

**Basics in Inorganic Chemistry**  
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**Lecture - 13**

**Problem Solving Approach**

(Refer Slide Time: 00:17)

**Magnetism**

Orbital  
Contributions in  
Octahedral  
Complexes

Ion	Config	OAM?	$\mu_{spin}$	$\mu_{obs}$
Ti(III)	d <sup>1</sup>	yes	1.73	1.6-1.7
V(IV)	d <sup>1</sup>	yes	1.73	1.7-1.8
V(III)	d <sup>2</sup>	yes	2.83	2.7-2.9
Cr(IV)	d <sup>2</sup>	yes	2.83	2.8
V(II)	d <sup>3</sup>	no	3.88	3.8-3.9
Cr(III)	d <sup>3</sup>	no	3.88	3.7-3.9
Mn(IV)	d <sup>3</sup>	no	3.88	3.8-4.0
Cr(II)	d <sup>4</sup> h.s	no	4.90	4.7-4.9
Cr(II)	d <sup>4</sup> l.s	yes	2.83	3.2-3.3
Mn(III)	d <sup>4</sup> h.s	no	4.90	4.9-5.0
Mn(III)	d <sup>4</sup> l.s	yes	2.83	3.2
Mn(II)	d <sup>5</sup> h.s	no	5.92	5.6-6.1
Mn(II)	d <sup>5</sup> l.s	yes	1.73	1.8-2.1
Fe(III)	d <sup>5</sup> h.s	no	5.92	5.7-6.0
Fe(III)	d <sup>5</sup> l.s	yes	1.73	2.0-2.5
Fe(II)	d <sup>6</sup> h.s	yes	4.90	5.1-5.7
Co(II)	d <sup>7</sup> h.s	yes	3.88	4.3-5.2
Co(II)	d <sup>7</sup> l.s	no	1.73	1.8
Ni(III)	d <sup>7</sup> l.s	no	1.73	1.8-2.0
Ni(II)	d <sup>8</sup>	no	2.83	2.9-3.3
Cu(II)	d <sup>9</sup>	no	1.73	1.7-2.2



So far today I think magnetism wise we dint discuss too much, we have introduced the topic magnetism where the origin of the magnetism coming or magnetic moment coming into the molecule. It is the molecule unpaired electron that is responsible. Number of a unpaired electron should technically give you the clear cut idea what is the magnetic moment going to be; there is some more to it.

Of course, in reality we know that it is orbital angular momentum and the spin only values that should give you that should combine, but you do not need to combine because it is

somewhat restricted. The still somewhat allowed that is where when it is allowed then you have a better value or the higher value for magnetic moment right?.

And when that spin only plus orbital angular momentum is coming into picture that is what we have introduced, but we will be discussing from here on in the next class ok. Now we will have two more still topic one is this magnetism, the next one will be by an organic two classes we should be able to finish.

Student: Sir.

Yeah.

Student: (Refer Time: 01:28) comparative complex is not credit then we have associated managing the (Refer Time: 01:35).

Yes that is a good question. Sure it I think if I am getting; I think in the beginning I did not get your point at the end what I get is. So, you have to think the total ensemble. Like if of course, if a molecule one molecule had some magnetic moment, another molecule associated with it has another magnetic moment you have to basically assemble.

Yes at the end at the very last at the end we will see, it is not the individual magnetic behaviour will matter it is the total collective molecule whatever molecule you are associated with. If it is only one type of molecule one center, then that is of no problem, but the moment you have let us say cluster ok. One thing is attached via another thing through another thing then things are more complicated.

So, that is what that is where I would like to take you to at the end of the magnetism. So, they can two magnet can communicate through a mediators one spin up, another spin up is it going to be magnetic moving moment going to be addition of these two can they talk with each other and reverse inverse.

Let us say, this is up in between these two magnet there is something which is communicating between the two. Can that communicator influence the total magnetic behaviour? So, there is magnetic communication that is actually the basis for you know more fun in this area.

We will not discuss a lot of case maybe one or two case we will discuss and then live. So, I think is that the type of queries you are having or maybe I have taken you to a different direction. Some something later I initially I could not hear you, but at the end I think I heard you correctly ok.

Now, hopefully the next part will not be that long another 20 minutes or so, or 30 minutes maximum depends on how you would; this is the third tutorial which is on coordination compounds, you have the printout the question.

Student: (Refer Time: 04:04).

