Fundamentals and Applications of Supramolecular Chemistry
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Week 08
Lecture 37

W8L37_Supramolecular chemistry of complexation of Anions

So, hello everybody, let us now continue our discussion on anion binding. So, today we will be discussing the factors that govern anion binding. We have already looked in detail at the factors that control the binding of cations with different hosts, and what we realize is that the concept of pre-organization is important, which we will revise again now.

So, the concept of pre-organization was found to be extremely important when it came to the binding of cations with different hosts. Number 2 was the electrostatic complementarity, which was the next important factor, and the third important factor was the solvation dynamics. That means you have both the solvation of the guest and the host, and it is necessary to desolvate the cation before it can effectively complex with the host to form the host-guest complex.

So, pre-organization, electrostatic complementarity, and solvation dynamics were very important to the binding of cations with a suitable host. Now, when it comes to anions, the discovery of anions as guests, this work can be traced back to 1968 when H. E. Simmons and C. H. Park actually started looking at anion binding in a series of molecules called kapatinands.

So, let us look at what these kapatinands look like. So, these are my kapatinands, where we have the bridgehead nitrogens.

These are the bridgehead atoms, and they are protonated. So, first of all, it is preferable to have a cationic host or a neutral host that has the electrostatic complementarity to bind anions. And here n can be equal to 0, 1, or 2.

So, we have 1, 2, 3, 4, 5, 6, 7, 8, 9. So, if n is equal to 0, the number of bridgehead atoms is 8; if n is equal to 1, the number of bridgehead atoms is 9; and if n is equal to 2, then the number of bridgehead atoms is 10.

And number 2, we need large-sized hosts, keeping in mind that generally, anion size is greater than that of cations. So, these two features have to be kept in mind when we are going to design a suitable host that will function in a complementary manner with the anions, which will be the guest molecules.

So, there are some important things we need to keep in mind before we consider anion binding. Anion binding is going to be more challenging compared to cation binding because anions are relatively large in size, and they can also come in different shapes and sizes. In the case of cations, we preferably had spherical-shaped cations, which means we had a positive ion that is either, divalent, monovalent, or trivalent.

But in the case of anions, we are going to have different shapes and sizes, and the charge density distribution is going to be different; therefore, this will affect or influence the nature of binding of the anion with the different cationic hosts. The second thing we have to keep in mind is that when you have a cationic host, you also have the counterion associated with the cationic host.

So, now you have two different anions: one associated with the cationic host and the other the anion of interest, which has to preferably bind with the cationic host. So, there is now going to be a competition between these two ions, and essentially what the binding constant indicates is the preference of one anion over the counterion, which influences the binding processes with the cationic host. So, these are some of the challenges that anions will face, and the second important problem we have is that anions have strong solvation.

So, there is a high solvation energy associated with putting an anion in aqueous solution or in a particular solvent. So, these solvent molecules have to be removed before the anion is free to effectively get encapsulated by the neutral or cationic host. The third important thing is the pH of the solution, which plays a very important role.

Why? Because of the operating pH in which the experiment is going to be performed, the anion should exist at that pH, and also the host has to be protonated. Either it should be partly protonated, or we can have a neutral host to start with.

We can have either a partly protonated host or a completely protonated host, which is of a cationic nature. So, the pH at which the host exists may not necessarily be the pH at which the anion will exist, because at low pH, the anion will get protonated and form the neutral species.

So, there is also a competition of pH here, and that is a very important factor when we want to study anion binding kinetics or anion binding thermodynamics with neutral or cationic hosts. And keeping these things in mind, let us slide right down. So, the important factors of consideration are: number one, anions come in different shapes and sizes.

For example, we can have spherical chloride, bromide, iodide, and fluoride. We can have the linear CN^- and the linear azide. We can have the trigonal planar carbonate ion and nitrite ion, and we can have the square planar $[PtCl_4]^{2-}$. We can have tetrahedral anions, for example, sulfate and phosphate. We can also have perchlorate, perbromate, and iodate.

We can have octahedral anions like PF_6^- or $[FeCl_6]^{3-}$, and we can also have biologically relevant phosphates, for example, $[P_2O_7]^{4-}$. Additionally, there are the oligomers of these phosphate ions, which are biologically relevant in nature as well.

So, we can have all kinds of anions of complex shapes and sizes, and all these anions would like to have a suitable host that can effectively encapsulate them and form a supramolecular host-guest complex. The second factor we need to keep in mind is that the anions have higher degrees of solvation energy, and energy must be spent for the process of desolvation.

