Coordination Chemistry
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Lecture - 19
Jahn-Teller Effect

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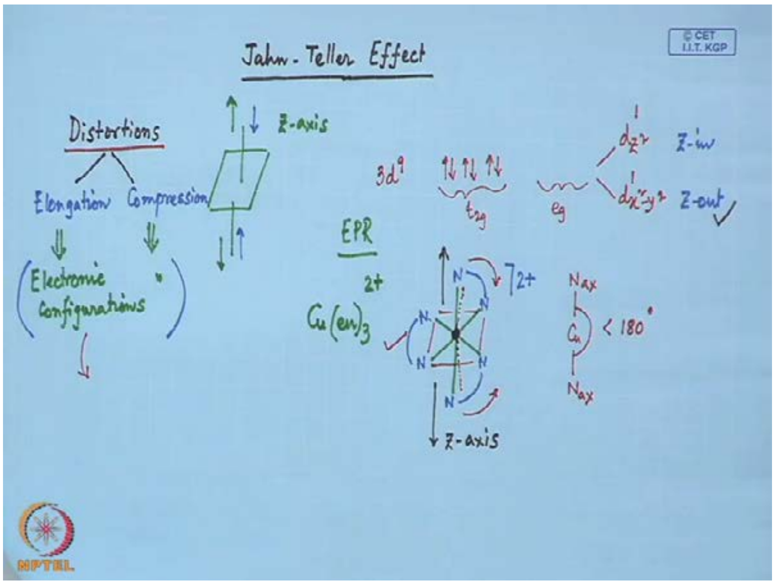

Good evening, everybody. Today, we will talk about some other type of distortion, which we will consider as Jahn-Teller effect. For the two types of distortions, what we have seen so far, which are basically tetragonal type; and if we consider in an octahedral geometry that considering the z-axis, which is either elongated or compressed. So, we will have elongation as well as compression. So, in these two cases, what we see that depending upon the amount of distortion in a particular direction that means the z axis, if we have elongation as well as the compression in another case, we will definitely get different electronic configurations here also, the electronic configurations for both these two cases would be different. And this basically results from a corresponding distortion over there. So, this Jahn-Teller effect, what we will see that depending upon the electronic configuration for some systems say d 4 or d 5 system, we will get a lower energy situation, where the distortion is automatically coming into the system or the molecule or the ion.

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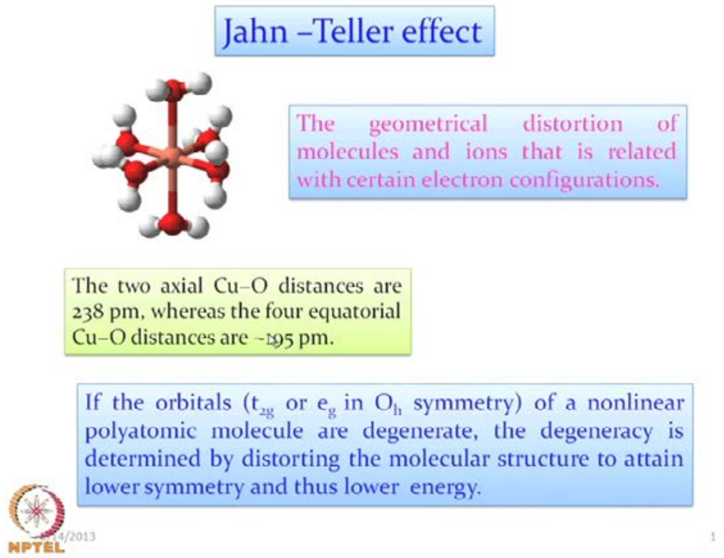

Jahn –Teller effect

The geometrical distortion of molecules and ions that is related with certain electron configurations.

The two axial Cu–O distances are 238 pm, whereas the four equatorial Cu–O distances are ~195 pm.

If the orbitals (t_{2g} or e_g in O_h symmetry) of a nonlinear polyatomic molecule are degenerate, the degeneracy is determined by distorting the molecular structure to attain lower symmetry and thus lower energy.

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What we see that in this particular Jahn-Teller effect, the geometrical distortion of molecules or ions, that is related with certain electronic configurations. So, if we now focus our attention on the electronic configurations; and those electronic configurations would be related to the reverse one, that means, the distortions. So, how the different electronic configurations, which are known as the corresponding electronic configurations, which would be Jahn-Teller sensitive. So, Jahn-teller sensitive electronic configurations will give rise to certain amount of distortion within the molecules. So, we get certain elongated or compressed situation for this effect. So, we have in octahedral symmetry, what we have seen that, we can have the t 2 g and e g set of orbitals. They are splitted already in a particular octahedral symmetry.

So, if they are present in non-linear polyatomic molecule and if they are degenerate; that means, within the t 2 g set, we have the d x y, d x z and d y z orbitals; and in the e g set, we have the d x square minus y square and d z square orbitals; that means, one is the triplet state; another is the doublet one. And here three orbitals are degenerate. And in this particular case, we have two orbitals, which are degenerate. So, the degeneracy is determined by distorting the molecular structure to attend low symmetry or thus low energy situation. So, this distortion will cause or will just lift this particular degeneracy; that means, they will no longer be degenerate; that means, t 2 g set will have further splitting and the e g set will have further splitting. And unequal occupancy of those splitted levels will give rise to a low energy situation. And as a result, we have the splitting. And the splitting we know that, originating from the lower symmetry from the octahedral symmetry.

If we have a corresponding hexaaquacopper ion, because we are talking this in terms of the corresponding 3 d 9 ion; and the 3 d 9 system is gentle and sensitive. So, when we have a typical octahedral geometry, because we are not restricting anything, only the 6 water molecules are surrounding the copper 2 ion. But in this particular situation, we will find that the molecule, which is non-linear polyatomic molecule and the 2 degenerate sets: the t 2 g set and e g set will undergo corresponding splitting. And as a result, we have a corresponding elongated situation – the figure – the molecular structure of this system tells us that, along the z-axis, we have two longer copper oxygen bonds compared to the equatorial four copper oxygen bonds. Therefore, we have the two axial copper oxygen distances, which are 2.38 angstrom; that means, these are comparatively longer corresponding to the four equatorial one. These four equatorial copper oxygen distances are in the range of 1.95 angstrom. Therefore, we have a tetragonally elongated situation due to unequal occupancy of the e g level. So, we have two electrons in one particular level and one electron in the other level. So, that is why it gives rise to the corresponding elongated situation.

