Biological Inorganic Chemistry Professor Debashis Ray Department of Chemistry Indian Institute of Technology, Kharagpur Lecture - 5 Coordination Chemistry in action

Hello, good afternoon everybody. So, we will be continuing to the fifth class on Biological Inorganic Chemistry what we are talking about. So, today's, we will be finishing the module one where we will be talking about the coordination chemistry in action. So, how we can utilize some amount of basic informations on coordination chemistry towards the goal, which is your module one, that is the chemistry of the different light processes.

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So, what we will be looking at is that, firstly, we will see that when we consider some bond is forming between the metal ion and some donor. So, we will be talking little bit about the nature of the bonds, the basic concepts, what we should have, otherwise is very difficult, how many bonds are forming at a single time, when the metal ion is getting inserted within a biological environment.

Then what are the available donor groups within a particular ligand and we all know that just from the very first day, we are talking about the water molecule, so water molecule itself is a very good ligand. So, in aqueous environment, we have seen earlier that in aqueous environment, if you can have plenty of water molecules surrounding the metal ion, when the metal ion is first entered in that particular biological environment.

So, if the metal ion is there and is a naked one or the bare metal ion, it will not remain as MN plus species like that of your AP 2 plus species or AP 3 plus species, it will try to attract as per their character, the metal ions corrector, large number of four to five to six water molecules surrounding that.

So, when those water molecules are surrounding that particular metal ion center we will get a particular geometry, the polyhedral arrangement. So, we will be talking little bit about the coordinates in geometry, how we can concept about the octahedral geometry, because in the biological world, what we will find, unlike our laboratory species or the laboratory molecule or laboratory prepared coordination compound, where we all know that in a test tube if we just simply drip a pinch of ferric chloride, we know that if the ferric chloride is giving ferric ion in the solution.

So, all the water molecules surrounding that ferric ion will come and bind to that particular central FE3 pass ion to give you 6FEO bond in geometry, which will be termed as the octahedral geometry. So, we should always have some good idea about what is the basic structure of an octahedron.

Then little bit we will talk about the redox behavior, because in most of these cases, we will find that some of these metal ions when they are not behaving for some acceptor molecule for (())(3:28) molecule in hemoglobin and myoglobin, they can also function as a redox species such that you can have a very good amount of electron transfer reactions which are required for our survival.

Then, lastly, very briefly again, the catalytic potential of these metal ions centers will be discussed. So, what do you find a very complex molecule now, I am showing you that is if this is a complex molecule and if we get the structure of that, so how we can find out, so this one, how we can find out this particular huge molecule. So, large number of amino acids are surrounding over there and little bit we have discussed about your corresponding this ribbon shape, what is that alpha helix and beta seed.

So, this helical arrangement of the protein backbone, the polypeptide backbone and you have the spear like of this particular metal ion will be showing. So, this particular metal ion, so where it is, is a three dimensional huge structure and maybe it is inside that particular structure or maybe on the surface of that particular species will be there.

So, how that particular metal ion can form all these, how the bonds are forming, whether you can have a redox behavior and the catalytic potential whether you expect from that particular metal ion or not, what is that? This is nothing but a manganese, sorry magnesium 2 plus center which is a cofactor in an enzyme.

So, because the meaning of these metal ions will start as a very good cofactor for the metal enzyme activity that means it must have some role to play for its enzymatic activity and if it is magnesium 2 plus and we all know that magnesium 2 plus cannot undergo electron acceptance and the electron donation behavior, so it will not function as a redox catalyst. So, we will talk giving some examples of all these things.

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So, the electron, the electron pairs mostly which we consider as the simplest definition for considering the negatively charged cloud if you can have and that occupies a definite but arbitrarily defined region of space relative to the nucleus is a typical definition how we can define a electron or electron pair.

So, in that particular region we call those region is occupied by the orbitals and it can have a maximum occupancy which is 2. So, a pair of electron that is why it comes, a pair of electron of opposites spin can function as a donor molecule on the atom where you are having that particular pair of electron available (())(6:21) your water molecule.

