

The Self-Assembly Process of a Nanojar Megan Aardema and Dr. Douglas Vander Griend

A nanojar is a structure made up of 31 copper (II) ions, 31 hydroxides, and 31 pyrazolates. When certain dianions are present with the components in solution, they form ring structures with 6-10 or 12-14 copper-hydroxide-pyrazolate units. Three of these rings stack on top of each other, forming a jar around the center dianion, completely isolating it from further reactions. Nanojars were discovered by Dr. Gellert Mezei at Western Michigan University. Dr. Mezei confirmed their structure with x-ray crystallography and mass spectrometry, so my goal this summer was to learn more about the assembly process of the 94-piece nanojar and the intermediate structures that form.

Dr. Mezei found evidence of a trimer species (made up of 3 copper ions, 3 pyrazoles, and 4 hydroxides) as a key intermediate to the nanojar. This summer's work focused on the formation of the trimer from the individual components and in the future I'll work on the process of complete nanojar assembly from the trimer species. The formation of the trimer involves 10 pieces coming together, so even that is a very complicated process.

To study this system, I performed spectrophotometric titrations. I titrated solutions of base and pyrazole into solutions of copper. As the copper coordinated to the various ligands, the newly formed species absorbed light differently and there was a change in the color of the solution. Using a computer program developed by Professor Vander Griend, I was able to take my titration data and work backwards to learn more about what was in solution. The computer program helps us determine how many species are formed that contribute to the changes in absorbance. It can mathematically calculate the absorptivity of each species and the equilibrium constants for the reactions between them, and that information can help me identify the specific species that are in solution.

I did many titrations this summer to learn about different aspects of the system. The first several titrations were performed using diglyme as the solvent because the system is only soluble in water up to the formation of the trimer. There was a small amount of water in the diglyme solutions, however, and this additional ligand increased the number of possibilities of intermediate species, making these species difficult to identify. I simplified the system by working with water as the solvent up to the trimer formation. This allowed me to focus on the interactions between copper, hydroxide and pyrazole. My data showed strong evidence for the existence of the trimer. It's likely that the trimer has additional hydroxide or nitrate groups coordinated to the outside and I was unable to definitively determine what those groups are, but I am confident that a trimer of some kind is present in addition to one or two additional copper/pyrazole species.

Participating in research this summer has taught me a lot about problem-solving in the lab. I ran into problems with solubility and with our autotitrator and worked with other lab members to address them. Spending the summer doing science confirmed for me that I want to continue learning chemistry after Calvin.