because this 5 k for this particular compound is closed to liquid helium temperature, which is 4 Kelvin and this can be measured nicely at liquid nitrogen temperature and this liquid nitrogen temperature gives the corresponding measurement at 77 k and we have almost two lines.

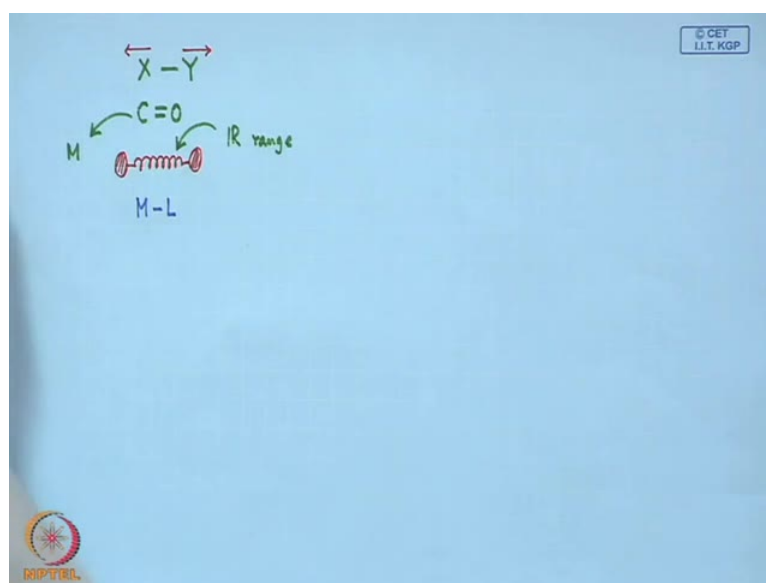
And as we move up we get at 180 k, the values are this this particular splitting is increasing. At 184 k we have 1, 2, 3, 4 all four signatures that present. Similarly, for 186 also, this is range what we have seen in one other previous examples. That around 185 Kelvin the corresponding transition is taking place from low spin to high spin. So, the magnetic susceptibility data what you have seen earlier in one other example this similarly, applicable for Mossbauer spectroscopy data as well. And when we have exclusively the low spin situation we have the splitting like this, but as we move up we go for further splitting and the signature for the high spin is also coming.

That means at this temperature range we have both high spin as well as low spin molecules. So, the molecules were entirely low spin at low temperature at liquid nitrogen temperature. As we rise the temperature, so some of the low spin molecules are transforming to high spin and they are in a dynamic equilibrium, that is why we are getting the signature for the four lines in the Mossbauer spectra, two for the low spin species and two for the high spin species.

And as we move upward and when we reach around 2, 300 k, that means a room temperature, exclusively reaching at room temperature the corresponding the spectrum is for the corresponding ferrous iron in high spin state. So, we have the different splitting and separation for these two lines which can be characterized for the high spin state of the molecule and which has been achieved at 300 k. So, that is why this spectroscopic data, Mossbauer spectroscopic data are nicely explaining the corresponding data or the corresponding explanation, what we get for the magnetic through the magnetic measurements.

So, those magnetic moment measurements are not so clearly seen that which particular point, we have the corresponding transitions and whether the situation is an equilibrium. But here we say that all the four lines and the corresponding equilibrium between the low spin and the high spin states are present in this particular temperature range. So, next we will just see another spectroscopic technique, which is very much similar to the infrared stretching frequencies, which is Raman spectroscopy. So, how Raman spectroscopy can be useful, for determining some of these useful compounds in the high spin and low spin state.

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So, whenever we have a covalent bond or the coordinate bond such as X and Y are bound together, it can be for simple molecule like carbon monoxide also. Then we will find that this particular one fixed with this covalent bond and they are vibrating along the bond axis. So, we have two balls basically, these balls are X and Y and they are connected through a spring which is the corresponding bond, so corresponding stretching frequency as we gives the radiation in the higher range. The higher frequencies are useful and can be absorbed by this particular bond stretching for the atoms which are connected together.

So, similar thing is also can be obtained if we have either this particular molecule serving as a ligand bond to metal system, so this can be a ligand which can be bound to metal center or there are some other cases where we can have the corresponding stretching

frequency between the metal and the ligand. And Raman spectroscopy is another technique close the related to the FTIR further infinite spectroscopy where we can monitor the corresponding M L bond distances, where we sub seen that M L bond distance are changing at as we move from high spin to the low spin state.

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Raman Spectroscopy

Due to the change in the M-L bond distance between the HS and LS state, the vibrational modes of the M-L are going to be affected.

Raman spectroscopy can be used to identify the spin state which is predominant in a SCO complex.