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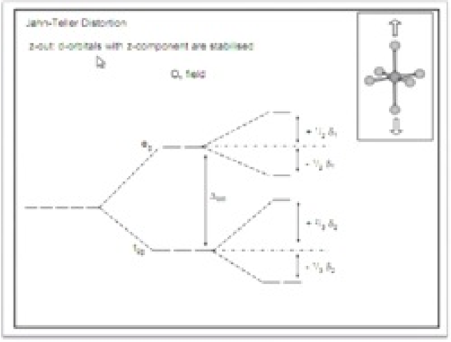

Jahn-Teller Distortion

z-out: d-orbitals with z-component are stabilised

O_h field

We have this since the elongation. This is the elongation axis along the z-axis. So, it is basically compared to the octahedral situation, is the z-out situation. So, d-orbitals with z component are stabilized. Since we have the longer distance of copper oxygen for this, we get the corresponding situation, where we have the corresponding splitting basically; that means these two levels: one orbital and the other orbital. So, this z-out, which the z component is stabilized; that means this is d z square orbital and this is d x square minus y square. So, in that particular situation, in the lower end also, we have two orbitals in the lower end, where we have the z component; that means, the x z and y z; that means, x z and y z orbitals are stabilized since they have the z components and since we are doing something, where z component is to be stabilized.

And, this is therefore, the x y. So, the amount of stabilization for this particular electronic configuration for copper 2 plus is due to the corresponding occupancy for two electrons in these two levels and one electron in this particular level. So, unequal occupancy in the e g level, which are not half filled or full filled, which is partially filled. So, we will give rise to the corresponding stabilization of minus half delta 1. So, this particular one, which is facing the ligands directly will have higher amount of splitting. That is why the corresponding splitting is delta 1. So, this is delta 1 splitting and this is delta 2 splitting. And we call this splitting from the t 2 g and e g set in an octahedral geometry is due to the corresponding Jahn-Teller distortion.

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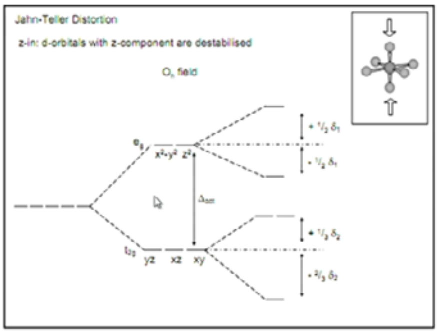

Jahn-Teller Distortion

z-in: d-orbitals with z-component are destabilised

This distortion further gives rise to the other situation; that means, where we have the tetragonally compressed situation, where the z-component had destabilized; which is very much similar to that, what we have observed in case of the corresponding tetragonally elongated and tetragonally compressed situation. So, this is basically equivalent to the tetragonally compressed situation, where these two orbitals, the z component would be destabilized; that means, this will be the z d z square orbital and this is the d x square minus y square orbital. So, we can have when we have the 3 d 9 electronic configuration; what we see that, we have the four levels; that means, the t 2 g level, which are filled; and after splitting also, they all are filled; and in the e g set, we can have two situations; that means whether it is one electron in the d z square level and one electron in the d x square minus y square level.

These are the two situations, where z component is stabilized. Basically, z is the lower energy. So, d x square minus y square is the higher energy. So, d x square minus y square 1 configuration would be for z-out situation. So, this is for z-out situation and this is for z-in situation; and which is very much similar to that of the corresponding tetragonally elongated and tetragonally compressed octahedral distortions. So, in this particular case also, the occupancy in the z square level and the occupancy in the x square minus y square level further can also be clarified if we go for the corresponding spectroscopic technique. So, electron paramagnetic resonance is one such technique, where we can measure the corresponding electronic paramagnetic resonance spectrum for the copper ion. So, in these two cases, we can have two different types of spectrum for clear identification of the situation, where the electronic configuration is d z square 1 or d x square minus y square 1. So, this is basically the corresponding one for the compressed situation.

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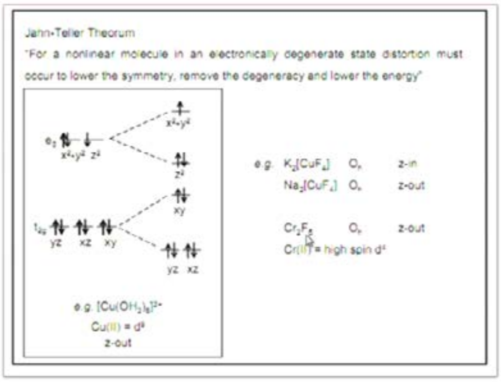

Jahn-Teller Theorum

"For a nonlinear molecule in an electronically degenerate state distortion must occur to lower the symmetry, remove the degeneracy and lower the energy"

e.g. $[Cu(OH_2)_6]^{2+}$
Cu(II) = d^9
z-out

e.g. $K_2[CuF_4]$ O_h z-in
$Na_2[CuF_4]$ O_h z-out

Cr_2F_6 O_h z-out
Cr(II) = high spin d^4

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And, for other situations, where we can have K 2 Cu F 4 – the tetrafluoro copper salt – potassium tetrafluoro (( )); which is potassium tetrafluoro (( )) and sodium tetrafluoro (( )). So, interestingly, within the crystal lattice, basically, these moles are showing Cu F 4 and Cu F 4 situation. But due to the different types of crystal packing in this particular situation, this Cu F 4 and this Cu F 4 also interact with other flourine atoms from the adjacent molecules such that this copper center would be octahedral Cu F 6. So, 4 from the same molecule, that means, the same copper environment and 2 is basically to other flourine atoms are being shared from the upper side and the lower side in the crystal lattice. So, this is basically the most compressed one; where, we have the potassium is in the crystal lattice also, which is z-in situation. And when we take the corresponding sodium salt, it is basically the z-out situation. Similarly, for Cr 2 F 6 also, we have the corresponding chromium 2; and this particular chromium 2 is in the high spin d 4 situation, which is also very much relevant for the z-out situation. And we have the sharing for the corresponding chromium around the 4 flourine atoms. So, this particular one is shared from the adjacent molecule.