No problem, I have that question here all right. Tutorials if you want to go I have no problem, but I think it is important later I will try to get it done very quickly. Tutorial questions were uploaded in the model and nowadays all of you are having Smartphone.

Student: (Refer Time: 04:28) Wi-Fi (Refer Time: 04:29).

So, if you have Wi-Fi connection.

Student: (Refer Time: 04:31).

You could have downloaded earlier.

Student: Sir, but I am just going to write (Refer Time: 04:35).

Do not come to my office to download it now ok. Just take it is one of you should have been able to download it. If you are really dying I you could have ask me I could have send you or give you a printout ok. Anyway that does not matter too much it is in there. If you like I can give you the print out the next time.

Student: Sir (Refer Time: 05:04).

Which going to pay for it.

Student: [laughter].

We can give it I think I can pay for it. Of course, you are paying IIT right no problem. So, first question crystalline silver oxide is diamagnetic explain?

(Refer Slide Time: 05:23)



**Q01. Crystalline AgO is diamagnetic. Explain.**

- AgO  
As per formula, oxidation state is +2

Electronic configuration should be  
Ag: [Kr] 4d<sup>10</sup> 5s<sup>1</sup>  
Ag(II): [Kr] 4d<sup>9</sup>

↑    ↑↓   ↑↓   ↑↓   ↑↓   ↑↓   ↑↓

- Mixture of Ag<sub>2</sub>O and Ag<sub>2</sub>O<sub>3</sub>



Student: (Refer Time: 05:23).

Question number 1 ok. So, sometime you have to be a little bit causes some not all of the question either in the exam or in tutorial are going to be straightforward, there is something more into it. So, silver oxide you just calculate you figure out, what is the silver oxidation state do it. Plus 2 what is the electronic configuration?

Student: (Refer Time: 05:52).

Time up. Silver oxidation state is plus 2 sure it is a d 9 electronic configuration d 9 on electronic configuration means one unpaired electron.

Student: Yeah.

So, it should be paramagnetic diamagnetic means to spin right pair or un list pair spin how it is? This is where I was saying it is a trick question.

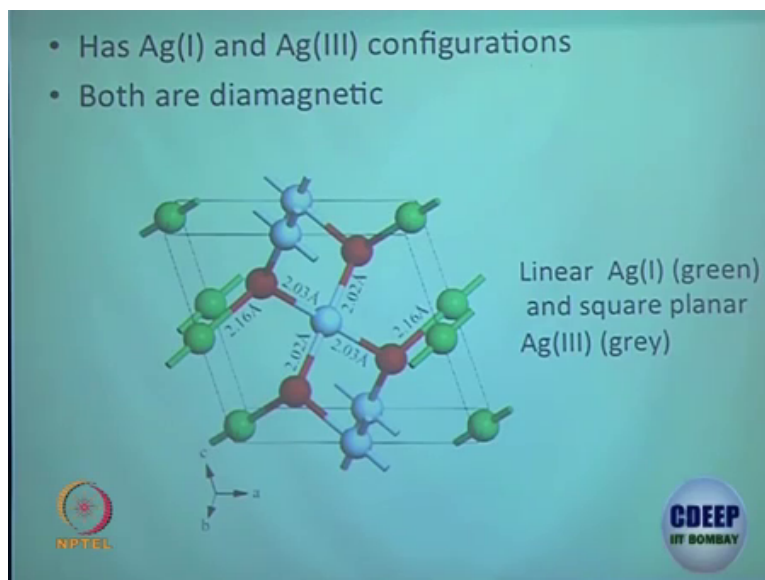
Student: Sir.

So, it see it is a mixture of sorry.

Student: One is plus 1 other is plus 3.

That is what it is. So, that is where it is a trick question. So, it is a mixture of Ag<sub>2</sub>O and Ag<sub>2</sub>O<sub>3</sub>. Now you have to look back at each of them let me try to discuss.

(Refer Slide Time: 06:39)



You have to look back each of them silver plus; silver plus 1 plus and silver 3 plus.

Student: (Refer Time: 06:48) Sir how did you decide that it is occupied O 2 minus (Refer Time: 06:53) O 1 minus.

O 1 minus is usually not possible.

Student: (Refer Time: 06:59) (Refer Time: 07:00).

You want to no do not worry I will give you.

Student: (Refer Time: 07:05).

I will upload since I have made the slide I will upload ok. No need to I mean if you bothered, if you are bothered to take the picture and take it, it is a public domain thing why should I not upload it ok. No need to just think little bit silver 1, please if you want to get it done quickly, either you answer quickly or I give you the answer and go I will upload the slide.

