Supramolecular Chemistry-I

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Week - 01

Lecture - 01

Good morning, this is Professor P. K. Bharadwaj, your instructor for this course, supramolecular chemistry-I. I was a professor at IIT Kanpur till the end of 2020 and since then I am staying in Kolkata, retired. In this course, I shall be discussing principles of supramolecular chemistry. This is very important to understand what are supramolecular compounds and what they can do for you. So this supramolecular chemistry is based on three principle ideas.

One is by Paul Ehrlich, who discussed what was called antibody-antigen, all of you perhaps know it. Then Alfred Werner gave what we know as coordination chemistry. And another important idea was by Emil Fisher. His idea was what we call lock and key concept.

So, these three gentlemen and their ideas gave us the modern day supramolecular chemistry. Now, why we study supramolecular chemistry? We study to understand how physiological processes take place in bio-systems. See, bio-systems is all supramolecular chemistry. Number two is in drug design, we borrow it from Paul Ehrlich's receptor idea and then in materials domain, we can design many soft advanced materials based on supramolecular bonding like molecular photonic devices, molecular machines and so on. So, as we go along, we will learn little bit of these things.

And then what is happening is in the beginning supramolecular chemistry was not a very coherent subject. It became a coherent subject once one after another instrumental facilities became available like high field NMR, high resolution X-ray and so on. So, once they were discovered, then we could have a now a coherent subject of study. So first, what is a supramolecular chemistry definition? The definition is due to Professor Jean Marie Lehn who got Nobel Prize in 1987. The original definition of supramolecular chemistry of Jean Marie Lehn states that it is the “chemistry beyond molecules” where two or more molecules or chemical species undergo association through intermolecular forces to form an organized entity of higher complexity.

So, these are the keywords chemistry beyond molecules and their association through intermolecular forces to form an organized entity of higher complexity. And of course, it

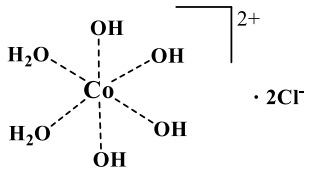
is also understood that when you get an organized entity of higher complexity, it will have properties which will be quite different from either. If there are two chemical species, then unless there is a new property, a useful property or a property which we can use, there is no point of studying association.

So, this is the original definition of supramolecular chemistry. Now, let us see what these intermolecular forces are. First is the strongest intermolecular forces i.e. ion-dipole forces. The energy of this ion-dipole interaction is in the range of 50 to 200 $kJmole^{-1}$. Then, there are dipole-dipole interactions. This dipole-dipole is about is quite low 5 to 20 $kJmole^{-1}$. Then, there is dipole-induced dipole and induced dipole-induced dipole. These two are also called van der Waals interactions. These are about 2 to 5 $kJmole^{-1}$ and then hydrogen bonding that is about 5 to 20 $kJmole^{-1}$.

Besides, another interaction is there that is called π-π stacking. π-π stacking is like if you have a benzene and other benzene comes parallel to the previous one. So, the way they stack is called parallel stacking and they can stack also like one benzene ring is perpendicular to another. This type of stacking is called herringbone stacking. So, π-π stacking are of two types. Their energy is small; about 2 $kJmole^{-1}$. A supramolecular compound is formed because of the partners. One partner we will call host and another partner we will call guest. So, when host and guest come together they are in contact over a large surface. If they are in contact over a large surface area then there will be many, hydrogen bonding interactions, and also many van der Waals interactions and many π stacking interactions between partners. And all these interactions make the total energy very high. Therefore, it is very important that whenever you have a supramolecular compound, your host and guest should come in contact with each other over a large surface area to maximize their interactions. What is mean by large? Hundreds or thousands of these interactions.

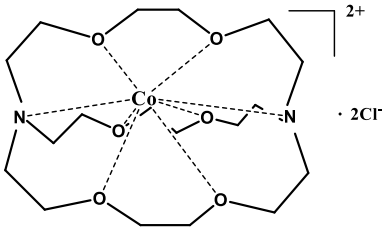
But you have to understand that the original definition of supramolecular compounds although is based on electronic structure of the systems, there are more and more compounds that might be regarded as supramolecular based on their properties. So, as you go along I will give you certain examples and qualify what I am talking about.

You understand that supramolecular compound is originally based on electrostatic interaction between partners. However, right now say somebody will say that I work in supramolecular chemistry what does this mean? It does not mean that he has a host and a guest they come together make a new compound and all that as per the original definition of Jean Marie Lehn. But there are some other compounds they also fall under supramolecular category. So, let me give you examples there will be several examples on that.



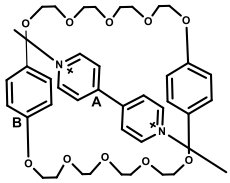
A Coordination Complex

This compound is known as a coordination compound. It is hexaaquacobalt(II) chloride. So, it is a chloride salt. But, how about this compound?



A Cryptate: supramolecular

This is called a cobalt(II) cryptate. This is also have coordination bonds. Cobalt(II) is bound to six oxygen atoms and weakly to two nitrogen atoms. So, this compound even though bonding is similar with hexaaquacobalt(II) chloride complex is a supramolecular compound not a coordination complex. Why is that so ? Because its property is very different. I will discuss about the difference in properties of this kind of compounds when we come to cryptands. Now, take another structure:



2-Pseudo-rotaxane

This is called a pseudo-rotaxane. So, I will stop here today because as we go along I will discuss. So, this pseudo-rotaxane is just a chemical adduct because they are not connected and there is no intermolecular bond and all that. I will be discussing this in the next class. Thank you.