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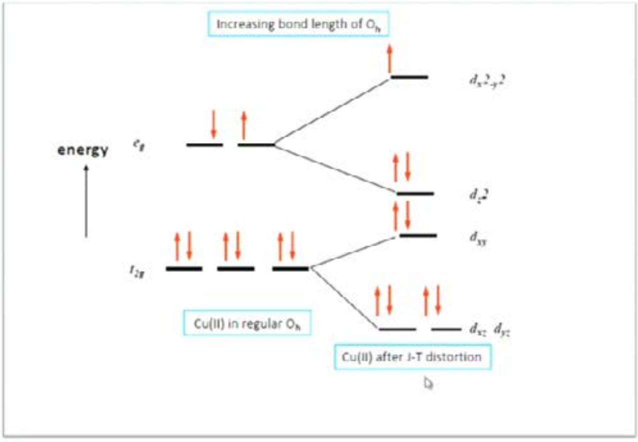

We have all these examples for this typical situation for these distortions. So, what we see that, in case of copper, which is also the copper in hexa-aqua molecule that, 9 electrons what we can have, these nine electrons are there, so this particular one. So, this copper 2 in regular octahedral geometry, there would be one more electron here. So, we can have 6 plus 3 – 9 electrons over there. So, this is paired and this is the unpaired one. So, when they are doublet and they are degenerate, we do not know which one is d x square minus y square and which one is d z square. But after splitting, we can clearly identify the corresponding number of electrons since it is a corresponding situation where we have the elongation. So, increasing bond length of the octahedral; that means, the corresponding distortion along the z-axis. So, z components are stabilized; d z square would be stabilized; and d x z and y z are also stabilized. So, we have the single unpaired electron in d x square minus y square. So, that is the corresponding situation, what we have seen in case of z-out.

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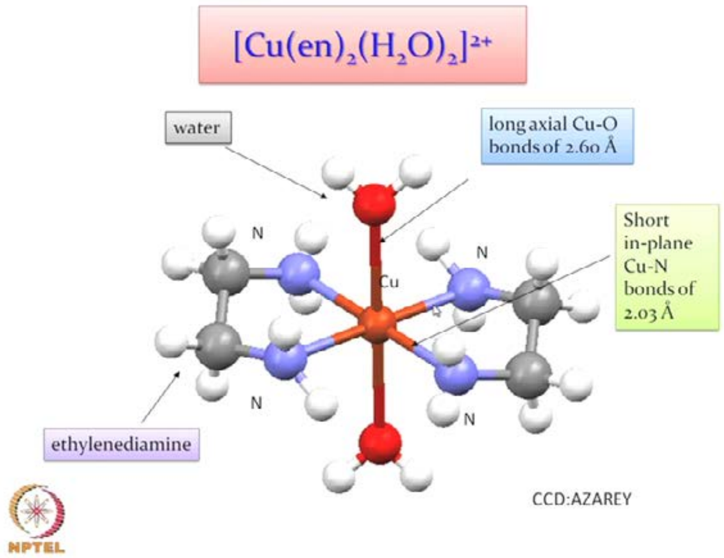

$[Cu(en)_2(H_2O)_2]^{2+}$

water

long axial Cu-O bonds of 2.60 Å

Short in-plane Cu-N bonds of 2.03 Å

ethylenediamine

CCD:AZAREY

What happens if we go for the bidentate ligand? When we have the bidentate ligand like this; that means, if we have the corresponding bis-ethylenediamine copperdiaqua molecule; where, the two corresponding water molecules are there, which are in elongated detection. So, long axial copper oxygen bonds, what we have seen in case of hexaqua molecule also. So, it is in range of 260 picometer or 2.60 angstrom. And the short in-plane copper nitrogen bonds are in the range of 2.03 angstrom. So, they are shorter in-plane; this copper nitrogen bonds are shorter. And we have the corresponding longer distances along this particular axis, which is the corresponding elongated axis. And we have the bis-ethylenediamine molecule for this sort of distortion. So, when we have the chelate rings also, we see the distortion, because the chelates are only restricted within the plane, which is the corresponding square plane; and the axial directions are free for water co-ordination.

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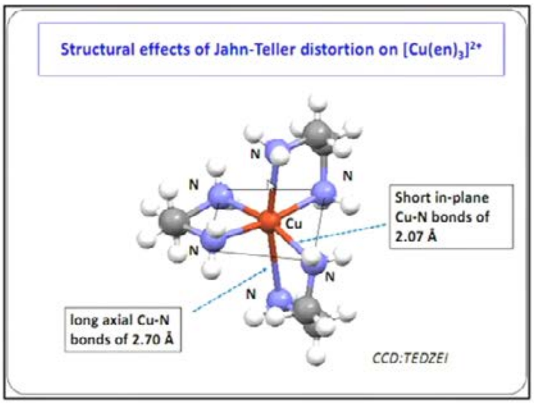

Structural effects of Jahn-Teller distortion on $[Cu(en)_3]^{2+}$

Short in-plane Cu-N bonds of 2.07 Å

long axial Cu-N bonds of 2.70 Å

CCD:TEDZEI

But, this is also true when we have the corresponding copper tris-ethylenediamine molecule. So, in octahedral geometry, when we have the tris-ethylenediamine copper molecule; that means, 6 copper-nitrogen bonds can be formed from the binding of one chelate, then the second chelate and the third chelate, which has a 2 positive charge. So, what we see that, this particular one if we find that, if this particular direction; again, we will consider this particular one; that means, the situation is z-out situation. So, these two axes; that means, the z-axis will try to elongate; that means, these two copper-nitrogen bonds will be longer compared to other four.

So, when this particular bond will try to be longer compared to this bond; that means, within the chelate ring, this is the copper position. So, we can have this copper-nitrogen bond is longer compared to this copper-nitrogen; which can be nicely compared if we just go for the in-plane short bonds for this bidentate ethylenediamine ligand, because here two copper-nitrogen bonds are in the square plane. So, these two bonds will be shorter. But the situation for these two ligands are different; we have one long bond and one short bond; similarly, one long bond and short bond. So, as a result, this particular chelate ring will be distorted towards this side and this particular one will be distorted toward this side; that means, we can have corresponding this bond will go towards this side and this bond will also go towards this side, because it is already chelated; it is not free like free water co-ordination. So, due to that, basically, is this particular one; that means, this nitrogen-copper-nitrogen axis.

Ideally, if we do not have any distortion related to this lengthening of this nitrogen in the trischelate molecule; what we see that, this is close to 180 degree. But when we just move from this right-hand side direction, and this is also moving towards this square plane, we have something where we get a corresponding nitrogen-copper-nitrogen axial. So, this is axial and this is also axial. So, nitrogen axial, copper and nitrogen axial angle should then be less than 180 degree. So, here we see that, this is the corresponding long axial copper-nitrogen bonds, which are much more than what we have seen just now for the aqua copper molecule, which was 2.60 angstrom. But it would be 2.70 angstrom. And also, the short in-plane copper-nitrogen bonds, which were below 2 angstrom in the aqua molecule; but it is above 2 angstrom; it is 2.07 angstrom. Then this particular picture clearly shows that this particular direction is moving towards on the right-hand side and this is also moving towards this direction towards the chelate ring direction. As a result, we have this nitrogen-copper-nitrogen angle less than 180 degree. So, we see also, for the trischelate molecule for copper, we still have the corresponding distortions related to the Jahn-Teller distortion.