For example, the delta G hydration for the potassium ion is around 300 kJ/mole, but it is minus 465 kJ/mole for fluoride.

This is because of the higher charge density. That means the amount of electrons per unit volume, which refers to the charge density, is much higher for fluoride because fluoride is a small anion, and therefore the charge density residing on the surface is greater compared to that of a potassium cation. So, it is associated with such a high magnitude of solvation, and this magnitude of solvation energy drops from -340 to -315 kJ/mole for the large-sized cation that is bromide.

The third important thing is that the anions stay deprotonated only in a small range of pH. The receptors or the host molecules might not be completely protonated in this pH range in which the anion exists in the desired form.

Okay, so this is something that has to be kept in mind, and the fourth most important point is that the anions are coordinatively saturated. That means they have the necessary coordination around them. So they are coordinatively saturated, and they bind through weak interactions, like hydrogen bonds and van der Waals interactions.

So, it is of interest to enhance the binding of anions with the cationic host while employing, for example, stronger hydrogen bonds and stronger interactions so that the binding is much more efficient. And also, to start with, let us take an example of the binding of an anion.

Now, the binding of an anion, unlike that of a cation, does involve a conformational change. For example, the kapatinands are not pre-organized hosts. Ok. So, there is a change in conformation of the kapatinand when it binds with the chloride ion. So, let us look at this conformational change.

To start with, this is the conformation we have; this is an anion. We have 1, 2, 3, 4, 5, 6, 7, 8, 9. So, when we have this 8, 8, 8, this is 1, 2, 3, 4, 5, 6, 7, 8, 9, but when we have the 8, 8, 8, there is no binding. So, you can see this is the out-out conformation; the N-H is outside, but now this is the in-in conformation.

So, there is a change in the conformation of the kapatinand, where the anions were initially present surrounding the cationic host, but now they are pulled into the cavity, where the anion is stabilized by the [N+H]Cl- hydrogen bond.

This is the charge assisted. So, when you have this kind of hydrogen bonds, then there is stabilization which takes place. So, what is now proposed is that we need to design the anions and cations that are complementary to these anions. The chemical design in anions post-binding is very important. Number 1 is the negative charge on the anion.

So, to start with, we know that because electrostatics plays a role and electrostatics is non-directional in nature. Therefore, if you have, say, different anions present in solution, then both the anions—say you have two different anions—will be attracted towards the host because the anions are non-directional in nature.

The interactions are electrostatic, which are non-directional in nature, and therefore there will be no selectivity observed, to start with, if you have a mixture of anions, particularly of the same shape and size.

For example, if you have fluoride, bromide, or iodide, then the chances are that all these anions will be attracted towards the host simultaneously. But what has been observed in the case of kapatinand is that when you have the [8.8.8] kapatinand, there is no binding, but when you have the [9.9.9] kapatinand, this is the binding constant for chloride, and when you have the [10.10.10], which is a larger sized host, it binds chloride, bromide, and iodide, but with no selectivity.

So, this is the problem. Now you have a much larger host, which has a bigger void. And if you have different anions present in the solution, for example, chloride, bromide, and iodide, then it will be able to bind chloride, bromide, and iodide with equal efficiency, and therefore there will be no selectivity observed.

Because, to start with, the anions have a negative charge, they are spherical, and they are attracted to the cation via electrostatics, which are non-directional in nature. Therefore, we must see that in order to have selectivity, you will actually have to play with the solvation processes or the cationic host so that you can achieve preferential binding. So, this is a challenge with anions.

Number 2 is whether we can look at the Lewis basicity. Now, the vast majority of anions, we know, are Lewis bases because they have lone pairs of electrons, okay. And so, what we can have now is that we can have the host that has Lewis acidic sites, for example, boron, mercury, or tin, which can now coordinate with the Lewis basic sites and form host-guest complexes. And these kinds of interactions are called anti-crown interactions.

So, what we can now see, for example, is that we can have this kind of host when mercury is the Lewis acid, and we can add the bromide anion. It has been observed that the bromide now interacts with the mercury atom, and it sits in a pyramidal geometry. The equilibrium distance between mercury and the bromide ion is 3.1 angstroms. A true covalent bond between mercury and bromine is 2.54 angstroms.