Now, silver 1 is going to be d 10 configuration that is diamagnetic. This is silver 1 two of the silver 1 one is oxide another over here this is silver 3 plus oxide is always minus 2, 6 minus. So, it has to be silver 3 plus silver 3 plus means what? One b 8 configuration right. So, d 8 configuration can be diamagnetic ok.

Student: (Refer Time: 08:09).

D 8 going to be square planar.

Student: But open minds to be.

Ah.

Student: So, (Refer Time: 08:22).

Because silver is in high oxidation state it is a. So, this is where some time the problem comes either the high oxidation state. So, it is the combination of both. The ligand should be strong field or.

Student: (Refer Time: 08:37).

Metal should be high oxidation state or in the combination of higher oxidation state and strong field ligand then you are going to get that ok.

Student: Sir what is the os of it ag Ag<sub>2</sub>O?



Sorry.

Student: What is the os of Ag<sub>2</sub> Ag Ag<sub>2</sub>O?

Oxidation state. Ag<sub>2</sub>O plus 1 silver is in plus 1, oxide is oxide all oxide water all oxide metal any oxide you see is minus 2. Water if you split, h plus h plus oxide 2 minus right now that is fine. So, there the geometry as you can see over here silver is linear and silver 3 which are in gray in here it is going to be square planar square planar oxide oxide oxide oxide silver is in the middle ok.

(Refer Slide Time: 09:33)

• Q02. Work out the hybridization and geometry for the following complexes using the valence bond approach.

(a) Ni(CO)<sub>4</sub>; (b) [Ni(CN)<sub>4</sub>]<sup>2-</sup>; (c) [CoCl<sub>4</sub>]<sup>2-</sup>; (d) OsO<sub>4</sub>; (e) VOCl<sub>3</sub>; (f) [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>; (g) [Ag(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>; (h) [Pt(PPh<sub>3</sub>)<sub>4</sub>]; (i) (Cr<sub>2</sub>O<sub>7</sub>)<sup>2-</sup>

Ni(CO)<sub>4</sub>

Ni atom  $3d^8 4s^2 4p^0$  Ni in Ni(CO)<sub>4</sub>  $3d^8 4s^0 4p^0$

$sp^3$  hybridization

Ni(CO)<sub>4</sub> has a tetrahedral structure and is diamagnetic (no unpaired electrons).

[Ni(CN)<sub>4</sub>]<sup>2-</sup>

18e<sup>-</sup>  $3d^8 4s^2 4p^0$   $3d^8 4s^0 4p^0$

18e<sup>-</sup>  $3d^8 4s^2 4p^0$   $3d^8 4s^0 4p^0$

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Now, that is you know that is some question which is directly. I think these questions are something we have given earlier also same questions for the tutorial. Now what work out the hybridization and geometry for the following complexes using the valence bond approach.

Student: Tetrahedral (Refer Time: 09:53).

First one is.

Student: Tetrahedral.

Student: Tetrahedral (Refer Time: 09:59).

The second one is.

Student: (Refer Time: 10:01).

Why is that?

Student: (Refer Time: 10:03).

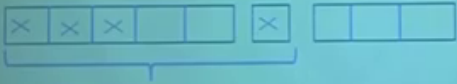
Fantastic. So, nickel is in zero oxidation state and then therefore, you I think this is may not be feasible, four of them  $sp^3$  hybridization four of the 4 of the ligand  $sp^3$  hybridization it is going to be tetrahedral nickel tetra cyanide it is going to be strong field ligand and they are by the pairing will occur by valence bond approach we are going to discuss it by valence bond approach and you know that sparing will occur the hybridization will be then  $dsp^2$  that is going to be the square planar. Of course, you can explain it better by crystal field theory, but that is.

Student: (Refer Time: 10:56).

(Refer Slide Time: 10:57)


(c)  $\text{OsO}_4$   
Electronic configuration  
 $[\text{Xe}] 4f^{14} 5d^6 6s^2$

**Ionic approach:** Oxidation state of Os(VIII)  
Electronic configuration:  $[\text{Xe}] 4f^{14} 5d^0 6s^0$





$d^2S$  hybridization Tetrahedral

**Covalent approach:** Covalent bond  
Electronic configuration:  $[\text{Xe}] 4f^{14} 5d^6 6s^2$



$d^2S$  hybridization Tetrahedral



 The remaining four electrons form  $\pi$  with oxygen



All right. Now I think I will skip this is the summary what is given here.