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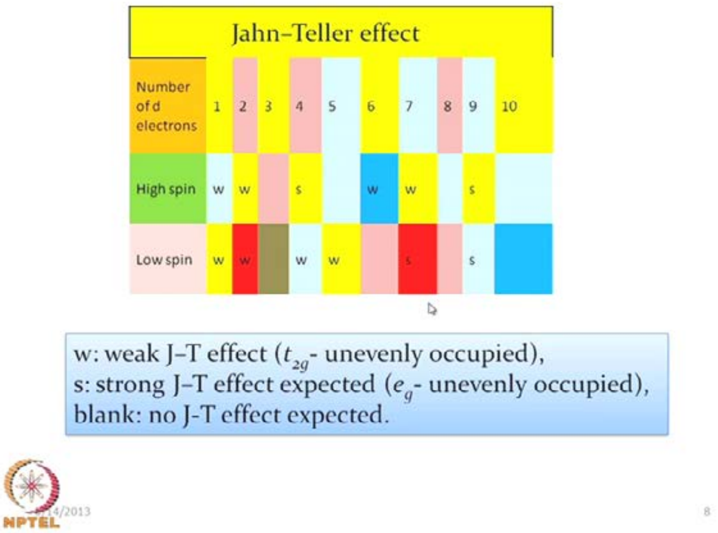

Jahn–Teller effect

Number of d electrons	1	2	3	4	5	6	7	8	9	10
High spin	w	w		s		w	w		s	
Low spin	w	w		w	w		s		s	

w: weak J–T effect (t_{2g}- unevenly occupied),
s: strong J–T effect expected (e_g- unevenly occupied),
blank: no J–T effect expected.

What we see that, for the different d electrons starting from the d 1 system to d 10 system; and we have two situations: one we already know that, for the octahedral complex with geometry, if the geometry is octahedral one, we have the situations like the high-spin situation and the low-spin situation. And just now, we are discussing about the d 4 system and this is the corresponding copper. So, in the copper case, which is not related to its high-spin and low-spin electronic configuration, it has only one electronic configuration, which is purely the corresponding 3 d 9 electronic configuration. And we have in both these two cases, correspondingly, it is giving strong Jahn-Teller effect. So, this strong Jahn-Teller effect for 3 d 9 system is therefore expected, because e g, which is unevenly occupied. So, the e g level now, in case of copper 2 plus, we have 3 electrons. And those three electrons would be unevenly occupied for this e g level. And that is why we get that, the e g level will undergo the corresponding distortion, which is the corresponding JT distortion.

So, where the entries are not there, we do not have any Jahn-Teller effect expected further. And for other cases; that means, we have the corresponding low spin d 7, low spin 3 d 7 system, which is cobalt 2. So, cobalt 2 also can give rise to strong Jahn-Teller effect and the high spin d 4 system. So, these are the cases. So, 3 d 9, 3 d 7 and 3 d 4 situation – we can have the corresponding strong Jahn-Teller effect.

But, what is our weak Jahn-Teller effect? The weak Jahn-Teller effect is due to the uneven occupancy in the t 2 g level, which is not facing the ligands directly, because we all know now that, in octahedral geometry, the e g orbitals are facing the corresponding ligands directly along the three cartesian axes: x, y and z. But in case of t 2 g, the electrons are there, but these orbitals are in between the cartesian axes. Such as, if we have the d x y orbital, which is between the x and y axis and which is in between and which is not propelling the ligand electron density much more; so whatever Jahn-Teller effect we can see due to the uneven occupancy in these levels; that means when we have one electron in the t 2 g level, two electrons in the t 2 g level; or, here also, after fulfilling this one; that means, the five electrons made out for all levels. Then the sixth electron and the seventh electron is coming in again into the t 2 g level. So, these all will basically give a every weak Jahn-Teller effect for these situations. So, we can get some effect; we can get some distortion; and some of these effects are stronger what we see in case of the copper. The most renowned example is the copper 2 plus. But in other cases, the distortion is very less and that also can be observed due to the different electronic transitions in optical spectroscopy also.

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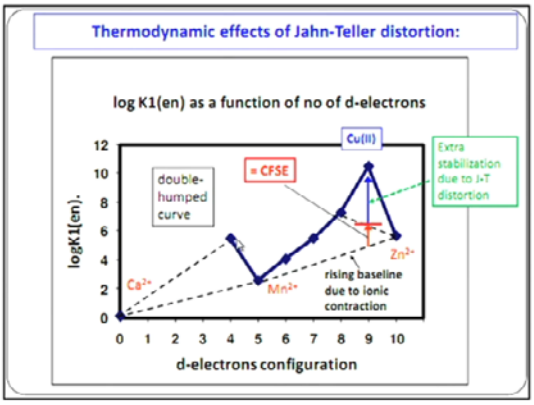

Thermodynamic effects of Jahn-Teller distortion:

We can also have some idea about the corresponding effect due to the distortion. The thermodynamic effect that we will see also afterwards that, the binding of the ethylenediamine to all these molecules starting from the main group element, the calcium to scandium, titanium, anadium, chromium, manganese. So, these are the things that where we can have the corresponding double-humped curve we can get. So, this double-humped curves are also very much useful for the corresponding metal oxygen bond in the solid state. That we will discuss afterwards. Similarly, for the different aqua molecules, we can have the corresponding hydration energy. And hydration energy also follow similar double-humped curve; where, we see that, some amount of crystal field stabilization, which is operating as we move from d 1, d 2, d 3 to d 4 situation. And there also, as we move up to this particular d 8 or d 9 situation, there is a gain in the crystal field stabilization energy. And due to that gain, we basically get some extra stabilization due to the corresponding gain through crystal field effect.

Here basically for this log K1 en is a function of number of d electrons. So, the corresponding binding constant for one ethylenediamine binding can be monitored depending upon the number of d electrons present. So, it is moving. As we move from calcium to manganese to zinc, it is basically rising. And the rising base line is due to the ionic contraction, because the more number of protons and electrons are there. So, higher nuclear charge will basically go for ionic contraction and size is less. And we can have some higher values for this log K i values.