So, this particular species what you can have these two electrons, which are there you can have the pair of electrons, so these pair of electrons can be on water molecule, can be on ammonia, we all know that the ammonia is the pyramidal molecule. So, you have the nitrogen and NH NH NH on this particular nitrogen, you have a pair of electrons, so is basically pointing towards up.

So, these pair of electron can be donated to give you a coordinate bond to the metal ions center. So, that basically gives us the formation of that particular coordinate bond. So, what is that bond? It is nothing but a special type of arrangement for a covalent bond, we all know that hydrogen atom, one single species of hydrogen atom and another hydrogen atom can form a HH bond.

So, HH bond having a single bond, so bond order is 1 because the hydrogen atom having one is 1 electron and another hydrogen atom having another one is 1 electron can overlap to each other giving the molecule orbital configurations, where the molecular orbital the bonding molecular orbitals, one is the occupied orbital, another is the anti bonding orbital.

So, the bonding molecular orbital will fill with this pair of electrons. So, that bonding molecular orbital will next be available for your donation to the metal ion center. So, it can be donated to the metal ion center which can function as a acidic center or Lewis acid center. So, if we can have these ligands, so these ligands will be classifying these ligands both its electron property as well as the structural property.

So, electronically how we can classify them as it depends on the number of electrons to be donated to the central metal ions center. So, iron you have, if 6 water molecules you bring around that particular FE3 plus ion. So, each and every water molecule can donate the pair of electrons to your iron center.

Then structurally that means, how many connections you will be able to make up when nothing is available only the water molecules are available. So, when 6 such water molecules are available surrounding your iron center, so you will have to play 6 iron oxygen bond in a 3 dimensional arrangement because you cannot put 6 bonds in a plane like that of your benzene molecule, which is C6H6.

So, we have the carbon carbon bond, 6 carbon carbon bonds we placed in a plane. So, that is why the benzene molecule is a flat molecule is the planner molecule. But when you bring the FE3 plus it has the D electronic configurations and the D electrons we know they are occupying these orbitals basically.

So, these orbitals are there and it is in three dimensional space in X, Y and Z axis. So, if you have that particular three dimensional element and these D orbitals can accept those electron pairs if they are vacant. So, this particular arrangement, the polyhedral arrangement containing 6 such FEO bonds will give you a structural feature. So, the structurally you can have 6 connections in a three dimensional space, and you get a typical octahedral.

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Then when you dissolve basically just now, what do I am telling out this that water molecules are effectively complex basically to these water molecules. So, when we use some other ligand say ammonia we bring some ammonia if the coordination power of ammonia molecule is higher than that of water. So, if we add ammonia to a solution in a test tube containing say copper, we know from our school days that the copper dissolved in water, say copper sulfate taken in water,

sample of water in test tube we know a coloration So, faint green color you can have with that particular arrangement.

Now, if you put or if you add dilute ammonia. So, is concentrated is 50 percent diluted say ammonia solution and you add drop by drop. So, you will get some color change is a blue coloration due to the formation of new copper nitrogen bond instead of copper oxygen bonds which are present originally in case of the copper present in water medium.

So, what we are doing, we are doing this particular thing basically, we are going for displacement of already bound water molecules if it is a multidentate ligand it will have some other property the stability will be more but as these are monodentate ligands like ammonia we will get 1 is to 1 replacement of the individual water molecules by ammonia.

So, instead of copper oxygen bond now, we can have the copper nitrogen bonds and that basically give us the stable complexes, the arrangements for these would be stable then similar systems with non or fewer chelates, so that we will see if we can have it bidentate ligand, so bidentate ligand like and like that of your if we can have we all know that you can have NH2, NH2, so NH2 and NH2.

