Inorganic Chemistry of Life Principles & Properties Prof. C. P. Rao Department of Chemistry Indian Institute of Technology, Bombay

Lecture - 10 Stability and lability

Welcome you all to the next lecture on the Inorganic complexes or primarily the coordination chemistry aspects pertinent to the this particular course which is Inorganic Chemistry of Life.

In the previous class we have looked at various characteristic of the coordination complexes in terms the ligands and towards the end I talked you about spectro chemical series and the effects of the ligands on the splitting energy. So, the highlights split to the least this is compared to the oxo ligands, compared to the nitrogen ligands, compared to the carbon ligands. I also mention to you that these can be explained not by the electro negativity principle, but by their pi acid, pi based characteristics.

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Now, so, this junction let me introduce what is the acid and base mean by. So, the metal ion is considered as a Lewis acid and the ligand is considered as Lewis base ok.

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Melalion: Lewis acud Ligand : Lewis base

So, what is Lewis acid and what is Lewis base? So, I am sure everyone of you know that what is a Lewis acid what is Lewis base, but nevertheless to bring a recapitulation let me tell you that Lewis acid is the one where you will find a low line empty orbital, means an orbital which is empty which is ready to accept electron pair. On the other hand Lewis base is the one where you have a filled electron or electron pair which is higher energy therefore, is ready to donate. So, ready to donate ready to accept.

So, accepting is coming to the Lewis acid donating is coming to the Lewis base character of this. And this is an important concept that you need to keep in mind when we are looking at. All the metal ions are Lewis acids and all the ligand on Lewis basis. So, ligand is coming from for example, in the biological systems. What are the ligands? We have seen the carboxylate group is a ligand, a thiol function is a ligand, a phenolate function is a ligand, an a mean function is a ligand.

So, all these kinds of ligands are all the Lewis basis. And the metal ions of course, we have the ion 2 plus, ion 3 plus, o copper 2 plus, or zinc 2 plus, nickel 2 plus, manganese 2 plus all of these So, therefore, this should be clear to you when you are studying the inorganic chemistry of life o biologically organic chemistry aspects. So, therefore, I have introduced this concept.

Please do a bit of exercise. So, that you get familiarize with these by looking at some of the examples these ok. What I explained to you earlier the highlights the weakest in terms of splitting energy and the carbon ligands like cyanide in carbon monoxide at the strongest to split the binding energy. And therefore, the once which split large will try to impose pairing of the electrons whereas, those which split to less extent will not impose any bearing at all.

So, therefore, you will have the high spin complexes coming from these ligands and loose pin complexes coming from these ligands ok, and that is one thing is good enough.

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Inorganic Chemistry of Life					
Polarizability: Hard and soft					
•The polarizability of an atom is its willingness to be distorted field generated by the neighbouring atom or ion.	l by the electric				
•Small & highly charged cations have greater polarizing abili	ity				
•Large & highly charged anions are easily polarized	Ionization limit				
•High IE, smaller size, low polarizability makes Harder •Low IE, larger size, high polarizability makes softer					
•The lighter atoms of a group are chemically harder •The heavier atoms of a group are chemically softer	(a) (b)				
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Now, there is another aspect that we need to understand about the inorganic complexes or coordinate complexes. So, the coordination complexes inorganic complexes what we need to know additionally is that the hard and soft character of both the Lewis acid as well as the Lewis base. Just now I have already defined to you Lewis acid as well Lewis base.

So, to explain its hardness and softness, we need to look at the following aspects. So, let me the note of caution this hardness and softness is not a mechanical hard mechanical soft it is a chemical hard and chemical soft aspects of that which is dependent on the polarization as well as the polarizability.

So, atom is the one which is having a nucleolus and electronic cloud. So, if the electronic cloud is distorted a lot then the size of the ion will be increasing and that becomes more softer in a chemically ok. And on the other hand if you have a smaller size smaller

electron cloud then you have a strong you know capturing by the nucleus, so they if such kind of things will tend to be hard chemically hard in nature. So, this means what is important is polarizability and polarization.

So, when you take an ensemble of a molecule or an atoms a each atom or each molecule this is the field of all the other molecules So, what field? Electric field of all that. So, therefore, this electric field try to distort the electron density of the central one. So, if it is able to distort quite well it is you know its ability to for distortion is quite lot and that is referred as the polarizing ability of this.

Polarizability to what extent can atom can get polarized, an ion can get polarized, a molecule can get polarized - by the surrounding electric field which is generated by the neighboring atoms neighboring ions neighboring molecules. So, therefore, you can take it as kind of a rule of thumb.