Now, in this particular case also, we see some amount of stabilization in case of copper, which is above this dotted line; which is due to the corresponding crystal field stabilization energy in 3 d 9 situation. So, there is the gain in energy due to crystal field splitting. And that gain in corresponding energy for crystal field splitting is reflected; and the log K1 value can go from here – the dotted line to up to this point. But experimentally, what we get; experimentally, this value is much more; it is close to 10. And this increase in these values from say 6 to 10 is due to the corresponding Jahn-Teller distortion. So, the stabilization what we get is experimentally that can be verified if we determine the corresponding log K1 value for the binding of ethylenediamine to the copper center, is due to the corresponding extra stabilization for the Jahn-Teller distortion. So, we get this much amount of stabilization.

So, the situation for copper 2 in 3 d 9 electronic configuration is that, it is the most stable situation after distortion. Similarly, in case of 3 d 4 situation, what we also know that, it has also stabilization due to Jahn-Teller effect and that basically gives us some amount of stabilization. And we have a double-humped curve. Therefore, where the peak is here for 3 d 4; and the second peak is at 3 d 9 due to copper 2. So, any kind of physical information, what we get due to that Jahn-Teller stabilization is reflected from determining the log K1 values for ethylenediamine coordination or binding.

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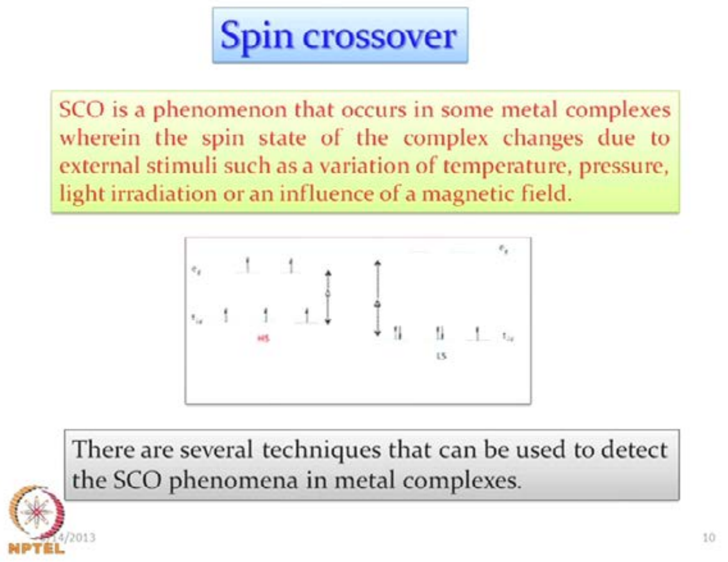

Spin crossover

SCO is a phenomenon that occurs in some metal complexes wherein the spin state of the complex changes due to external stimuli such as a variation of temperature, pressure, light irradiation or an influence of a magnetic field.

There are several techniques that can be used to detect the SCO phenomena in metal complexes.

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Next, we will just move on to another situation, what we are just discussing for the corresponding spin state.

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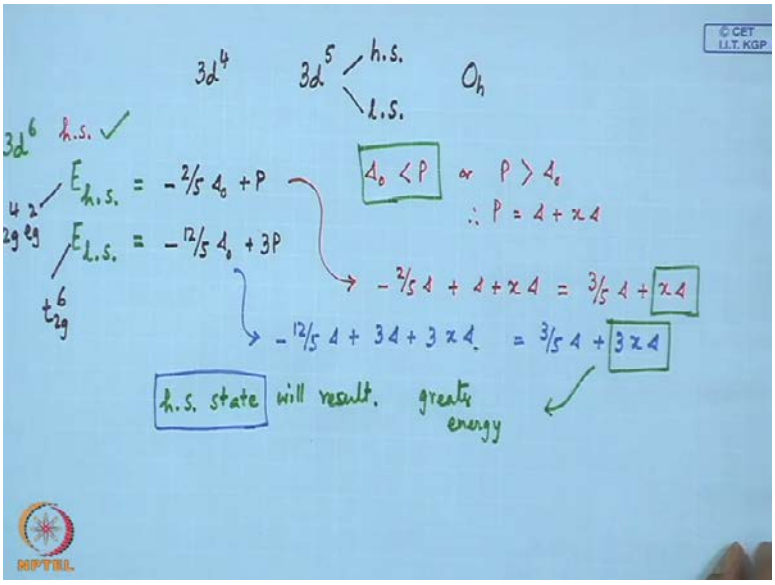

$3d^4$ $\quad$ $3d^5 \begin{cases} h.s. \\ l.s. \end{cases}$ $\quad$ O_h

$3d^6$ h.s. ✓

$t_{2g}^4 e_g^2$ — $E_{h.s.} = -\frac{2}{5}\Delta_o + P$

t_{2g}^6 — $E_{l.s.} = -\frac{12}{5}\Delta_o + 3P$

$\boxed{\Delta_o < P}$ or $P > \Delta_o$

$\therefore P = \Delta + x\Delta$

$\rightarrow -\frac{2}{5}\Delta + \Delta + x\Delta = \frac{3}{5}\Delta + \boxed{x\Delta}$

$\rightarrow -\frac{12}{5}\Delta + 3\Delta + 3x\Delta = \frac{3}{5}\Delta + \boxed{3x\Delta}$

$\boxed{\text{h.s. state}}$ will result. greater energy

Whenever we have any d-electron configuration say 3 d 4 or 5 or 6 or 7, we see that, in case of 3 d 5, we can have two electronic configurations in octahedral field. So, the field is octahedral. So, we have the corresponding high-spin configuration and the low-spin configuration. And in case of 3 d 6, we have determined earlier that, for 3 d 6, the energy for the high-spin situation and the corresponding energy for the low-spin situation can be determine nicely if we know the corresponding amount of splitting. So, this has two different types of configurations: one is that corresponding t 2 g 4 e g 2. And in case of this low-spin, it is t 2 g 6. And these two situations can very nicely be handled if we determine the corresponding values for the high-spin and the low-spin configuration. So, in this particular case, it is two-fifth of delta o plus P. And in this case, it is minus twelve-fifth of delta o plus 3P, because we have three electron pairing. So, in this particular situation, if we just consider the 3 d 6, we have a high-spin configuration. And in high-spin configuration, we know that, the delta o is less than P or P is greater than delta o.