(Refer Slide Time: 10:59)

$\text{Ni(CO)}_4$	Ni(0)	$d^{10}$	$sp^3$	Td
$[\text{Ni(CN)}_4]^{2-}$	Ni(II)	$d^8$	$dsp^2$	sq planar
$[\text{CoCl}_4]^{2-}$	Co(II)	$d^7$	$sp^3$	Td
$\text{OsO}_4$	Os(VIII)	$d^0$	$d^3s$	Td
$\text{VOCl}_3$	V(V)	$d^0$	$d^3s$	Td
$[\text{Pt(NH}_3)_4]^{2+}$	Pt(II)	$d^8$	$dsp^2$	sq planar
$[\text{Ag(NH}_3)_2]^+$	Ag(I)	$d^{10}$	$sp$	linear
$[\text{Pt(PPh}_3)_4]$	Pt(0)	$d^{10}$	$sp^3$	Td
$[\text{Cr}_2\text{O}_7]^{2-}$	Cr(VI)	$d^0$	$d^3s$	Td



Yes that is where over here.  $\text{OsO}_4$  electronic configuration is going to be  $4f^{14} 5d^0 6s^2$  ok. This is what is little bit difficult over here to do it why vvt. Anyway if you do it by ionic approach osmium 7 plus, it is going to be  $4f^{14}$  osmium sorry osmium is going to be  $8 + 6 + 2 = 16$ . So,  $4f^{14}$  total it is going to be  $d^3 s$  hybridization and it is going to be tetrahedral.

We do not call it  $d^4$  or anything it is going to be  $d^3 s$ ; 3 of  $d$  and one of  $s$   $d^3 s$  that is going to be tetrahedral by covalent approach similarly you can look at and you can tell that it is going to be  $d^3 s$  as well. It is little bit on a borderline explanation its say when these are a little bit older approach vvt approach. So, the explanation is going to be little bit skewed at some point, but this is you can kind of make sense for both of them ok.

Now, this is most of them are clear cut tetrahedral square planar, tetrahedral square planar, linear tetrahedral tetrahedral. Linear is the silver ammonium where another molecule will be



coordinating anyway this is you should be able to find out by whatever you have done earlier. Tetrahedral place should not be a problem square planar are the one where you have the stronger ligand ok.

If it is a d 8 configuration that is where the square planar comes into picture, but the real reason that valence bond theory wise exploration was simply given it is a strong field ligand and thereby it should be paired off and shown that is what you have learned in the valence bond approach, but by crystal field approach, we have shown how things are going in terms of electron distribution how orbitals are splitted and thereby why we are saying that d 8 is going to be the square planar one.

(Refer Slide Time: 13:33)

**Q03. While the most stable chloride of Zr is  $ZrCl_4$ , that of Pd is  $PdCl_2$ . Why?**

- The third and high I.E. of the d-block metals increases with increasing atomic number. Owing to the large  $Z_{eff}$  making it more energetically unfavourable to attain oxidation state above +2.
- Further the d-orbitals become more core-like towards the end of the series and so are less effective in stabilising higher oxidation states.



Now, while the most stable chloride of zirconium is zirconium tetrachloride that of palladium is palladium chloride  $PdCl_2$ .

Student: (Refer Time: 13:48) relative effect.

Yes, it is also called relativistic effect what is that anyone wants to answer?

Student: (Refer Time: 13:57).

Sorry.

Student: (Refer Time: 14:00) (Refer Time: 14:04).

No it is its more of a d orbital see what we have seen so far it is there are let me tell you, there are palladium is going to be down the periodic table. Show you have already seen this z effective because those orbital the higher orbitals whichever getting involved, they are not neutralizing the positive charge effectively.

So, as we were discussing in the very early class first class or so, z effective is going to be very very strong. The moment z effective is going to be strong, they will be pulling out pulling in those d orbitals which are going to participate into the plus 4 oxidation state. Up to plus 2 is ok, but plus four another two electron release although technically possible since z effective is very high, it is going to not allow those electron last two electrons to get oxidized to palladium something like plus 4 relatively speaking.

So, those due to the high z effective, you are not going to participate very strongly or those plus 4 oxidation state achieving becomes difficult. This is what it is called relativistic theory or relativistic effect or so, called inert paired effect. As you go down in the periodic table, the participation of the electrons becomes less and less. I mean if from first row to second row if you go there you do not see much effect, as you go down below further it becomes more prominent right.

