

Fundamentals and Applications of Supramolecular Chemistry
Deepak Chopra
Department of Chemistry
IISER Bhopal
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Lecture 42

W9L42_Self Assembly in Metal-Ligand systems forming Racks, Grids and Ladders

So, let us continue our discussion.

So, in the previous lecture, we looked at the design principles that must be followed in constructing a larger discrete species, wherein the information is already contained in the system in terms of the ligand design and the metal design, and we proposed different strategies here. Now, before we go into the actual systems, there are a couple of things we need to keep in mind.

So, firstly, when you have a ligand, it can be monodentate, bidentate, tridentate, or tetradentate, depending on the number of donor atoms. So, we can have multidentate ligands or we can have monodentate ligands, which depend upon the number of donor atoms that can be given to a particular metal center.

But here we refer to a new term called topicity of a ligand, which is actually the number of distinct binding sites available in a ligand, and in this regard, we can have monotopic, ditopic, and tritopic ligands.

Monotopic ligands have only one binding site; essentially, these are the terminal ligands, and they can also serve as protecting groups on metals that form larger species.

Then we can have polytopic ligands that contain multiple binding sites available in the ligand. It contains multiple binding sites, which enable the formation of complexes having more than one metal center. So, multiple metals can be included in a polytopic ligand to form resulting species having more than one metal center.

As I told you, we use the word 'n' topic here, which refers to the number of distinct binding sites, and this is not the number of individual donor atoms available for coordination.

So, this is our fundamental difference between the denticity of a ligand and the topicity of a ligand. So, we can now look at the formation of first racks, ladders, and grid structures, all of which are closely related to each other because they consist of a regular array of metal ions that are joined by rigid, linear, and multidentate ligands.

So, this is the construction blocks. This is the construction mode of formation of this rack, ladder, and grids.

Let us look at this process. So, we can have a ligand backbone, which is now called ditopic. Now, why is it called ditopic? Because this is one distinct binding site; this is another distinct binding site. This particular binding site can have different kinds of donor atoms. It can have 2 donor atoms, 3 donor atoms, or 4 donor atoms.

It can also have different kinds of donor atoms, but essentially it is a ditopic ligand because it has 2 distinct binding sites, labeled 1 and 2. And this is a monotopic ligand. This is also a monotopic ligand. It has one binding site. Similarly, we can now understand the construction.

This is referred to as a 2-rack, where the number 2 refers to the number of rungs, which are attached, essentially referring to the two monotopic ligands that are attached to the ditopic ligand. So, you also have to keep in mind that these are arranged perpendicular to each other.

So, the ditopic ligands or the polytopic ligands run like this, and the monotopic ligands actually come and join at certain discrete nodal points, where the coordination is completed.

They act as the rungs, and these are the monotopic ligands that bind at very specific sites to give you a rack-like arrangement in a perpendicular fashion, resulting in a 2-rack. We can now have a similar arrangement, where I can now extend the concept, where now I have a metal here, a metal here, a metal here.

Now we can see that this is referred to as a [2.2]-ladder, where this number 2 refers to the number of rungs, and this is a ditopic ligand.

Now, because it has two coordination points, we also have this as a ditopic ligand, or it is a polytopic ligand. Now in this case, it is ditopic, so how many such numbers are there? This is one; this is one. So, there are two such numbers, or the two numbers of polytopic ligands which are present.

So, this forms a [2.2]-ladder, and then we can have a grid-like structure where we have a metal sitting here. And now you can see that when a metal is sitting here, we will have one horizontal bar like this, and then there will be a vertical bar below this. So, below the plane is a vertical bar, and above is a horizontal bar. For example, say each point has two coordination numbers.

So, in total, there are four coordination sites, or it is essentially topicity, one for each.

Overall, we can see that this can form a $[2 \times 2]$ -square grid. This is a 2×2 square grid, and you can actually now have, from here, a distortion of the square grid that can give you a chiral grid where, for example, you have this particular arrangement. So, this will give a square grid. It starts from the top, but then it goes to the bottom.

This is top, this is bottom, this is bottom, this is top; this gives you a chiral grid. So, at every point, you have got top, bottom, top, bottom. So how do we start now creating this necessary structure? So first of all, the design principle was that we used the ligand. Now the design can be applied to different molecules for the construction of this rack, ladder, square grid, and chiral grid. So first let us see how it originated.

First, we start with this particular ligand, which is called phenanthroline. And here you can see that the number of donor atoms, that is, the denticity, is 2, but the topicity is only one. That is, there is only one distinct binding site. Here, this is the distinct binding site where the two nitrogen atoms can now bind to a metal, say, for example, a silver ion. So, this is a convergent ligand, and now we can have another ligand, for example, a bipyridine.

This again has donor atoms. So, this has topicity one, and now we can combine it with $[AgL_4]^+$ or $[CuL_4]^+$, where L is a monodentate ligand. So, naturally, the monodentate ligands will be displaced. The driving force will be the chelate effect, where we form the rings, and it will form now, so we have the silver ion here, and now this is a tetrahedral complex. So, this will now form, and we will have the phenanthroline ligand in this direction, and this will come perpendicular.

So, you can see that the bipyridyl ligand is now coming perpendicular to the phenanthroline ligand, thereby forming a distorted tetrahedral geometry. So, this was the first example, which was conceptualized and essentially consists of a locking of the metal ion via the two ligands in perpendicular orientation.