So, like ammonia, so, it can form so you have two lone pair of electrons. So, here also you can have two lone pair of electrons, you have the copper 2 plus, so what is this arrangement. So, we have seen that you can have the water molecules and water molecules are displaced. So, you can bring something which is ethylenediamine, so which is NH2 CH2 CH2 and NH2 and that NH2 CH2 CH2 NH2 is basically your this part, so is CH2 CH2 and NH2.

So, this can function as a multi, multi means is a base now, is a bidentate ligand. So, it can occupy two adjacent positions around these copper center, the same copper center. So, if you have water around copper, so, that will be displaced by ammonia, then if you add ethylene diamine eN, which is abbreviated as small e and N. So, ethylene diamine can also displace the ammonia already bound to this particular copper center.

So, what we get, basically we get then that there will be an increase in entropy from net increase in the number of unbound molecules because during this particular complexation reaction, what do we get during that particular complexation reaction if you say that water is there and many water molecules are surrounding your copper center then you directly add instead of ammonia you add directly the ethylene diamine, again a very dilute solution of ethylene diamine.

So, the water molecules will be displaced and this free water molecules will be released in the medium. So, the non chelating ligands that means the water, usually water that is why because in the aqueous medium in our living system also, those water molecules will be released from the coordination sphere of the metal ions.

So, already you have a coordination sphere in presence of the water molecules and those water molecules will be released. So, many number of water molecules will be released because if you attach two of these ethylene diamine molecule, the formula of the species will be CUEN whole 2.

But at the same time you will be removing four water molecules. So, many number of water molecules will be released. So, the number of particles released in the medium is more, that is why there will be a energy gain from the entropy point of view. So, the entropy will increase and you will have the stabilization. So, not only the energy contribution from the enthalpy point of view, but also from the entropy point of view you can increase the corresponding stabilization.

Then what are the donor groups you can have? So, these donor groups we can have basically, we will be talking again only three simple donor groups, one is nitrogen, another is oxygen and another is sulfur. And many biological or not biological molecules can have all these N and O when you have the simple amino acid like glycine, we will know that that NH2 end of the glycine can bound to the metal ions center like that of the other end is your carboxy end.

So, you will have a NO bidentate ligand like that of your ethylene diamine. So, like this ethylenediamine you can have NH2 CH2 COOH. So, you can have the corresponding glycine coordination in a similar fashion. So, now we see that bidentate classification is your ethylenediamine iupac name is one to ethane diamine, which is abbreviated as eN and the formula.

Then if we increase it one step further, it will be a tridentate ligand, and that tridentate ligand basically gives us a diethylenetriamine or 147 triazaheptane we call as a iupacname. So, 147 triazaheptane, remember, it is a linear one. But the corresponding one if you cyclize it, so, is

NH2 CH2 CH2 NH CH2 CH2 is a linear one, but this is a completely different one, which is known as tacn, which is triazacyclononane is the cyclic ligand. So, we will see what are the advantages of using this particular cyclic ligand compared to the linear ligand, and as we have seen the linear ligand can have advantages over the simple monodentate ligands.



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Similarly, we can have another group of ligands which are your, the Binap ligand is 2, 2 prime bis diphenylphosphino 1, 1 prime binaphthyl. So, you have the naphthly function binaphthyl function so, coupling up two naphthyl units then you can have PPH2 substitutions PPH2 so these are artificially prepared or laboratory prepared ligand these are not biological ligand, but it is a very useful ligand.

So, what is the three dimensional structure of the ligand we can understand from the particular arrangement of these atoms in this molecule. Similarly, again we know the very famous complex like that of your nickel dmg, what is the dmg ligand so you should know, how to draw the dmg structure and when one of these is a dimethylglyoxime, so two glyoxime units are there, but when it is bound to the nickel center, it is binding to the nickel center in this particular form that means one of the oxime function NOH function will be deprotonated.