So, therefore, although higher oxidation state is technically feasible, but practically it becomes difficult to access. Those removing those electrons last third electron fourth electron

becomes extremely difficult because  $z$  effective is higher this is going to pull in very tightly. These are becoming more of a core like  $d$  electrons become more of a core I mean why it is difficult? It is it becomes part of the core. So, much attracted it does not want to leave those or the atom is not going to leave those one.

(Refer Slide Time: 16:43)

Q04. When high pressure is applied, what type of electronic configuration is favoured for a  $d^5$  transition metal complex (Octahedral, weak field ligand)?

Low spin; because it leads to low electron density between the metal and the ligand (i.e., along the bond axis).

$d^5$ : HS

$d^5$ : LS

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Next question number 4. When high pressure is applied what type of electronic configuration is favoured for a  $d^5$  transition metal complex? When high pressure is applied what type of electronic configuration is favoured for a  $d^5$  transition metal complex? It is you are going to put high pressure you are going to take out the electron from those let us say  $d_{z^2}$  orbital which is shown in there and thereby you are going to kind of pair of the electron.

So, because it leads to low electron density between the metal and the ligand that is along the bond axis, you are going to end up pairing. So, you will get the low spin complex.

Student: Not clear sir.

Not clear? When high pressure is applied I will tell you it is not clear to me as well let me see, what type of electronic configuration is favoured for a d 5 transition metal complex. So, d 5 you are going to have two configuration right  $t_{2g}^3 e_g^2$  and another configuration is going to be  $t_{2g}^5 e_g^0$  right.

Now, I think it is you are going to apply more field means you are going to split between the  $t_{2g}$  and  $e_g$  level if you are pulling out, you are going to separate out the  $t_{2g}$  versus  $e_g$  still not clear? I am getting more confused I will bring it back leave it. I think pulling based it is clear that you pull out then you decrease the electron density along the axis, th can you explain? Low electron density between the metal and the ligand that is along the bond axis what exactly is happening?

Student: This is m a along the axis how much I am telling this is m a along the axis. So, we bond the electron cloudy repulsion is there. So, while repulsion is there then this energy we are increasing. So, (Refer Time: 19:14).

Repulsion between what?

Student: Ligand and metal.

Ligand and metal.

Student: (Refer Time: 19:19) vector.

Ok.

Student: When you are compressing these two (Refer Time: 19:23).



So, when you are compressing wait I am not clear you when you are compressing between these two then?

Student: (Refer Time: 19:32).

Repulsion force to be much more.

Student: Then repulsion ligand donating electron right (Refer Time: 19:49).

Hm.

Student: There is a eighteen concept by (Refer Time: 19:50).

Fine. I will I think it is still not clear unless I am 100 percent clear I am not fine it is its interesting.

Student: (Refer Time: 19:58).

I think you are saying exactly what he is trying to say, but explaining the explaining becomes little bit difficult. Let me digest it little bit better I will come back ok.

(Refer Slide Time: 20:17)

**Q05. Provide reasons for the fact that a number of tetrahedral Co(II) complexes are stable, whereas the corresponding Ni(II) complexes are not.**

The CFSE of  $d^7$  tetrahedral complex is greater than that of  $d^8$  tetrahedral complex.  
Similarly, the CFSE of  $d^8$  octahedral complex is greater than that of the  $d^7$  octahedral complex.

Octahedral Vs Tetrahedral

**Table 19.2 Ligand-field stabilization energies\***

d <sup>n</sup>	Example	Octahedral	n	LFSE	Tetrahedral	n	LFSE	
d <sup>0</sup>			0	0		0	0	
d <sup>1</sup>	Ti <sup>3+</sup>		1	0.4		1	0.4	
d <sup>2</sup>	V <sup>3+</sup>		2	0.8		2	0.8	
d <sup>3</sup>	Cr <sup>3+</sup> , V <sup>2+</sup>		3	1.2		3	0.8	
		<b>Strong field</b>			<b>Weak field</b>			
d <sup>4</sup>	Cr <sup>2+</sup> , Mn <sup>2+</sup>	2	1.6		4	0.4	4	0.4
d <sup>5</sup>	Mn <sup>2+</sup> , Fe <sup>3+</sup>	1	2.0		5	0	5	0
d <sup>6</sup>	Fe <sup>2+</sup> , Co <sup>2+</sup>	0	2.4		4	0.4	4	0.4
d <sup>7</sup>	Co <sup>2+</sup>	1	1.8		3	0.6	3	0.6
d <sup>8</sup>	Ni <sup>2+</sup>	2	1.2		2	0.4	2	0.4
d <sup>9</sup>	Cu <sup>2+</sup>	1	0.6		1	0.4	1	0.4
d <sup>10</sup>	Cu <sup>+</sup> , Zn <sup>2+</sup>		0	0		0	0	0

