

The Self-Assembly of a Nanojar
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A nanojar is a supramolecular structure made up of 31 copper (II) ions, 31 hydroxides, 31 pyrazolates and a dianion. When these 94 pieces are in the correct ratios in solution, they form a stack of three rings, each with 6-10 or 11-14 copper-pyrazolate-hydroxide units around the dianion to form the complete nanojar. Nanojars were discovered by Dr. Gellert Mezei at Western Michigan University, and their structures have been confirmed by mass spectrometry and x-ray crystallography. My project this summer was to study the self-assembly process of nanojars in solution and to identify intermediate structures.

Spectrophotometric titrations were the primary method of studying this system. I titrated solutions of hydroxide into solutions of copper and pyrazole. As the copper coordinated to the ligands, the complexes absorbed light differently than the individual components, resulting in a change in the color of the solution. Sivvu™, a program developed by Professor Vander Griend, was used to analyze this titration data. Sivvu™ mathematically determines how many factors are contributing to the changes observed in a solution's absorbance. I can predict a set of chemical species and the equilibria between them. Sivvu™ then modifies the equilibrium constants in my predicted reactions until the model accounts for as much of the data as possible. Corresponding molar absorptivity curves and concentration profiles for the species are produced, along with a residual value that represents how well my model fits the data. This can be repeated until a low residual value is found, indicating that the predicted model and the actual data match each other.

My focus this summer was on varying the parameters of my titrations to learn as much as I could from them. I found that the addition of acid or water leads to coordination of these additional ligands to the copper, interfering with the coordination of pyrazole and hydroxide and therefore altering the color changes of the solution as well. Very few solvents were useful for titrations because both the individual components and the forming complexes needed to be soluble in the solvent. Acetonitrile, which was previously used for mass spectrometry, reacted with copper-pyrazole complexes over time so it could not be used as a solvent for UV-Vis.

Mass spectrometry of copper and pyrazole solutions with various amounts of hydroxide gave us additional insight into the assembly process. In Mezei's previous mass spectrometry, there was evidence for a trimer species (three coppers, three pyrazoles, and one hydroxide) as a key intermediate to the complete nanojar. I found that in a copper-pyrazole solution with no added hydroxide, almost half of the copper in solution was already involved in a trimer species. Additionally, there were two forms of the trimer – one with three pyrazoles and two nitrates around the outside and another one with two pyrazoles and three nitrates. As more base was added, more trimer was formed, but we were unable to detect the full nanojar because of the excess cations from hydroxide additions.

Recent studies have suggested that there is a kinetic component to this system as well. The absorbance of my solutions changes significantly within the first few hours, so titrations that allow the system time to equilibrate will need to be performed for more accurate analysis.

This summer, I gained independence as my understanding of the project increased. I developed patience and persistence because I had to repeat titrations several times until the data was usable. I saw the value of collaboration in research through discussions both with other lab members and people from other labs about our projects.