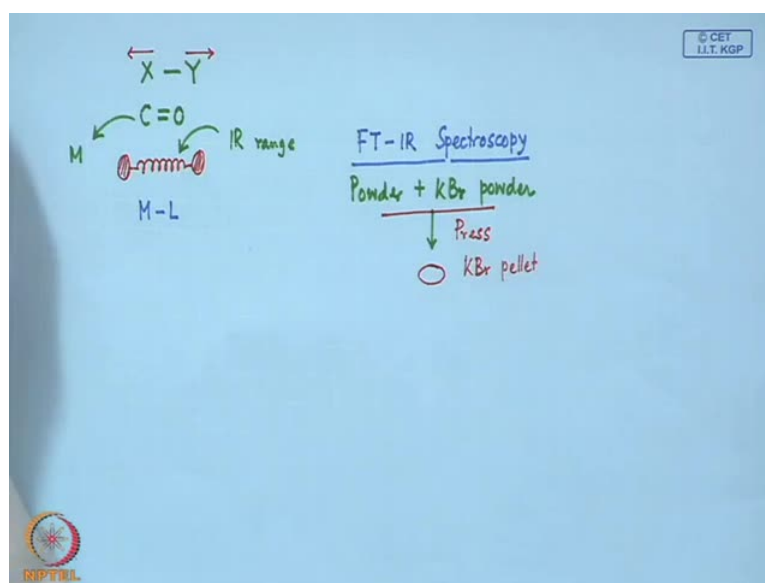
The spin crossover phenomenon is very sensitive to grinding, milling and pressure but Raman spectroscopy has the advantage that the sample does not require further preparation.



And the vibrational mode which is associated with the M L bond is definitely be affected or changed as we move from the high spin state to the low spin state. So, this particular simple assumption is useful to tackle this particular complex situation for the spin crossover complexes by using the Raman spectroscopy's. So, it can therefore, be used to identify the spin state that which particular spin state is dominating in a SCO complex. So, whether at a particular temperature it is the low spin complex, which is exclusively present in absence any high spin species or as we increase the temperature the situation is changing more, and more low spin complexes are getting changed to the high spin one.

And we are ending up close to the room temperature with all the molecules transform from the low spin form to the high spin form. So, this spin crossover phenomenon is very sensitive where we see that incase of I R, we have to go for the corresponding sample preparation.

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So, FTIR spectroscopy is particularly useful when the sample can support the corresponding powdering or the milling or the grinding with K B r because here in FTIR, we take the powder sample mix with some specific amount of, what I am saying? Bromide powder and we mix it in modern vessel and then we go for the corresponding press and we make a dick shaped K B r pellet. So, this K B r pellet, so this K B r pellet is formed and this particular pellet is basically being inserted to the machine to record the corresponding FTIR spectra.

So, our sample for knowing these things, that means the grinding with k v r powder and then corresponding placing it in the corresponding ham place, so it is within the press. So, we go for placing this particular material and such that we get a nice K B r pellet and this K B r pellet is then inserted in the machine. So, if our sample is not rawest, not very much strong to support this particular processes for recording FTIR spectrum, is not suited for measuring the corresponding spin transition and the spin crossover phenomenon. As a result we use only the Raman spectroscopy because in this spectroscopy we there is no need for making this K B r pellet because is the very sensitive one with respect to that.

So, the spin crossover phenomenon is very sensitive to grinding milling and pressure, so we grand with K B r during FTIR measurement when we go for the milling and the pressure. So, during this processes our compound might change from one particular spin

state to the other, but the advantage of Raman spectroscopy is that such sample preparation is not required, what we use for FTIR sample preparation. So, thus whatever sample we have for the measurement does not require further preparation like grinding milling and pressurization in the press, to get the corresponding K B r pellet.

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Raman Spectroscopy

Due to the change in the M-L bond distance between the HS and LS state, the vibrational modes of the M-L are going to be affected.

Raman spectroscopy can be used to identify the spin state which is predominant in a SCO complex.

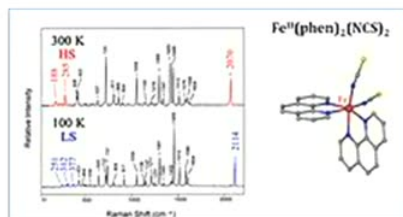
The spin crossover phenomenon is very sensitive to grinding, milling and pressure but Raman spectroscopy has the advantage that the sample does not require further preparation.

Highly colored samples may affect the measurements however.



So, the Raman spectroscopy is a very safe one to measure the corresponding frequencies for SCO complexes, but some of the highly coloured samples may affect the measurements, because the colour samples cannot be handled nicely in this particular spectroscopy.