\* n is the number of unpaired electrons; LFSE is in units of  $\Delta_o$  for octahedral and  $\Delta_t$  for tetrahedral complexes.

Now, provide reasons for the fact that a number of tetrahedral cobalt II complex are stable, where is the corresponding nickel II complexes are not anyone? Provide reasons for the fact that a number of tetrahedral cobalt II plus complexes are stable.

Student: (Refer Time: 20:35).

And whereas, corresponding nickel 2 complexes are not nickel 2 is what?

Student: D 8.

D 8;  $d^8$  tetrahedral yeah square planar more or tetrahedral versus octahedral even if you are considering and cobalt 2 plus tetrahedral and octahedral you are considering what you see that

is what you have to see. So, d 7 tetrahedral CFSE and d 7 octahedral CFSE. So, what you see overall is d 7 tetrahedral complex is greater CFSE is greater than the d 8 tetrahedral complex. Calculate the d 7 CFSE for tetrahedral field what is that d 7 CFSE? Minus 2 of dt right d 7 CFSE tetrahedral.

Student: (Refer Time: 21:37).

D 7 tetrahedral is high spin always high spin minus 12 right 12 dq what is for d 8 minus?

Student: Minus 8.

Minus 8 12 and 4 over there right minus 8 12 which one is more stable? D 7 is more stable. So, d 7 is going to be cobalt 2 plus d 7 is going to be tetrahedral you.

Student: 12241 into technique you know.

No I am asking you to compare tetrahedral versus tetrahedral; tetrahedral for d 7 tetrahedral for d 8. Octahedral for d 7 octahedral for d 8 you see the answer is within that ok. So, CFSE of d 8 octahedral d 8 octahedral will be just do the octahedral simple octahedral ok.

Student: (Refer Time: 22:43).

So, it is going to be.

Student: (Refer Time: 22:55) minus 1.

Minus 1.2 or 12 delta q or dq and what is for d 7?

Student: Minus 12. So, minus 12 (Refer Time: 23:09).

Minus no for minus 0.8 or 8 dq.

Student: D 7.

D 7. Calculate that is what I was saying maximum cases calculate the CFSE of both the geometry d 7 what is the geometry? D 8 what is the geometry? What is the splitting sorry what is the stabilization energy? This you should be able to do it in your dream.

Now, the statements here is correct CFSE for d 7 is more for tetrahedral case you have find out and CFSE for d 8 octahedral is more. CFSE of d 8 octahedral complex is greater than d 7 octahedral you calculate you will find. So, for this d 8 it is going to be minus 12 dq or minus 1.2  $\Delta_0$ . For d 7 it is going to be minus 8 dq or 0.8  $\Delta_0$  or  $\Delta_0$  octahedral right the fact is here. So, the answer is correct the experimental fact is also given over here which you can collaborate fine.

(Refer Slide Time: 24:31)

**Q06. Using the crystal field stabilization energy as criterion, indicate whether you expect the following spinels to be normal or inverse:  $\text{Fe}_3\text{O}_4$ ;  $\text{Co}_3\text{O}_4$ .**


Spinel by definition, the 3+ ion has to go to the  $\text{O}_h$  site leaving the 2+ ion in  $\text{T}_d$ .

$\text{Fe}_3\text{O}_4$  is composed of Fe(II)  $\text{T}_d$  and Fe(III)  $\text{O}_h$  ions with  $d^6$  and  $d^5$  configurations respectively. Since  $d^5$  has no CFSE, it is more advantageous to put it in a  $\text{T}_d$  environment than in  $\text{O}_h$ . In other words, by placing  $d^6$  ions in  $\text{O}_h$  environment there is more gain in more CFSE than keeping this in  $\text{T}_d$  environment.

Here the  $\text{Fe}_3\text{O}_4$  structure is inverse spinel.

