

Molecular Star

How a Molecule of the Year 2017 Was Made

Dillip Kumar Chand

In molecular self-assembly, molecules put themselves together in a predefined way by decoding the information already coded/stored in the molecules. Suitably selected chemical components are simply combined in a single-pot under proper environment. As a consequence, the participating components arrange themselves in a three-dimensional array. This work describes the philosophical approaches on the making of self-assembled coordination cages utilizing building blocks like palladium(II) and organic ligands. An exotic molecule of five-fold symmetry is considered as a particular example to describe the phenomenon.

1. Introduction

This report describes the making of a self-assembled coordination architecture that is named as a ‘molecular star’ since it resembles the shape of a star; more specifically a five-pointed star. This work has been already published in *Chemistry- A European Journal* in the September 2017 issue and was featured in the cover page of the same issue.

The beautiful architecture was also featured in the *Chemical & Engineering News (C&EN)* – a magazine owned by the prestigious American Chemical Society – under science concentrates in August 2017. The molecule was one of the seven molecules that made the list ‘Molecules of the year 2017’ by Editor’s choice, from the several molecules featured by *C&EN* throughout the year. Thus, the molecular star made the cover story of the final issue of *C&EN* that reviewed the ‘Year in Chemistry: The Science That Shone Brightest in 2017’. The description below covers the



Dillip Kumar Chand works in the area of supramolecular coordination chemistry. He is a recipient of the Alexander von Humboldt (AvH) Fellowship, and the Japan Society of Promotion of Science (JSPS) Fellowship. He is particularly interested in self-assembled coordination cages prepared using palladium(II) and non-chelating multidentate ligands. One of his molecules made the list of “Molecules of the Year 2017” that was featured in *C&E News*.

Keywords

Self-assembly, coordination cages, molecular star, molecules of the year 2017.



self-assembly process in general and the molecular star in particular.

2. Self-assembly

Cool molecules are featured by *C&E News*, a prestigious magazine published by the American Chemical Society. In the month of December, few molecules are chosen as the 'Molecules of the Year' by the Editors of the magazine. These molecules are then made available for public view and online voting. Seven entries were chosen by the Editors in the year 2017 that include the molecular star described in this report. The molecular star received 17% share of the votes and ranked third in the list.

The process through which objects put themselves together is popularly termed as self-assembly. Self-assembly is conceptually prevalent in matter ranging from atoms to molecules to biomolecules; it is also prevalent among universal objects and the universe itself. Specific arrangements of the constituents in a self-assembled system defines the overall architecture and are also responsible for the properties of the system. The phenomenon of self-assembly has been an area of intense study among researchers of various fields including chemical sciences. Chemists are interested in molecular self-assembly. In molecular self-assembly, molecules put themselves together in a predefined way by decoding the information already coded/stored in the molecules. Suitably selected chemical components are simply combined in a single-pot under proper environment. As a consequence, the participating components arrange themselves in a three-dimensional array. When molecules come together they, of course, interact with each other whereupon chemical bonding (weak and/or strong) happens. In the process of molecular self-assembly, the positions of the new bonds formed define the overall architecture of the self-assembled systems. If the nature of bonding is reversible, then the intermediate architectures will keep adjusting and evolving till it finds a comfortable profile for itself that is usually related to the thermodynamic stability of the ensemble. Weak or moderate chemical forces are reversible and dynamic in nature meaning the bond-making and bond-breaking processes can happen at ease. Therefore, utilization of the weak forces superbly allows self-healing of the intermediates. Metal-ligand interaction is one such force well utilized by many research groups world-wide to construct self-assembled coordination complexes. The chemistry of self-assembled coordination complexes has been immensely studied, and it has become possible to intercept the information stored in their constituent, i.e., the designer metal and ligand com-