Now, if we consider that, since P is greater than delta; therefore, if we can consider the P is equal to delta plus x delta. So, if we put these values for these, what we find that, in case of e high spin, the energy for this would be two-fifth delta plus delta plus x delta, which will be equal to three-fifth delta plus x delta. Similarly, we also can put for energy for the low spin. So, it will be minus 12 by 5 delta plus 3 delta plus 3 x delta, is equal to 3 by 5 delta plus 3 x delta. So, what we see now that (( )) the two values can now be compared by looking at the corresponding delta x values. So, this low spin we will have three-fifth delta plus 3 x delta; and the high spin has three-fifth delta plus x delta. So, this will have… Therefore, we can consider it has greater energy. Since it has greater energy; that means, we get the situation as the corresponding high-spin state. So, 3 d 6 will result high-spin state. So, if the condition is such that delta O is less than P, we have the corresponding high-spin state definitely.

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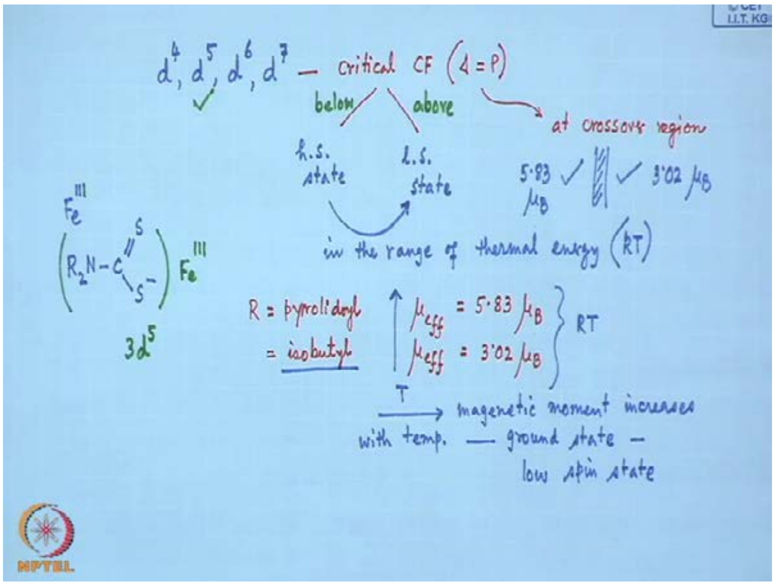

Now, we will see that, for situations like the corresponding configurations, it can be for 4 d and 5 d as well. For d 4, d 5, d 6 and d 7, if we see that, there is always a balance between the corresponding crystal field energy and the pairing energy. So, if there is a critical crystal field; at the critical field, we find that delta is equal to P; that means, this is at somewhere; where we can consider is at a crossover region; that means, we are moving from one direction to the other such that if on the left-hand side, the low spin state is of low energy; on the right hand side, it would be of higher energy. So, at this critical crystal field, we find that, below this critical field and above this critical field, we have two situations. And these situations are considered in such a way that, below the critical field, if we have the high-spin state is of low energy; and above this critical crystal field, the low-spin state will have low energy. So, at this particular point, we can have a crossover. And this particular crossover region can be found out; where, delta is close to P and which is in the range of thermal energy; that means, KT – in the range of thermal energy, which is nothing but KT.

How we get this thermal energy to change over from one particular form to the other; that we will find in case of this spin crossover. So, this spin crossover situation, we have see that this can be abbreviated as SCO. It is a phenomenon that occurs in some metal complexes. Not all metal complexes will keep the spin crossover situation, wherein the spin state of the complex changes due to external stimuli, such as variation of temperature, pressure, light irradiation or an influence of magnetic field; that means we are forcing, we are giving some external stimuli as temperature, pressure, light irradiation or magnetic field.

So, once we change the corresponding temperature; and as we have seen just now that, it is in the range of corresponding thermal energy; that means, the KT; that means, the KT can control the corresponding spin state of the molecule. So, there are some beautiful examples for all these molecules, where we will find that, this particular situation can be handled nicely by finding out the right ligand system and the right metal ion. So, we have this particular one. So, thermal energy can control this particular situation, where we can have this high-spin state, can go to the low-spin state, which is of low energy; that means, this delta is basically, now, close to the corresponding fearing energy.

And, as a result, we push these two electrons to the lower level for pairing. So, if they are close to this P; the P is close to this delta value; we do not know what should be the situation; whether it would be high-spin or whether it would be low-spin. So, there are several techniques also, how we can find it out the corresponding spin crossover or spin crossover molecules that can be used to detect the SCO phenomena in metal complexes. So, there are right number of these techniques, which can be applied to find out the corresponding spin crossover situation for these molecules.

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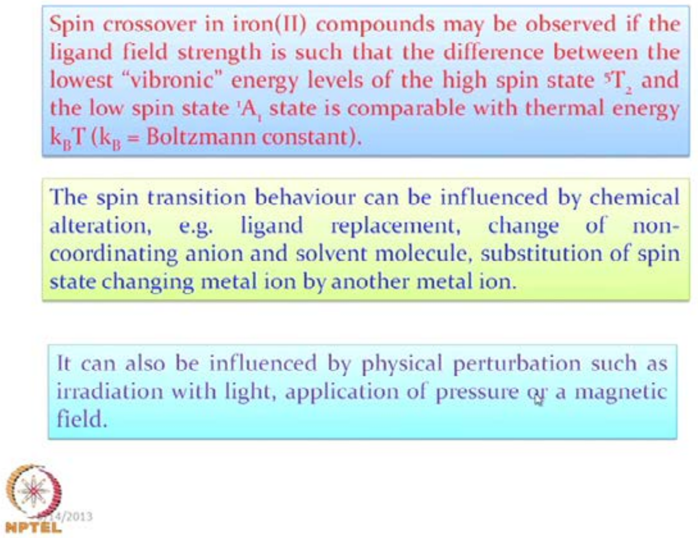

Spin crossover in iron(II) compounds may be observed if the ligand field strength is such that the difference between the lowest "vibronic" energy levels of the high spin state $^5T_2$ and the low spin state $^1A_1$ state is comparable with thermal energy k_BT (k_B = Boltzmann constant).

The spin transition behaviour can be influenced by chemical alteration, e.g. ligand replacement, change of non-coordinating anion and solvent molecule, substitution of spin state changing metal ion by another metal ion.

It can also be influenced by physical perturbation such as irradiation with light, application of pressure or a magnetic field.