$\text{Co}_3\text{O}_4$  has a similar structure with  $d^7$  and  $d^6$  configurations for 2+ and 3+ ions respectively. Co(III)  $d^6$  ion is low spin because (a) high charge (even with weak ligands like oxo) and (b) maximum gain in CFSE.

So the  $\text{Co}_3\text{O}_4$  structure is normal spinel.



Student: Sir, one not according to the last class.

Provide reasons for the fact that a number of tetrahedral cobalt complex are stable whereas, corresponding nickel II complexes are not that is the answer of course. This clearly shows that cobalt 2 plus preferred tetrahedral.

Student: And nickel II plus.

Nickel II plus are not preferring tetrahedral I am not saying what it is right. So, answer is now using the crystal field stabilization energy as criteria, indicates whether you expect the following spinels to be normal or inverse.

Student: (Refer Time: 25:16).

No calculate and figure it out. Another 10 minutes you should be done calculate quickly. See the this is what I was really trying to tell you that you should be able to calculate the CFSE really quick write down calculate. CFSE for Fe 3 plus what we have asked you to for normal and inverse spinel? You do not have to worry about tetrahedral you just think about octahedral. Fe 3 plus and Fe 2 plus octahedral and it is going to be high spin.

High spin octahedral case you just calculate should I calculate? No I can calculate Fe 3 plus is d 5 system high spin d 5 system is 0 t 2 g 3 eg 2. So, there is zero CFSE. High spin iron 2 plus that is d 6; d 6 means high spin t 2 g 4 eg 2. Fe 2 plus having minus 4 dq as a stabilization energy Fe 3 plus having zero stabilization energy. So, higher oxidation state is having less stabilization lower oxidation state is having higher stabilization you are going to get an inverse spinel I guess I was discussing in the class as well.

Student: (Refer Time: 26:55).

Now, Co 3 O 4 is a little tricky case because Co 3 is low spin.

Student: During for high charge and I iron cobalt d 6 ion is low spin because high charge even with ligand this is a tricky case. C o 3 plus has a similar structure with d 7 and d 6 configuration this is going to be a normal spinel d 7 d 7 is what? D 7 d 7 is what? Co 2 plus is d 7 iron cobalt d 7 is Co 2 plus if you Co 2 plus with oxide it is not going to be the.

Student: Low spin.

Low spin it is going to be the high spin. Co 2 plus lower oxidation state oxide is not that of a great ligand. So, it is going to be the high spin. Co 2 plus high spin d 7. So, it is going to be minus 8 dq.

Student: (Refer Time: 28:17).

Ok.


How about Co 3 plus? C o 3 plus it is going to be d 6 d 6 it is going to be minus 4 dq if it is high spin. 3 t 2 g 4 eg 2 t 2 g 4 eg 2 if it is high spin d 6 now the problem is that is minus four dq technically speaking it should be inverse spinel higher oxidation state is having lower stability compared to the lower oxidation state, but Co 3 plus this is an exception you have to kind of remember, but we will try in the exam we will try to give not such example Co 3 plus being high oxidation state and even with the lower oxygen lower even if the you know weaker field ligand such as oxide we still are going to get these normal spinel ok.

(Refer Slide Time: 29:19)

Q07. By showing the details, determine the CFSE for the following complexes:  
(a)  $[\text{FeCl}_4]^{2-}$ ; (b)  $\text{W}(\text{CO})_6$ .

$e^3 t_2^3$        $\text{CFSE} = -0.6 \Delta_t$

$t_2^6 e_g^0$   
 $\text{CFSE} = -2.4 \Delta_o$



Next few more questions left. By showing the details determine the CFSE for the following complex these are the very simple question. CFSE for  $\text{Fe}^{2+}$  plus  $\text{F e}^{2+}$  plus is  $d^6$   $c l$  is a weak field ligand, iron is  $2+$  low oxidation state. So, it is going to be the high spin  $d^6$  high spin,  $t_2g^4 e_g^2$ ;  $t_2g^3 e_g^3$  cancels out minus  $4 \Delta q$  all of you got it or should I wait little bit ok? 30 seconds the titanium titanium is going to be sorry not tungsten.

Student: (Refer Time: 30:09).

My bad ok. Tungsten; tungsten is going to be carbonyl is going to be strong field ligand almost the strongest you can get out there. So, it is going to give you low spin for  $\text{CO}$   $t_2g^6 e_g^0$ .

Student: (Refer Time: 30:33).

Ok.

Student: (Refer Time: 30:35).

Yeah.