The concept was now to extend this arrangement by using a polytopic ligand instead of a monotopic ligand. So, here you see this ligand has only one specific site of binding; topicity is one. If you can now extend this topic to multiple domains or multiple specific sites, then this will form a polytopic ligand, which can be used to form the ladder-like arrangement that can self-assemble to create much larger discrete species.

And people have now extended this concept; you can also now take a slightly different environment. So, we can now take a terpyridine. Now this is tridentate, but it is monotopic because this is the only specific distinct binding site where the metal ion can come and bind, okay.

And because their denticity is 3 and the topicity is 1, we can now use any octahedral complex. For example, we can take the $[\text{Ru-L}_6]^{2+}$ octahedral complex, and this can now form the complex.

Again, this tridentate ligand is in this particular orientation, while the other one comes perpendicular and forms this particular metal-ligand complex, which has the ligands in a specific binding environment.

So, this is again the perpendicular binding, and this perpendicular binding gives rise to the octahedral geometry, which is again a very specific mode of recognition. So, it is not necessary for you to have an ideal octahedron with idealized geometry.

You can have distorted variants, and the driving force is again metal-ligand interactions, which stabilize the much larger species formed from the ligands, and metal-ligand complexes that have these monodentate ligands or monotopic ligands that cannot dissociate and form much larger species.

So, this concept was now extended, to generate to start with. So, we can now look at this example of a 2-rack first, and what was done is that the concept was now extended to commission in this particular case again.

So now this is a very different kind of ligand, and here you see it has a density of 6, but topicity of 2. So, this is one region of binding, and this is the second region of binding; therefore, this is now my polytopic ligand. This can now complex with a ruthenium(II) ion, and here and here it can also combine with a ruthenium(II) ion, and this is the perpendicular orientation. So, this can give you a 2-rack, okay.

So, this is a polytopic ligand and this is the terpyridine, okay. And this is a monotopic ligand, as we saw that the terpyridine here has only this monotopic; it has only one binding site.

So, we use a monotopic ligand, as per definition, and a polytopic ligand to construct a two-rack species, and actually, the crystal structure has been determined for this particular species. It exactly resembles this particular arrangement, and then the counterions that have been observed stabilize this large cation RBF_4^- , PF_6^- , and CF_3SO_3^- . Now we can extend this concept to ladders.

So, in the case of a ladder, we have two polytopic ligands connected by a certain number of ditopic ligands. So, you see here, this was the ladder-like arrangement. We have this polytopic ligand disconnected by the ditopic ligand here.

And the nomenclature is represented in the form of $[2.n]$, where n is the number of rungs and 2 refers to the two sides to which the rungs connect.

So, you have this polytopic ligand, and you have two rungs that connect, with each rung being a ditopic ligand such that both sides connect to both sides of the polytopic ligand. So, we have this particular arrangement.

Let us look at a specific example where this is met. So, this was considered in the system where we have the following arrangement of the ligand. This is nitrogen here, nitrogen here, nitrogen here, nitrogen here, nitrogen here, nitrogen here, and we have now added 3 equivalents of this particular ligand.

So, this is a ditopic ligand and this is a polytopic ligand, and how many do we need, two to connect from both sides of the ladder? And we need the three rungs, so we have three equivalents of these, and then we need a template that is very important. So, now we need a metal ion to template this species.

So, we have a polytopic ligand and a ditopic ligand. We have to template them in a way that they come together to form the thermodynamically stable discrete species, and we now add a copper ion because the copper ion forms tetrahedral complexes.

And so now what happens is that we have the copper here; we have the copper here; we have the copper here, and this is going to bind with the nitrogen.

And here you will see that it forms a disc-like arrangement. So, we have this nitrogen here, and we also have the nitrogen here; we also have the nitrogen here. We have this, and then this again can come from here; this again can come from here.

This can form copper plus 1, and then we are going to have the same polytopic ligand on this side, which will coordinate with the nitrogens here. And then we will have a similar arrangement of this here, and then a similar arrangement of that there.

So, this will form a nice ladder-like arrangement where the two vertical sides are the polytopic ligands, and the horizontal bars are the rungs, which are actually the ditopic ligands that connect from either side.

So, this gives rise to a [2.3]-ladder, where 3 is the number of rungs and 2 is the number of polytopic ligands. So, we can form these kinds of large arrays and copper ion functions here as a template, and another very interesting example is where you can even generate a larger ladder. For example, you can now use the same ligand that I mentioned in the previous case.

So, now you can use the same ligand, and you can modify the rung. The rung can be modified as follows. We can use this particular species now. So, we now have this as one

topic, this is another topic, and this is another region. So, this is a tritopic ligand; we have now got a tritopic ligand, and this can now complex with a copper ion, with three such ligands.

So, you will have one on this side, one behind, and one on the other side. So, you will have these three vertical polytopic ligands, such that each binding site will satisfy the tetrahedral geometry, with copper (+1), and it will form a [3.3]-ladder. It will now form a 3.3-ladder, and this, you see, is actually a disc, like a tritopic ligand.

You have a disc, like a tritopic ligand, and the topicity is 3; this is a polytopic ligand, and it now forms the 3.3-ladder. So, these kinds of species will be templated by copper ions, which form tetrahedral building blocks and assemble these ligands: the polytopic ligand and the ditopic ligand, or with a certain number.

For example, the total number of species here is $3 + 3 + 3$ copper ions, which equals 9 species; the self-assembling is a very specific way to form these kinds of large discrete species. So, this makes us realize that self-assembly processes are very interesting.

We have now looked at essentially racks, ladders, and other variations as well. Now in the next lecture, we will look at a specific set of self-assembly systems called helicates and examine some examples related to these as well.

Thank you.