Small ions or small atoms highly charged cations they have a greater polarizing ability, but they will not get polarized they will polarize others they will not have, they will polarize polarizing abilities more, but polarizability is alone. Large and highly charged anions are easily polarized so that means, they get their polarizability is much greater on this. So, similarly if you can look at higher ionization energy, small size, low polarizability these are referred as harder, this is chemically harder.

Those having a low ionization larger size and a high polarizability they are softer. So, as I said both the Lewis acid can be harder, Lewis acid can be softer, similarly Lewis base can be harder, Lewis base can be softer. And as I said the metal is called the Lewis acid ligand is called the Lewis base therefore, you are looking at the combination of Lewis acid and Lewis base.

So, therefore, the hard acids will combine strongly with a hard bases and soft acids will combines with the soft bases. So, hard hard combination is stronger, soft soft combination is stronger.

Generally the lighter elements of a group when you look at the periodic table a group they are chemically harder and the ones which are down which are heavier in that group they are all softer in that kind of thing. So, same thing is explained by the diagram over here which compares the polarizability with respect to the ionization, so the ionization polarizability, ionization and polarizability. So, the greater ionization potential with the lower polarizability, lower ionization potential with greater ignitability, that is all the thing that we need know.

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So, this can be further explain by using the HOMO, LUMO kind of a idea. See acid the acid will have an empty orbital, and this is what you can look at. And the base have a failed one.

So, and, so this becomes hard when you have a greater gap and so, therefore, you can see that the hard base with the soft becomes you need a lot of a energy difference. A hard acid with a hard base does not require much of a energy variation so that means, energy comparability or low lying orbit the empty orbital and the fill orbital should have a comparable in their energies, if they have comparability in their energy of course, symmetry also important then you will have a easy overlap.

So, therefore, the hard acid hard base will have a better overlap. Whereas, hard acid hard base with a soft acid will not be so favorable ok, and similarly soft acid with a soft base there is a favorability.

So, therefore, soft acid soft base combination is better because their empty orbital and fill orbital respectively or in parallel in the reasonable energy comparison, in case of hard acid hard base again the empty orbital and the filled electron pair have a comparable energies, all that you need to keep that in mind is. The second thing that you keep in need to keep in mind is if the HOMO to LUMO gap is large then it is hard if the HOMO to LUMO gap is smaller then it is softer; So, harder and softer harder and softer kind of a thing that you can look at.

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So, this can also be a talk in a little different way this is nothing, but the difference in the ionization energy of a neutral atom and its anion. So, what is the ionization energy of the neutral atom? What is the ionization energy of its anion that difference? If difference is large then its hard if the difference is small it is a soft, just like the HOMO LUMO difference is small it is soft, ok. So, this can also be quantified by using the Pearson absolute hardness scale eta, so ion minus A by 2 ok, the HOMO energy and LUMO energy by 2.

So, it is, so hard acids tend to combine with hard bases preferentially soft acids tend to combine soft bases preferentially why I just now a explained to you the reason is that the hard acid having a empty orbital and the hard base is having a fill orbital these two orbitals have very comparable energy. Similarly, soft acid having empty orbital soft base is having a an empty or filled orbital these two having a very similar energies.

So, therefore, such kind of cases will give more you know preferential binding. So, soft acids of base combination is stronger, hard acid hard base some combination is again stronger in the complexations, ok. So, just give an idea as I said that the ions with the greater charge smaller size will be tend to be hard having the smaller charger and greater size of this will be softer and the anions more and more anionic charge will be softer more and more catatonic charge will be harder. So, just keep in that mind you can divide these into hard and soft with some kind of a border line cases.

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As you can see the it is a plus 1 sodium, lithium, potassium, magnesium, calcium, manganese, chromium etcetera. Border line you have a zinc, copper 2 plus, nickel etcetera and softer copper plus silver plus gold plus thallium plus they are all very large in size and smaller in charge.

So, this for large in size in smaller in charge, they will be tend to be more softer and the those which greater charge in smaller size even if the charges smaller the sizes also smaller then again hard, so they are hard soft. So, this is within that acids and this part is within the basis or ligands or anions. So, this is the Lewis base and this is for the Lewis acid.