Then, another very interesting group of ligand, I have chosen a selected group of ligand basically which is TP ligand, which is nothing but hydrotris(pyrazolyl)borate, tris pyrazolyl TP tris

pyrazolyl T and P from this name is considered as the TP ligand. So, is tris pyrazolyl borate or borato, so is the scorpion at ligand, so is like this.

So, is one three, so, three donor groups not like the linear one, not like the bidentate one or not like the macro cyclic ones. So, macro cycle is a cycle, but it is that that you have the boron here. So, then it is ending with the nitrogen of the pyrazolyl unit another nitrogen of this pyrazolyl unit another nitrogen of the pyrazolyl.

So, when it is coming to bind the metal ions center it is functioning as a scorpion, so scorpion you know, these are the thing it is bind, you just tag you, then the third thing will come, so is the scorpion type of binding or coordination to the metal ions center giving this class of ligand. So, these ligands can have very useful application.

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So, if we will now consider that how you prepare these solutions only one ligand is generally sometimes is a futile solvent molecules often coordinate resulting in higher coordination number. So, this is a very typical example we are looking for that if we start from here, because already I told you that you can have the coordination from 6 water molecules around the ferric ion center that means 6 are coming so like this, so 3 water molecules like this and another 3 from the top. So, center you have the iron center.

Now, the very simplest one where you can have only one ligand and is bound to a particular metal ions center is very difficult to get. But this is a typical example where we get a more complex structure, sterically hindered structure. And we get that is basically a thallium complex. So, thallium is a very big metal ion, 1 plus 1 oxidation state and it can have a affinity for forming two bonds like copper 1 CU plus but CU plus have a more standard coordination number of 2 only, is forming a linear molecule. If you have two water molecules, two cyanide ions or two ammonia, it can have a linear, copper is at the center, one ammonia and another ammonia in the cuprous state, not the cupric state.

But here if you can have these ball shape arrangement of the ligands some parts, since only two sides basically not that this like this. So, this is, if these two are perpendicular one and your metal ion will come to bind this particular nitrogen, so is triazapentadienly complex so this is the nitrogen, so nitrogen you do not have the H, so you will have a charge on this nitrogen. So, you have the overall charge 1 minus on the ligand. So, this particular nitrogen in a sterically crowded environment if it gets the metal ion like thallium it will form only a single thallium nitrogen bond.

So, this is a typical example of thallium nitrogen bond where coordination number one is satisfied. So, later on when we will talk about the myoglobin and hemoglobin, we will also find a typical example, by that time you just think of it that whether you can have a similar type of a mono dentate ligand from biological origin, which is a big, very big protein molecule or a polypeptide chain, but it can form only one bond to the metal ion center like this particular case.

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Then you can have another arrangement. So, this is a cyclic arrangement so on the tacn, so we just basically formed that particular tacn, so, this is the tacn backbone, then we can have three arms. So, ethanethiol arm on this nitrogen, second nitrogen and the third nitrogen when it is coordinating to the iron center, it is giving this particular again a octahedral arrangement and that octahedral arrangement is typically a different one because, now, we find that you can have a SSS phase and another NNN phase.

So, what is that is basically a big name basically try to remember the name because it is based on 147 triazacyclononane, but on 147 we have the substitutions which are two mercaptoethyl substitutions. So, if you have two mercaptoethyl substitutions on the NH, these are NH originally on the tacn ligand. So, you will get the corresponding CH2 CH2 SH, CH2 CH2 SH, CH2 CH2 SH, but following deprotonation this S groups will be S minus, then it is forming a complex with FE3 plus and this FE3 plus is giving this particular arrangement but 3 nitrogen can come through this particular phase.

So, this is one phase of the octahedron and the other S3 is the opposite phase. So, you get the trigonal phase, which is defined by the three sulfur donors one phase is S3 phase another is N3 phase defined by that three nitrogen atoms. But what is important, why we have highlighted one particular phase, not the other one?