Student: (Refer Time: 30:38).

Its usually we when we count we just count for  $d$ , until these like  $d^6$  that is why we are counting. Because the that was atomic orbital you have to take into the atomic orbital into the more of a complex orbital or molecular orbital.

We never so, far we never talk about  $d^2 s d$  you know atomic orbital wise it is correct  $d^4 s^2$   $d^4$ , but in reality when you are doing anything with the hybridization or anything with especially with in the complex section, you have to say it is a mixing orbital mixing is happening, you have to say it is a  $d^6$ . So,  $t_2g^6 e_g^0$ .



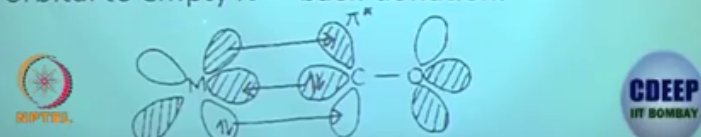
(Refer Slide Time: 31:37)

**Q08. Explain what is meant by the term “synergic bonding”?**

In the synergic bonding the  $\sigma$ -donation of charge from the ligand to the metal is reinforced by  $\pi$ -back-donation from the metal to the ligand.

In a valence bond model it may be represented by  $M\cdot CO^+$  and  $M=C=O$ .

The filled CO to empty M  $\sigma$ -donation. Filled M d-orbital to empty  $\pi^*$  - back-donation.



Now, explain what is meant by the terms synergic bonding. This is a textbook question synergic bonding I think you have studied for your exam before it is the; it is the pi bonding between the ligand.

Student: (Refer Time: 31:57).

Sorry sigma bonding between the ligand this ligand orbital and the metal orbital and pi back bonding between the metal orbital and the anti-bonding orbital of the carbon monoxide ok. It is written in the way I think you have studied before synergic bonding it is the ligand donates metal gives back. So, it is I am teaching that is what I was trying to say you. You tomorrow you will give me money that is the synergic bonding right.


(Refer Slide Time: 32:21)

Q09. The  $\text{Cr}^{2+}$  ion in  $\text{CrF}_2$  is surrounded by six fluoride ions. Of these, four are at a distance of  $\sim 2.00 \text{ \AA}$ , while the other two are at a distance of  $2.43 \text{ \AA}$  from the metal ion center. Explain this observation.

$\text{CrF}_2$ :  $\text{Cr}^{2+}$  is surrounded by 6 fluoride ions in an  $\text{O}_h$  environment.

$\text{Cr}^{2+}$  is  $d^4$  high spin;  $t_{2g}^3 e_g^1$ .

The unsymmetrical distribution of electrons in  $e_g$  leads to Jahn-Teller Distortion. This observation suggests that the  $e_g$  electrons in  $d_{z^2}$  orbital and  $d_{x^2-y^2}$  is empty.



Once you become trillionaire, I am sure some of you billionaire or whatever ok. Now the chromium 2 plus ion in  $\text{CrF}_2$  is surrounded by six fluoride ions, chromium 2 plus this is a clear cut I mean statement is given it is  $\text{CrF}_2$  we are saying, but it is surrounded by six ligands ok. It is surrounded by six fluoride of these four are at a distance of two Armstrong four are shorter and the other two are at a distance of 2.43 Armstrong explain this observation.

Student: (Refer Time: 33:09).

So, chromium 2 plus is surrounded by six fluoride ions in an octahedral environment, it is surrounded by six fluoride ion chromium 2 plus is what?

Student: (Refer Time: 33:25).

D 4 scandium titanium vanadium chromium d 4 s 2. So, 2 plus is going to be d 4 now it is going to be t 2 g 3 eg 1 right. So, the unsymmetrical distribution of electrons in eg orbital that is what we were trying to sell right. The e g orbital whenever you are having unsymmetrical feeling, then there is a possibility of further splitting of the eg orbital eg orbital can be splitted.

These observations suggest that eg electrons in dz two orbital, because the two of them are longer four are shorter two are longer little bit longer. Two longer means that directions it is getting stabilized the ligands are getting longer; that means, ligands are not coming close I think now.

I can explain little bit that question anyway, ligands are farther and therefore, z it is going to be z out right slightly z out and you are going to get dz square orbital stabilized. Ligand are far at the z direction therefore, dz 2 orbital is going to be stabilized slightly lower in energy and the electron. Since it is stabilized electron is going to go there because you it wants to achieve the stabilized state move on, that is it.