So, you can see that oxygen based one water ROH, OR minus they are all the hard side these are all oxide based ones then if you have a nitrogen based ones there somewhere in between or border line for intermediate. Then if you look at the sulphur based ones or carbon based ones these are all softer that we have seen already too, ok; So, therefore, hard base hard soft base hard acid soft acid. I hope this is clear to you. So, towards the end what you need to remember is the size and the charge if the size is large and the charge is smaller softer sizes small and charge is greater again is a harder, whether it is a anion or cation kind of thing, so you need to look at both of these, ok.

So, we have to try to finish quite a few aspects of this then how do we try to understand this into the metal ions into when you put them into biological systems or when you put into the biological you know systems like proteins and enzymes.

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Inorganic Chemistry of Life
Metal ions biology
Metal ion in the vicinity of biomolecular system
Stability: •Interaction, binding and thermodynamic stability of the ion-biomolecular complex formed
•Close proximity of the metal ion center can be visualized as a coordination complex that we generally treat in inorganic chemistry
• Follows coordination principles
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So, what you look at there? One is that the metal ion sits in the metal of protein or metal of enzyme and does not sit ideally as I have shown you already is bonded to the side chain, residuals of the protein and form say coordination complex. So, it interacts it binds therefore, it is a thermodynamic stability is associated with this, and of course, the surrounding groups which have coming from the protein will also apply certain kind of criteria conditions on the metal ion in terms of the geometry and in terms of the crystal fields splitting other kinds thing, so it all follows the coordination chemistry principles what you want.

So, now, what we saw is the situation where you have a metal of protein you have metal ion sitting in this that is not sufficient enough that tells you about the only thermodynamic, but what you require is kinetics. Metallo enzymes are what? There are catalytic, they show reaction, they are not just like that sitting ideally there. So, therefore, the metallo enzymes and metallo proteins having a metal ion metal complex inside the protein and the protein comportment, but they do show a function.

To show a function you need the reactivity, and this is the reactivity which we are talking about in terms of the lability aspect of it. So, this is a absolutely important.

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Again it depends on the what is a find of a coordinations sphere that you have what is the charge of the metal ion centre, what is the size of the metal ion centre and what is the protein influence all of these again influence influence the lability, all those parameters which are influencing the stability also influencing the lability as well in a different way.

So, one of the ways of understanding the lability is that suppose you have a coordination complex having a ligand bonded to the metal centre if such a ligand can be exchange by an outer ligand or outer act ion or outer molecule and the rate at which it can be a exchanged is the one which you can talk in terms of the lability or rate exchange or rate of reactivity. So, all the these things.

Generally one would measure you take a metal ion with a coordination sphere of water and you take a labeled water in the bulk and see how well a labeled water is exchanging with the water which is bound to the metal centre that kind of a rate. So, the greater the rate of exchange between the coordination sphere and the bulk is the kind of rate of exchange that you can explain in this. So, the facile other kind of a things is redox. So, during the reactions large number of reactions in metallo enzymes the metal ion undergoes the redox not necessary in every case, but large number. So, metal ion can go oxidized can undergo reduction, so redox process will have. Also how well the redox process is favoured by the protein enzyme, is they are still bound to the enzyme, can the enzyme allow the next higher oxidation, can the enzyme allow next lower oxidation state.

So, if the enzyme can allow both of these then you have a facile redox process in these things too. So, they capability to act as a Lewis acid into activate the how well they will activate the organic moiety. In this organic moiety is the protein. And organic moiety is the small molecule which comes and binds to the metal centre for activation or for recognition purpose, all of these are important in the logical aspects of that.

So, we have looked at the stability, we have looked at the lability. So, let us look at the stability aspect with their little more quantitative aspect of it.

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There, that the y axis is the log of k formation. So, that is formation constant the logarithmic value; that means, 10 powers are taken by logarithmic. So, they becomes the 3 means power 3, 10 power 6, 10 power 9, 10 power 12 and log k will become 3 6 9 and 12 and you take these ligands and add these ions and all of these are taken as a divalent divalent ions. So, Ba 2 plus Sr 2 plus, not the Ba atom Sr atom calcium atom is a ions.

Now, if you add this one and you will form some kind of a complex. So, take oxygen based the black one here it starts from here and as you go from barium to strontium to calcium to magnesium to manganese etcetera etcetera its going and increase into the maximum at copper and this decreases. Now, if you take ethylene diamine nitrogen ligand it is starting from somewhere much lower than this and then increasing here, and if I take the one nitrogen ligand other oxygen ligand are combined.

So, as you can see in all the cases as you go from left to the right there is a increase in the formation energy, of the formation constant in all of these and it goes to a peak value around the copper and then goes down I will explain you this in a while that is too with all this. So, we have taken oxygen base ligand, we have taken a the 2 nitrogen ligands, we taken 1 oxygen, 1 nitrogen, 2 nitrogens and then 1 nitrogen, 1 sulfur.