The back is your sulfur. So, the triangles are of different sizes. Now, you will try to remember it, try to know it nicely and try to explain it. Why the ones triangle is bigger compared to the other triangle because it is composed of nitrogen, but it is part of the macro cyclic ring. But sulfur ends are free and sulfurs are bigger. That is why the S3 triangle is bigger compared to your N3 triangle. So, that is why you get some asymmetry within the geometry, octahedral geometry around this particular Rn center which is not symmetric like that of your (())(23:52) ferric ion.

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	Redox chemistry
The nature of the ligand do profound effect on the red	onor atom and the stereochemistry at the metal ion can have a lox potential of redox-active metal ions
	Eq. relating the standard redox potential to the observed redox potential by Walther Nernst in 1881
$Ox_1 + ne^- \Leftrightarrow \operatorname{Red}_1$	$E_{h} = E_{0} + RT/_{nF} \ln \left[Ox_{1}\right]/_{Red_{1}}$
Electrochemical techn thermodynamics but immediately precede	niques are used to know not only about the also the kinetics of chemical reactions that or follow ET (e.g., protonation or substrate

Then we will just quickly see the redox chemistry that the nature of the ligand donor atom how the nature of the ligand, the stereochemistry can porter the corresponding behavior of the metal ion for electron transfer. What is that electron transport, because if you have an oxidized species OX1 can accept n number of electrons giving rise to your reduced form and we can have a equation, what is that equation, relating the standard redox potential which is we all know is the famous Nernst equation.

It is Walther Nernst who gave that particular equation in 1881, see around 140 years back we have seen that particular arrangement for this particular equation of Nernst question. So, this is the form. So, this is in square bracket, this is, some error is there So, is not, is OX1 is in square bracket, red one is also the reduced one species is also in the square bracket, such that you can correlate the cell potential with that of your standard potential which is your E0 value.

So, why do we do this? Experimentally we can measure the E0 values and we can have some idea about the thermodynamic electron transfer behavior but also the kinetics, the rate of electron transfer also we can see and sometime we can have something which can go for your electron transfer behavior protonation or substrate binding following your electron withdrawal or electron donation to the system.

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So, these are some very useful examples of these reactions, the redox reactions only we can have the reactions in the gases because in the biological world we will find that many such molecules will be releasing. So, the NO also our system, our body can also produce NO, so the reactions in the gases the electron transfer reactions, we should know, because we all know that the oxygen is also a gas and we accept oxygen through myoglobin and hemoglobin.

Similarly, this can oxidize some organic substrate and in solution we all know the typical reactions in your inorganic chemistry classes you have seen these that the reaction between iron and chromium or the reaction where the chromate is used as an oxidizing agent, but sometime in solids also like your batteries, we know that the batteries are solid material. So, the batteries, these are lithium batteries this is a typical example can be given to you as a lithium battery. So, some reaction whether is a anode reaction or cathode reaction, we can have such reactions, where it can react with that of your LiCoO2 with the carbon, simple carbon carbon powder or carbon nanoparticle or carbon tube, giving you a lithium carbide and your cobalt oxides.

So, in that tetravalent state or some other oxidation state can be in the lower oxidation states also. Similarly, the ferric oxide can also have, but how we can correlate these for your biological systems. So, in the biological system, we have seen somewhere that we are talking about WOC, which was your water oxidation center. So, if that water oxidation center is only discussed there, that is the manganese bearing center. So, you have to know a little bit about the manganese biological chemistry.

So, you can have four manganese centers of different oxidation state, one is the in the pentavalent, others four, three are tetravalent. When they react with water, basically, this particular reaction is responsible for the liberation of your O2 molecule. So, while doing so, not only it is changing the oxidation state of the system, so you are all these oxidation states of the four manganese are getting reduced by one step. That is why is the four electron transfer reaction and that four electron transfer reactions, basically, manganese centers are getting reduced.

So, it is a water oxidation reaction, where your two water molecules will be oxidized to generate the protons as well as the dioxygen molecule from that particular medium. So, that is why we know that the photosynthesis is always associated with liberation of dioxygen molecule or water molecule.