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So, what we see that the sen, thyaneto compound two phenonthrolin, two thyanet is there in the sis position, two thyanet groups are present. And we can have the corresponding frequencies, the figure is not very much clear. But what we see that we are basically going for some of these frequencies, some of these stretching frequencies for this bond basically iron nitrogen, iron nitrogen from thyanet and within the thyanet also because what we have seen here for carbon monoxide, this is also true for NCS.

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The handwritten notes describe the preparation and IR analysis of a thiocyanate complex. At the top, a general bond $\text{X}-\text{Y}$ is shown with a double-headed arrow. Below, a metal-ligand bond $\text{M}-\text{L}$ is shown with a green arrow pointing to a $\text{C}=\text{O}$ group, which is associated with an IR range. The notes then show the reaction of KSCN or NH_4SCN with a ligand to form $\text{N}-\text{C}=\text{S}$. The resulting complex is $\text{Fe}-\text{N}-\text{C}=\text{S}$, where the $\text{C}=\text{N}$ and $\text{C}-\text{S}$ bonds are highlighted. A note states that the IR frequencies for these bonds will change. The preparation procedure is outlined as: Powder + KBr powder → Press → KBr pellet. The final complex is shown with checkmarks for LS and HS states. A small box in the top right corner reads '© CET I.I.T. KGP'.



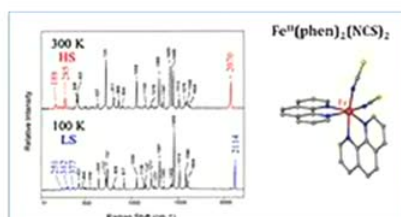
So, NCS is a thyanet anion binding towards iron, we can have the corresponding stretching frequencies for C double bond or triple bond N, as well as stretching frequency for CS. So these are the two characteristic stretching frequencies present. If we can monitor these two nicely in the parent salt, that means it can be potassium thyanet or ammonium thyanet. So, for these two values are known, when it is not bound to iron center, but when it is bound to iron center we can compare these stretching frequencies. That means this C N stretching frequency as well as C S stretching frequency will change due to coordination.

And how much it is changing, that will again depend on whether we have a low spin compound or a high spin compound. So, for low spin compound where thyanets are bound to the iron site we have the corresponding or rather characteristic stretching frequencies for this particular spin state. Similarly, the other values that we are getting for the HS complex will also be characteristic for the high spin compound. So, what are we taking? We are taking the Raman spectrum at 100 K and at 300 K. So, at 100 K the corresponding signatures, what we are getting over there particularly this particular value at 2, 1, 1, 4 due to the corresponding C N stretching frequency of the thyanet, which is characteristic for the low spin compound.

And that value signifies that at 100 Kelvin, we have the compound exclusively in the low spin state that means the LS form can be generated at 100, 100 Kelvin and as we go up and we have seen that around 185 Kelvin, the spin transition is taking place from the low spin to the high spin and there basically we get this corresponding signatures for the high spin signals. So, high spin signals appear because the number of electrons occupying the different d levels are different, in case of this particular iron center also. As we move for the high spin so easy level are getting occupied so the interaction with that easy level electron to that of our NCS ligands are different and the stretching frequency that means the electron is being pushed.

Some of the electronic charge is being pushed to the orbitals of the thyanet groups and those electrons basically can modify the corresponding stretching frequencies of these thyanet groups. And this particular stretching frequency is going downward from 2, 1, 3, 4 to 2070, so that downward movement of these particular stretching frequencies signifies that, we have a high spin situation for this particular molecule.

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Fe^{II} complex in the HS and LS state, a shift from 2114 cm^{-1} to 2070 cm^{-1} corresponds to changes in the stretching vibrational modes of the thiocyanate ligand from a LS state to a HS state, respectively.



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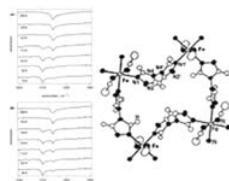
So, whatever high spin iron 2 complex we have, we can have high spin and low spin state and a shift from 2114 centimeter inverse this is 2114 to 2070 centimeter inverse the upper one the red one corresponds to the changes in the switching vibrational mode of the thycanet ligand from a low spin state to high spin state respectively. So, that gives us the clear indication that as we move from a high spin situation to a low spin situation, the corresponding iron thycaneto stretching frequencies are rather the corresponding C N and C S combined stretching frequencies are changing. And this is very much characterized for the C N stretching frequency within the thycanet group and is changing from 2114 centimeter inverse to 2070 centimeters that is the lower value for the movement from a low spin to a high spin state.