So, this kind of non-covalent association takes place, and these are referred to as anti-crown interactions, where you have a Lewis acidic site in your host that can interact with the Lewis basic site, for example, anions, and form this kind of host-guest species. The nature of the binding of the anion actually depends upon another very important factor, which is the contact surface area, because these have electrostatics as the primary driving force.

Once the anions come in the vicinity of the host, they would like to maximize their contact with the host. Therefore, the surrounding surface area becomes very important, and one should be able to polarize the electron density of the anion to effectively complex the anion with the host. So, the polarizability of the anion is important because we are looking at weak interactions of the van der Waals type.

So, van der Waals interactions essentially depend upon the fluctuating electron density, and when the atoms come close to each other, it is the anion that, if you can polarize the electron density associated with these anions, will contribute to enhanced binding. Therefore, a greater area of contact between the anion and the host leads to enhanced binding. The fourth important factor that must be kept in mind when designing a suitable host for anion binding is solvation.

So, the anions are strongly solvated by the solvents, and solution-anion complexation measurements will influence the magnitude of the binding constants in which these are carried out. So, anions are strongly solvated by the solvents, and hence solution anion complexation measurements will influence the magnitude of the binding constant in which these are carried out.

So, for example, the binding constant is approximately 10 to the power of 2 to 10 to the power of 3 for the halides, and it can also be measured in different solvents where the magnitude of the binding constant is greater in DMSO, greater in acetonitrile, greater in chloroform, and greater in CCl4. So, this is the order of the binding constant for a set of halides in different solvents.

So, this kind of complexation behavior is of relevance, which is influenced by the solvents and the magnitude of the binding constant increases when you change the solvent from DMSO to MeCN, to chloroform to CCl4. Now, let us look at one example, to further understand, the role of pH which is extremely important here. A simple change in pH is the next important factor.

So, we looked at all these factors: negative charge, basicity, polarizability, and solvation. We also looked at the pH; that is, we examined the important factors of consideration. So now let us look at what the role of pH is here. So, for this, we will again go back to our old example, where we looked at the soccer ball complex. Now, we can first consider the neutral complex.

We have seen that it is a very good receptor for the ammonium ion. We studied this when we examined the binding of the soccer ball with organic cations. So, we looked at the ammonium binding here. This was towards us; this is behind, and then these two are in the plane. Now, if we change the pH of the solution, that is, if we now go to a partially protonated host, we will see that they will function as a good host for water molecules.

So, we see this is the water molecule.It forms O-H...N hydrogen bonds and [N+H]...O hydrogen bonds. There are two of these that stabilize the solvent molecule, which is water. If you actually want to consider an anion, then we will have all four of them protonated. Then we can have the chloride sitting here, and this forms the [N+H]...Cl- charge-assisted hydrogen bonds.

So, as you change the pH of the solution, that is, if you make it more and more acidic, you are lowering the pH of the solution; then the active species, depending on the pH, can function either as a good host for ammonium ions, for water molecules partially protonated, and when fully protonated, it can be a very good host for your chloride anion.

So, these are called tetrahedral receptors, and in this case of tetrahedral receptors, they have a very good affinity for ammonium, water, or chloride ion.

The log K value, when measured in methanol and water, is equal to 4, and the selectivity factor for chloride over bromide is 50. That means now you can see here that we bring in the concept of selectivity.

So initially, we were saying that when you have different kinds of anions, the kapatinands for fluoride, bromide, and iodide were not very selective; they were all undergoing encapsulation by the kapatinand.

But now, here we can see that the host has been designed in such a way that there is a greater affinity and selectivity for chloride over bromide. The optimal distance is 3.09 angstroms between hydrogen and chloride. And these correspond to the fact that the host is now also more pre-organized.

There are more electrostatic interactions. There are greater binding sites. All this promotes enhanced binding. So, we now have a more pre-organized host. Number one: greater positive charge on the host, greater number of binding sites, and all these are responsible for the enhanced binding of the anion. In the case of bromide, the binding is not very strong because it forms longer N-H ...Br distances; therefore, this is not an optimal match for the cavity size, and the extent of binding is weaker, resulting in lower selectivity.

So, the cavity dimensions here are more appropriate for chloride, whereas the distances are much longer for bromide, and therefore, this is not an optimal match based on the cavity size that is created. Hence, the action of binding is weaker, resulting in poor selectivity of bromide compared to that of chloride. So, with this in mind, we will now close this lecture, and in the next lecture, we will look at the other factors that influence the processes of anion binding.

Thank you.