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So, the reactions in aqueous solution always we considered that and we find that somewhere we will get that the influence of the complexes in reactions. So, whether this particular reactions the

complexation reactions, whether that can be beneficial or not, that will also see in reference to that of your reaction of the hydrogen for electron transfer.

So, the standard reduction potential for hydrogen we all know is considered as the 0.0 volt. But if you change the pH value, but as a pH7, which is our biological pH, our blood pH can vary from 6.8 to 7.2. So, in that particular average value of 7, we see that the reduction potential is a negative one, so it is minus 0.421 volt.



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So, the biological redox spectrum is a little bit complicated. So, we can have a huge range of these molecules do not worry for this particular diagram, we will come again and again with this, but this is the introduction part that how we can handle the electron transfer reactions with respect to the E0 values. The thermodynamic quantity for your electron transfer behavior.

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,			Iron-porphyrin complexes
Compound	I	E_0' (mV)	of catalytic biochemical
hexaaquairon(II/III) [(H ₂ O) ₆ Fe] ²⁺¹³⁺		771	processes
tris(2,2'-bipyridine)iron(II/III) [(bpy) ₃ Fe] ^{2+/3+}		960	
hexacyanoferrate(II/III) [(NC)6Fel4/3-		358	
trisoxalatoiron(II/III) [(C2O4)3Fe] 4/3-		20	
			· · · · · · · ·
emoprotein iron(II/III) emoglobin syoglobin di kasawi tara (UDD)	170 46	Axial : His/- His/-	mino acid ligands
temoprotein iron(II/III) temoglobin nyoglobin orseradish peroxidase (HRP) vtochrome <i>a</i> .	170 46 -170 400	Axial : His/- His/- His/- His/-	mino acid ligands
emoprotein iron(II/III) emoglobin yyoglobin orseradish peroxidase (HRP) ytochrome a _j ytochrome c	170 46 -170 400 260	Axial : His/- His/- His/- His/- His/-	mino acid ligands
temoprotein iron(II/III) temoglobin nyoglobin orseradish peroxidase (HRP) ytochrome a _j ytochrome c ytochrome b ₅	170 46 -170 400 260 20	Axial : His/- His/- His/- His/- His/Ma	mino acid ligands
emoprotein iron(II/III) emoglobin ayoglobin orseradish peroxidase (HRP) ytochrome <i>a</i> , ytochrome <i>b</i> , ytochrome <i>b</i> , ytochrome P-450	170 46 -170 400 260 20 -400	Axial : His/- His/- His/- His/- His/M His/Hi Cys ⁻ /-	mino acid ligands

So, we can have also the biological molecules where the hemoproteins we will be using and the E0 values and we will be considering these with respect to your hexaaquairon species. The first one is your hexaaquairon species, how we can go for the other ligand bond species, the hexacyano, the trisoxalatoiron and all this.

So, iron-prophyrin, the heme protein can also involve in the catalytic biochemical processes, a large number of biochemical reactions we can have from hemoglobin to cytochrome p450. And we will see all these one after another in terms of its corresponding E0 values and the environment, the coordination environment. So, if you change the coordination environment we will definitely go for a change in the corresponding electron transfer values or that redox potential values.

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So, in conclusion, what we have understood from this particular class that how important is your the corresponding bond formation between metal ion which is MN plus with that of your L. So, metal ion ligand interaction can be assessed by knowing the E0 value, by knowing the stability, by knowing the structure.

Then the electronic and structural effects what we can have in the coordination sphere. So, that is also important and we can have the secondary interactions like the binding of DMG, we can have hydrogen bonding interactions. And finally, the concept of electro-protic equilibrium where you can have the electron transfer as well as the proton transfer in that particular medium. So, we have seen all these four things nicely.

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So, we can have again the references from Wikipedia and the books of Crichton. And lastly, thank you all for your attention. Thank you very much.