So, like magnetic moment like Mossbauer spectroscopy, Raman spectroscopy also supporting and Raman spectroscopy is also very much significant in identifying the corresponding spin state change from the low spin to a high spin situation.

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Fourier Transform Infrared Spectroscopy (FT-IR)

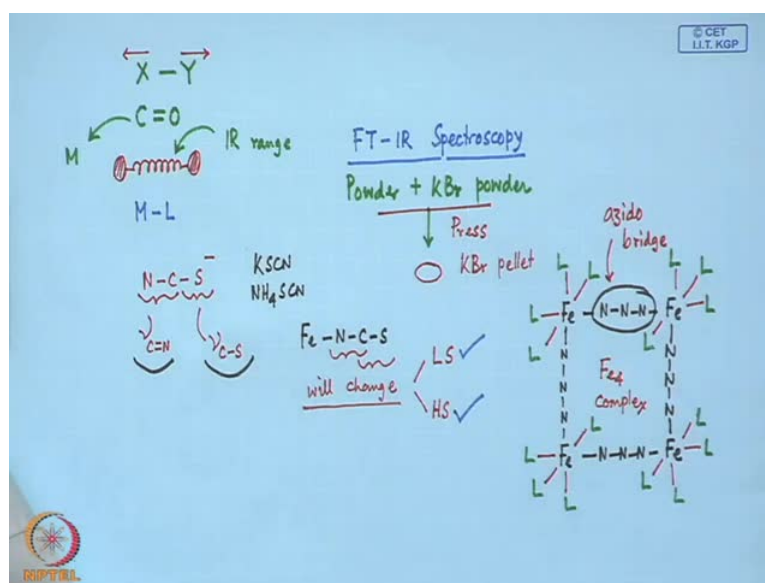
Transitions from a HS to a LS state cause a decrease in the M-L bond distances.



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Similarly, the other one though the particular technique requires the corresponding mesing, milling and grinding, but FTIR technique is also useful like Raman because Raman, what we just told you that is a complimentary technique, so this can also monitor the corresponding transition from high spin to low spin or the visa versa. So, if we have a well connected tetra nuclear system, where four iron centers are present, these at four corners tetra nuclear species. And in this tetra nuclear species some bridging groups are present. So, this is basically the bridging unit, so we have four bridging unit. So, it is a basically a rectangular set molecule and that rectangular set molecule, this particular iron center is breezed by this group and is also breezed by other group. So, how we get this things because this is a very simple practice where we have iron thycanet groups.

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If we can go from iron thycanet to some iron iron azide function. Azide is nitrogen triple bonded system, which can reach the second iron center. Similarly on the others axis if we can have the second iron and on the other corner we have fourth iron, so this will also be connected by another azide group. So, this entry unit is known as the corresponding azido bridge. So, when we have this particular connectivity for a F e 4 complex, we can have other free positions. So, four other free positions we can have and there we just basically place the monodentate ligands. So, all different monodented ligands can be placed over there, so giving rise to a very nice F e four complex. So, that is the situation over here and if we measure and if we monitor the corresponding signal corresponding to the high spin, and low spin compound and there will be change from a high spin to a low spin situation.

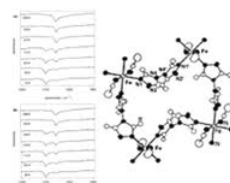
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Fourier Transform Infrared Spectroscopy (FT-IR)

Transitions from a HS to a LS state cause a decrease in the M-L bond distances.

As the temperature decreases, the Fe-N bond distance decreases. Therefore the CN stretching band shifts to higher frequencies.

In the HS state, the CN stretching band at 2054 cm^{-1} is predominant at higher temperatures.



IR absorption of the CN stretching vibration of $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ at different temperatures in the cooling mode (a) and heating mode (b).



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So, here the cyanide groups are attached to this particular iron sites. So, C N can be monitored this particular form the thyanet groups. So, this C N stretching vibration of $[\text{Fe}(\text{btr})_2(\text{NCS})_2] \cdot \text{H}_2\text{O}$ is the another Ligand. set, but of similar type what we have seen for phenanthroline. And water is the water of crystallization at different temperatures in the cooling mode and the heating mode. So, as we go for cooling and we come back again through the heating mode, basically give rise to the corresponding change in the Fe N and the corresponding C N stretching bands, which is shifting from the change from one spin state to the other spin state.

So the high spin state the C N stretching band has 2054 cm^{-1} is predominant at higher temperatures. So, just now we have seen that how we monitored as the temperature variation here, also the heating mode and the cooling mode can be monitored for monitoring the corresponding stretching frequency for the high spin state, as well as for the low spin state.

Thank you very much.