As you go from oxygen is a very hard kind of a thing and when you go to the next one having 1 oxygen, 1 nitrogen little bit of soft character is introduced. When you go to the both nitrogens little more soft character than the oxygen is introduced, when you go to the 1 nitrogen and 1 sulfur you see here 1 sulfur 1 nitrogen and then much more soft character. So, that as the soft character is increased that is the formation constant is gone down and on this side the formation constant is gone up you see that. So, these are barium strontium calcium magnesium and these are manganese ion cobalt nickel.

So, therefore, transition metals behave differently because of their d electronic configurations of this. So, this kind of a stability or is explained by Irwing William and this is known as the Irwing William series of divalent cation things. And this can be understood from the following kind of a ionic radii plots and the lattice energies radius versus the hydration energy of this.

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You see that its going down as you add 1 electron, 1 electron, 1 electron etcetera go into the d 5 system, again d 6 onwards go down and the minimum that is coming over here. So, therefore, it is based on the electron connectivity in the d system that is all you can say and then goes back to this.

So, if you do not have this 5 orbitals, then filling one one each then followed by the second one you would have got like you would have got this along with this particular the dotted line. The other one is that if there is no the spin problems then you would got into these one. So, therefore, this kind of a ionic radii or the lattice energy or hydration energy can explain.

So, here lattice energy as you see it is exactly the reverse of this one and goes down and again reverse. So, the maximum value, here obviously, in the negative side minimum value and maximum value and that is why what you are finding in a transition metal. So, in the transition metal it is dependent on the d electron filling. So, therefore, you see the kind of a trend that you see here, so this kind of a trend ok.

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And we talked about the lability just this gives you a quantification the lability.

Let us look at the top tire here the top yeah before going to that let us see this scale the scale centre point is 10 power 0, as you go right side 10 power 2, 10 power 4, 10 power 6, 10 power 8, 10 power 10. What is this? This is rate. Rate is what? Per second, so rate is per second. So, this is a value per second. So, how do we understand? As I told you earlier you take let us say an aqua complex put into a d 2 o and see how the d 2 o is exchanging with the water or put into a o 18 water and see how the o 18 is exchanging with the metallo centre.

So, if you look at the alkali ions they are all having very high rate of exchange and you take alkaline earth ions divalent ions they have little bit lower, then you look at the some of the trivalence etcetera they have much lower. So, as this charge increasing their lability is going decreased as you go from here to here to here and as you go to this particular you know within the group within the group as you go from lithium to sodium to potassium to rubidium to cesium the rate of exchange is increasing.

So, what is changing? Not the charge. What is changing? It is the size. So, as the size increases and the charge remains the same that you have increase in rate of exchange. So, in another words in any of the group as you go from top to the bottom the size of base is increasing, this the charge is kept maintained constant. So, if you maintain the same

charge and the size as you go down the group then you have an increase in the rate of exchange of the reaction in that.

Similarly you can see magnesium calcium barium etcetera. You can see that again in the alkaline earth ions again the change we will explain the same kind of a rate of a rate of exchange.

So, now coming to some a transition metal ion here you can see some of the ions are in this side; that means, 10 power minus 2, minus 4, minus 6, minus 8, minus 10, this is not plus and this side is a plus 1. So, you can see that some of the ions which are there here, this is chromium 3 plus and if you look at the chromium 2 plus the chromium 2 plus is somewhere here. So, huge difference between chromium 2 plus and (Refer Time: 24:57). You see cobalt 2 plus here and cobalt 3 plus is not shown here, but it will be somewhere in this range this region.

So, therefore, we know that the chromium three is a very inert chromium 2 is very a labile. Similarly ion 2, ion 3 ion 2 is somewhere here, ion 3 is somewhere here. So, very close to the 10 power 2 and this is very close to the 10 power 6 or 7, there is about 10 power 4 difference between ion 2 and ion 3. That is why ion 2 is labile and ion 3 is inert. Cobalt 2 is labile, cobalt 3 is inert chromium 2 is labile, chromium 3 is inert ok.



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So, all of these so, you can see that how do you quantify the liability as a complexes.

So, how we quantify the lability of complex? How do we quantify the stability is a complex? Stability the complex is quantified by delta G is minus nFE. So, the greater the minus value of the delta G naught this E take is delta G naught minus nFE naught. So, therefore, if it goes by this more and more negative then it is more and more more feasible, more and more a stable kind of thing as you know from thermodynamic.