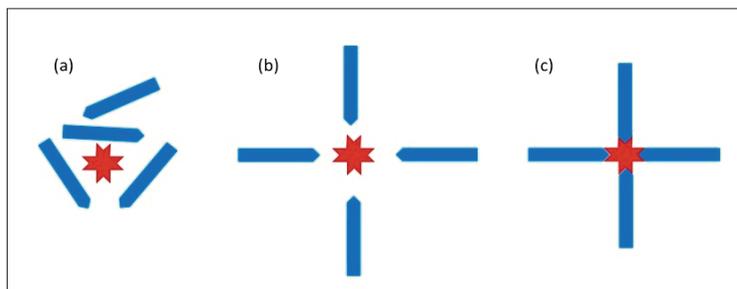


Figure 1. Cartoon diagram showing complexation of the acceptor, i.e., palladium(II) with donor, i.e., pyridine: (a) mixing, (b) approach, and (c) the assembly.

ponents. Thus, it is very often possible to predict the architecture of ensuing assemblies. Self-assembled coordination architectures are useful in various applications, mostly in host-guest chemistry and preparation of molecular machines.

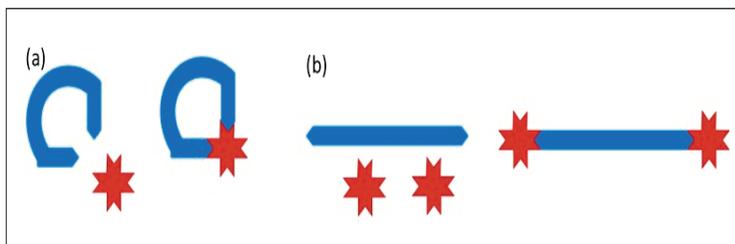
3. Palladium(II) Based Coordination Architectures

Let's consider the metal component as the acceptor and the ligand as a donor, as we know it in the classical coordination chemistry. To be specific, let's consider palladium(II) ion as the metal component and pyridine as the ligand. Palladium(II) is known to provide a square planar coordination environment and accept four ligands. The ligands are placed 90 degrees apart from each other on a given plane as shown in the *Figure 1*. However, if there is a requirement due to geometrical constraints, the coordination environment around the palladium(II) component might deviate from the ideal square planarity.

A mononuclear complex is formed due to the interaction of palladium(II) with the monodentate ligand (say pyridine). However, the phenomenon is slightly different if we allow complexation of palladium(II) with a bidentate ligand. A bidentate ligand has two donor sites, and it can be either chelating or non-chelating in nature. Chelating means, both the binding sites will go for the same metal unit (*Figure 2 (a)*) whereas non-chelating means the binding sites will go to different metal units (*Figure 2(b)*). Of course, all the four acceptor sites of metal components and two donor sites of the ligand component must be completely utilized



Figure 2. Cartoon diagram showing complexation of palladium(II) with bidentate (a) chelating and (b) non-chelating ligands. (only partial structures are shown).



to afford a fully evolved structure. Use of non-chelating ligands is particularly interesting because depending upon the number of donor sites (two, three, four, and so on) and geometrical shapes (direction of the donor vector), a large variety of designs are possible and are already known in the literature.

Objects with five-fold symmetry are common in real life. Particularly, there are many flowers with five petals, a variety of star fishes and so on. However, there are very few chemical structures with five-fold symmetry, e.g., cyclopentadienyl ion. The molecular star described here possess a five-fold symmetry and hence is unique with respect to its architectural beauty.

When ‘m’ equivalents of a metal (M) and ‘n’ equivalents of a ligand (L) put themselves together to afford a self-assembled architecture, the corresponding formula is usually designated as M_mL_n . In case of palladium(II), it could be claimed as Pd_mL_n . In this formula, the charge on the complex and the balancing number of anions are neglected. Since palladium has two positive charges, upon its complexation with a neutral ligand one should afford a complex having $Pd_mL_n(\text{anion})_{2m}$ composition where the anions are monoanionic. These complexes are called ‘homoleptic’ since only one variety of ligand is used. Construction of ‘heteroleptic’ architecture is a recent phenomenon, and it embraces the use of at least two types of ligands. Therefore complexation of palladium(II) with two types of suitably chosen ligands say L^a and L^b might afford a complex of $Pd_m(L^a)_x(L^b)_y$ formulation.