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And, when we find that spin crossover for several iron compounds can be absorbed if the ligand field strength is such that the difference between the lowest vibronic energy levels of the high spin state, which is 5 T 2, is the corresponding spectroscopic term related to the occupancy in the t 2 g and e g level. So, we find there that, the corresponding state of 5 T 2 and the low spin state, which is 1 A 1, because it has 5 spins multiplicity value. And here the spin multiplicity value is 1. So, it has high spin value, so this particular value, which is 2 S plus 1. So, it has two unpaired electrons for this S value. And we have this corresponding value for this; that means, the four unpaired electron is there; the capital S value is equal to 2. So, we have this particular situation. And this is the low spin state. And these two states are comparable with thermal energy KT, which is k B T; k B T is nothing but the corresponding constant named after Boltzmann. So, it is abbreviated as capital B also. Small k abbreviates with subscript; capital B gives the corresponding Boltzmann constant. So, these two states when they mix up and when one is of low energy than the other, we can change the corresponding situation from one state to the other.

Then, the spin transition behavior can be influenced by chemical alteration. We all know that the ligand replacement, the change of non coordinating anion, the solvent molecule, substitution of spin state changing metal ion by another metal ion. So, these are the things what we can use to control the corresponding spin transition whether we will be getting the corresponding high-spin molecule or the low-spin molecule. So, if we change the ligand system, the same iron 2; if we are restricting our attention on iron 2 compound itself. So, if we change the ligand system, the iron 2 can give rise to the low-spin compound as well as the high-spin compound depending upon the nature of the ligand. Then we can go for the change of non-coordinating anion, which is outside the (( )) which is not coordinating the metal ion, but which is influencing the corresponding crystal field for the crystal lattice. And it can also affect the corresponding spin behavior. Then the solvent of crystallization and sometime the substitution of the spin state is possible if we change the metal ion, the iron 2 by some other metal ion. So, it can also be influenced by the physical perturbation, what we have seen just now that, irradiation of light, application of pressure and magnetic field apart from temperature. So, apart from temperature, three other physical perturbations can be applied to see the spin state transition, which are the light, the pressure and the magnetic field.

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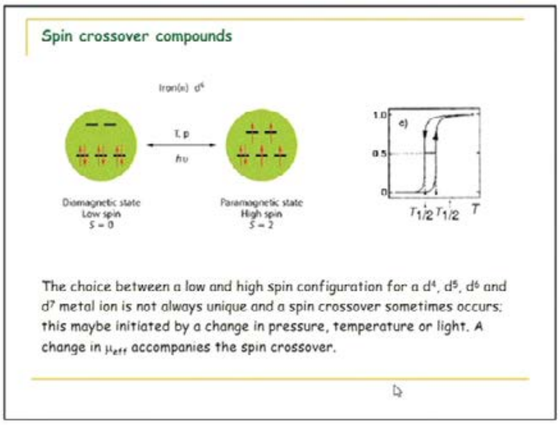

Spin crossover compounds

The choice between a low and high spin configuration for a d^4, d^5, d^6 and d^7 metal ion is not always unique and a spin crossover sometimes occurs; this maybe initiated by a change in pressure, temperature or light. A change in μ_{eff} accompanies the spin crossover.

So, a situation what we can get for the spin crossover compounds, which is a iron 2 compound, which is a 3 d 6 electronic configuration when it is low spin, where spin is equal to 0, which is the diamagnetic state; and when we move from there; that means, these two are in equilibrium from temperature, pressure or the light. So, these are the things, which can give rise to the corresponding transitions. So, we get the high spin state; that means two of these paired electrons can move to the upper state, where we get four unpaired electrons. That is why we have the spin multiplicity 5 due to S value equal to 2. So, S value 2 give rise to the corresponding spin multiplicity equal to 5. And we can monitor these by changing the temperature from this. So, you just go from there to… Then we move to the corresponding spin value; that means, when it is diamagnetic, which is 0; and we can have the corresponding maximum paramagnetism, which is close to 1. Then it is going to this particular path way and it is basically going for the paramagnetic situation.

Then again, if we cool down, it is taking a different pathway; it is not the same pathway. So, when we are moving from left to right, we are going through this pathway. The arrow shows the path, where we get the corresponding T half for the up spin. And when we are coming back; that means, lowering down the temperature, we have another T half due to the down spin, which is a different temperature. So, the choice between the low- and high-spin configuration for these molecules, what we are just telling you, that is, d 4, d 5, d 6 and d 7 metal ions, which have both the two situations; that means, the high spin and the low spin is not always unique; and a spin crossover sometimes occurs; that means, if we are not strictly getting a high-spin d 4 complex or a high-spin d 5 complex, we can get in same situation, the low-spin analogues. This may be initiated by change of pressure, temperature or light.

A change of mu effective accompanies the spin crossover. So, what we are getting a diamagnetic situation to a paramagnetic situation; that means, the corresponding magnetic moment; when we will study the corresponding magnetic properties of coordination compound, we will again come back to this particular aspect. That when we are measuring the mu effective value and there is a effect for the corresponding temperature, we should be very much careful whether we are going for a corresponding spin crossover compounds or something, other thing; that means, some anti-ferromagnetic interaction or ferromagnetic interaction are taking place between these two electrons occupying two different magnetic orbitals. So, if we have this particular situation for iron 2; iron 2 compound is there, and some well-known example for the dithiocarbamate; what we discussed earlier for dialkylamine, so the trischelate for that this N, N-diethyl – diethylcorbomate. And in this particular case, we get this as iron 3 compound. So, these are mono-negatives. So, charge is balanced, which is a neutral compound.

And, we have now for the next one – the second one – the 3 d 5 situation. So, these R values can be different types of these R groups depending upon the corresponding amine.

So, when R is equal to pyrrole groups or pyrrolidoyl – r r o l i d o y l – pyrrolidoyl, the corresponding mu effective value would be equal to 5.83 mu B – 5.83 Bohr magneton. But if we change the R group from pyrrolidoyl to isobutyl, the corresponding mu effective value for the same would be 3.02 mu B. So, simply by changing the corresponding R values, we get the corresponding situation for two types of magnetic moments when we measure these at room temperature. So, at room temperature, we can have these things; that means, if we now see that, we change the temperature; so if we change the temperature and the magnetic moment increases with temperature, this magnetic moment is going from 3.02 say to 5.83 for the same substitution.

These are the two situations; where, one is for the high spin and another is for the low spin; that means we have a crossover. And if we have a crossover region, the high spin will be on the left-hand side, which will be of the lower energy; and the low spin will be on the right-hand side. So, the high spin – that means, this 5.83 Bohr magneton will be on the left-hand side and this 3.02 is the corresponding low spin one will be on the right-hand side. So, if we increase the temperature, the magnetic moment increases. So, magnetic moment increases with temperature; that means, here we are; that means, we are having the low-spin state. So, ground state would be the low-spin state. So, we have the corresponding ground state, which will be the low-spin state.