From the kinetic lability that is this can be quantified from the crystal fields stabilization energy as the reactant minus the crystal stabilization as activated complex and this will give a measure. If this value is positive is labile more positive more labile less positive less labile, but if it is negative it is inert.

So, the opposite to labile is inert. So, labile very fast exchange inert is very slower change or lower change kind of thing. So, labile and inert are the two terms which used for kinetic and feasible non feasible at the terms which we used for the thermodynamics, so thermodynamic aspects of it and kinetic aspects of it too.

Lability of complexes						
	High Spin	High Spin	Low Spin	Low Spin		
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7		
d ^o	0	0	0	0		
d1	+0.57	+1.28	+0.57	+1.28		
d ²	+1.14	+2.56	+1.14	+2.56		
d ³	-2.00	-4.26	-2.00	-4.26		
d ⁴	+3.14	-1.07	-1.43	-2.98		
d ⁵	0	0	-0.86	-1.70		
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Let us look at this particular table for a while this particular table is given for different d configurations d 0, d 1, d 2, d 3 etcetera etcetera and it is also given for different spin states as well as the coordination numbers. So, there are three parameters spin state, coordination number and the d configuration there are 3. So, it is a kind of a 3 dimensional plot kind of thing. So, if you take the coordination number 5 you see these are the plus values that means, they are labile, this is a minus value that means, inert and

this is labile. We see there are same high spin with the coordination number 7 these are labile and this is inert.

So, similarly you can gauge which are the labile which are the. So, almost all d 1 d 2 for all the low spin high spin 5 and 7 they are all labile, and you go to the d 3 they are all inert moved from the high spin, and low spin and then d 4 is again a labile only for 5 coordination, but inert for the other one. So, it is not only dependent on the number of electrons present in the d, it also depend upon the number of coordination number as well as the spin state of it.

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Lability of complexes							
	High Spin	High Spin	Low Spin	Low Spin			
System	C.N. = 5	C.N. = 7	C.N. = 5	C.N. = 7			
d ⁶	+0.57	+1.28	-4.00	-8.52			
d ⁷	+1.14	+2.56	+1.14	-5.34			
d ⁸	-2.00	-4.26	-2.00	-4.26			
d ⁹	+3.14	-1.07	+3.14	-1.07			
 D ¹⁰	0	0	0	0			
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So, continuing to the same thing to d 6, d 7, d 8, d 9 etcetera, you can see that d 6, d 7 and for the high spin their this and high spin of this coordination number 5 coordination number 7 both of these are labile.

But when you go to the other part, that is the low spin part for the 5 and 7 that different. So, that mean because the electronic configuration is different d n is same, but electronic configuration is different. So, compare to d n you need to give importance to the electronic configuration as well and the coordination number, so all these are important. So, for when it comes to the d 8 all of them are inert all of them are inert. We come to the d 7 the 5 coordination, 7 coordination high spin or labile and 5 coordination low spin is also labile.

But a low spin is 7 coordination is again inert. So, therefore, you can see the inert and the lability is explained by the difference in the crystal field stabilization energy difference between the reactant and activated complex. I hope you just read a bit the from the known coordination chemistry things to make yourself familiar with this.



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And let us look at this one, this will explain you the kind of a thing labile and this is fast, this can be exchanged very easily and this is again labile and fast is going to be exchanged very easily too and these are the some other things.

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So, what we need to learn at the end is that in this particular class the let us take metal ion and water, water bonded to metal ion came polarize the H bond and give H plus and this depends on the what kind of a metal ion you have. If you have a calcium 13.4 pKa, manganese 11.1, copper 10.7, zinc 10.0.

So, from 14 pKa it goes to 10 pKa, that means, it becomes much more labile and can push the proton out. Similarly an imidazole bond one in the cobalt, nickel and copper. So, this means then when some other ligands are bound to the metal ion their polarization the OH bond varies and the stronger Lewis acid will polarize better and there can become instead of NH 2 as OH, instead of NH 2 as NH. So, such kind of species are dominant during the reactivity and I will explain when it comes to there, but at the time you should keep in mind the pKa.

So, with this kind of thing I will try to close for the coordination chemistry perspectives required for this particular course. And then in the next class I will talk to you about what kind of techniques are used for the gazing the inorganic ions and elements in the biological system. And so therefore, please sort of revise your coordination chemistry abilities using this as a background and going to the some of the very simple text books you can look at and then try to make yourself familiarize with this.

Thank you very much.