4. Making of the Molecular Star

The molecular star focused in this report was prepared by one-pot mixing of five equivalents of palladium(II), five equivalents of a linear non-chelating bidentate rigid ligand (L^a) and five equivalents of a bent non-chelating bidentate flexible ligand (L^b). The process afforded a beautiful five-pointed molecular star of $Pd_5(L^a)_5(L^b)_5$ formulation as shown in *Figure 3*. In this structure, the



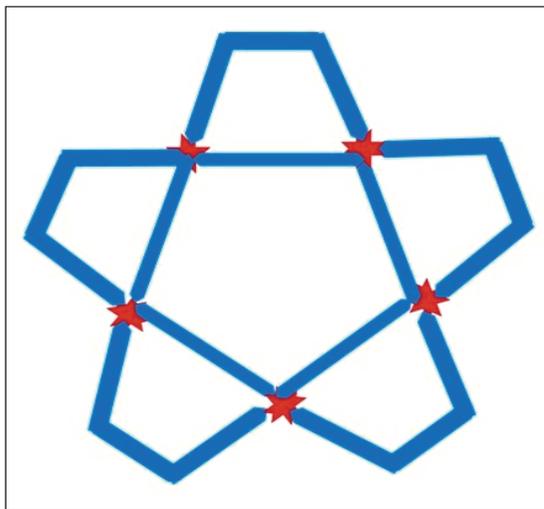


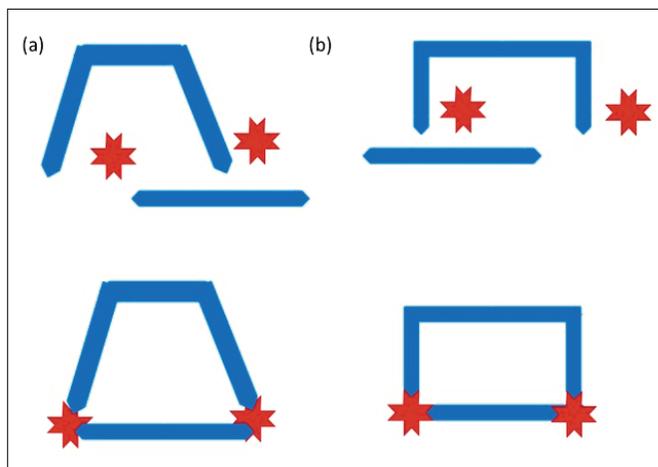
Figure 3. Architecture of the five-pointed molecular star.

bond angles described by ‘donor-acceptor-donor’ deviated from the ideal 90 degrees. The linear rigid ligand takes the role of the arms of the pentagonal core whereas the bent flexible ligand formed the peripheral decoration of the pentagon. The interior bond angles in equilateral pentagon are 108 degrees that matched with the interior angle of the pentagonal core of the star. The exterior angles in the equilateral pentagon are 72 degrees and that also matched in the molecular star. Overall, the architecture of the star is composed of five isosceles trapezia arranged in a specific manner that are glued by the palladium(II) centers.

The deviation of the bond angle from 90 degree in the molecular star is due to the constraint resulting from the geometry of the bent ligand that offered a somewhat divergent binding as shown in *Figure 4 (a)*. The diagram shown in *Figure 4 (b)* indicates the design of a bent ligand that could potentially offer parallel binding vectors and hence might not deviate from the ideal 90-degree bond angles. Choice of a bent ligand shown in *Figure 4 (b)* is likely to afford a square type core decorated by the bent ligands to produce an overall architecture arising from the arrangement of four rectangles.



Figure 4. Geometrical requirement of trapezoidal versus rectangular periphery of the core.



5. Remarks

Human beings have been impressed by geometry and beauty since ancient times. The roles played by synthetic chemists at the molecular level to construct architectures are also fascinating. The architectural designs take inspiration from real life objects. There are many real life objects that have five-fold symmetry, particularly flowers that possess five petals, whereas among the chemical structures there are only a few. The construction of a five-pointed molecular star is a small effort in this direction.

Suggested Reading

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