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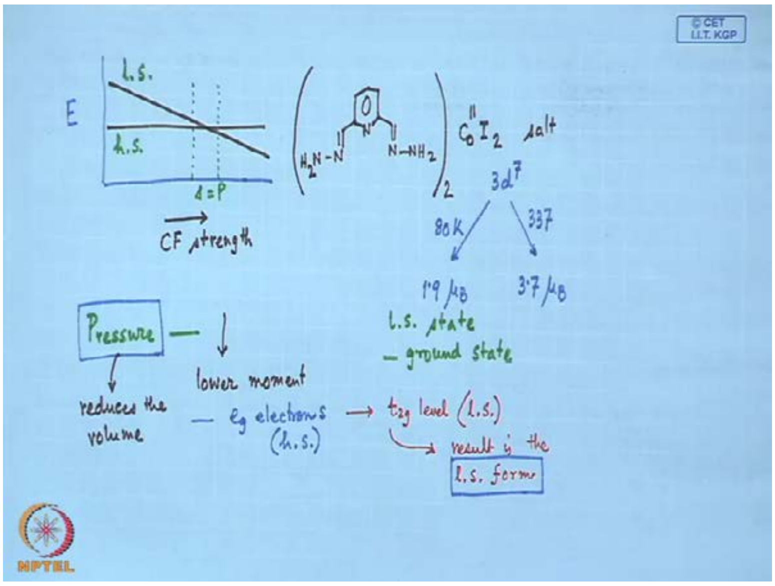

For this molecule, if we just simply plot the corresponding E values; that means, the energy values – E of the spin state – E of the low spin and E of the high spin; we will find there that, as we change it with respect to the corresponding crystal field strength – the CF strength; if this CF strength goes like this and if we find that the energy for the low-spin state decreasing sharply compared to the energy for the corresponding high-spin state, which is not decreasing so sharply; these are the energy values for the low spin and the high spin. And this is the corresponding crossover region. And at this crossover region, we have the corresponding delta value equal to P. So, as we move from here to here, just we get the corresponding value for this. So, at this region, the corresponding available thermal energy will be in the room temperature. And we move from there; the corresponding crystal field will just give for the corresponding change over. So, we see that, one particular state will be of low energy and compared to the other state. So, the corresponding value for also can be obtained.

And, if we just see another example, which is the corresponding hydrazone derivative of pyridine 2 6 dialdehyde, which is giving rise to the corresponding complex with cobalt 2; and since this ligand is a neutral one, we have the corresponding cobalt iodide salt. So, this one having a 3 d 7 electronic configuration; as we all know that, in this particular case also that, we can have two configurations: one is the low spin; another is the high spin. So, at 80 k – at 80 Kelvin, the value is 1.9 mu B – the magnetic movement value. And as we increase the temperature, we get the corresponding value as 3.7 mu B. So, again like that of the iron example, we find the low spin state is the ground state. So, the low spin state is the ground state. So, in this particular case and in some other cases also, not only the temperature; that means, if we change the temperature, the situation can change from one side to the other. But also, the corresponding pressure effect can also be seen that, how pressure effect can change the corresponding magnetic moment. So, when we put pressure to the corresponding compound and measure the corresponding magnetic moment, we get lower moment – a lower magnetic moment, because the exerted pressure reduces the volume, which can be the molar volume or the molecular volume.

And, as a result, the e g electrons, what we can have, which are directly facing the ligands, which can move the e g electrons, which are present for the corresponding high-spin configuration, can move to the t 2 g level, which is responsible for the low-spin configuration. And the result is the corresponding low-spin form. So, the exhaustion that gives when we exert pressure; there also, we see that, we will be able to get the corresponding low-spin form from the high-spin form. So, in this particular case, like the temperature, the situation is also close to the crossover region. And since the crossover region is susceptible for the change in the magnetic moment from one direction to the other, we get the corresponding spin change as well as the magnetic moment change due to the temperature as well as the pressure.

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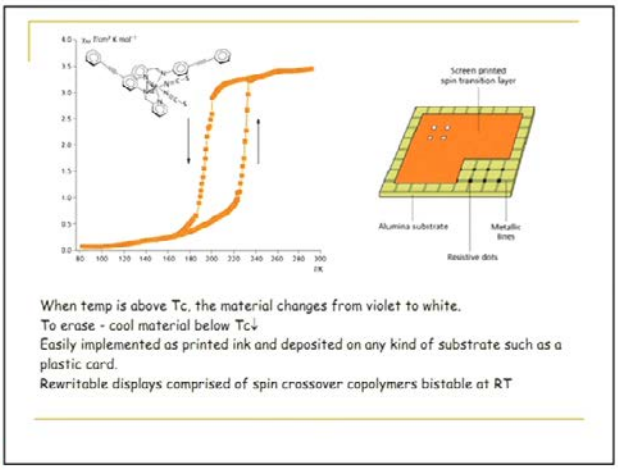

When temp is above Tc, the material changes from violet to white.
To erase - cool material below Tc↓
Easily implemented as printed ink and deposited on any kind of substrate such as a plastic card.
Rewritable displays comprised of spin crossover copolymers bistable at RT

One more example is there, where we have the corresponding iron compound. This particular case we can have, is a very complicated molecule though; but we have two thiocyanate coordination. And that thiocyanate coordination again gives rise to the corresponding hysteresis-type of loop; that means, as we change the temperature, the chi m value – this we are measuring the corresponding chi m value like the measurement of the magnetic moment at variable temperature. So, we just go like this. Again, on the right-hand side, we move to the high-spin state. And then when we come down, we go through some other pathway.

So, we find some hysteresis loop, when the temperature is above the T c, the material changes from violet to white. So, there will be a color change to erase-cool the material below the T c. There is the corresponding transition temperature, which can be used for lighting some materials. So, these are the most latest technologies people can use it that, the screen printed with based on the corresponding spin changes. The spin transition layer is deposited over there. Then we have the metallic line, alumina substrate and resistive dots. Easily implemented as the printed ink and deposited on any kind of substrate, we can go from printing such as plastic card. Rewritable displays comprised of spin crossover copolymers bistable at room temperature; that means, its stability at room temperature is different; that means, in one case, it would be stable in high spin; and in another case, it will be in the low-spin state. So, some more examples and some more physical characterizations for identification of this spin crossover molecules, and this spin crossover situation, we will see in our next class.

Thank you very much.