Announcement of Doctoral Oral Examination

Candidate: Pooja Singh
For the degree of: Doctor of Philosophy
Department: Chemistry

Title: Synthesis and Characterization of Heavy-Metal Oxoanion- and Phosphonate-Binding Nanojars

Committee: Dr. Gellert Mezei, Chair
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1 to 3 p.m.
1220 Chemistry Building

Nanojars are an emerging class of anion binding and extraction agents that exhibit exceptional anion binding strength and have potential applications in the recovery of toxic or valuable anions from water bodies. Nanojars of the formula \((\text{TBA})_2[\text{XO}_{3/4}^2-\subset\{\text{Cu}^{II}(\mu-\text{OH})(\mu-\text{pyrazolate})\}_n]\) (TBA = tetrabutylammonium cation; \(\text{XO}_{3/4}^2- = \text{anion}; \text{X} = \text{Se}, \text{Te}, \text{Cr}, \text{Mo}, \text{W}, \text{HP}, \text{HAs}, \text{HV}; n = 26 - 36\)) are synthesized from \(\text{Cu}^{2+}, \text{OH}^-, \text{pyrazole}\) and the TBA salts of various anions. Nanojars possess hydrophobic exteriors with an array of pyrazolate ligands and hydrophilic interiors with a sequence of hydroxide groups, which make them excellent incarcerating agents for anions with large hydration energy such as \(\text{SeO}_4^{2-}, \text{CrO}_4^{2-}, \text{MoO}_4^{2-}, \text{WO}_4^{2-}, \text{HPO}_4^{2-}, \text{HAsO}_4^{2-}, \text{HVO}_4^{2-}, \text{SeO}_2^{2-}\) and \(\text{TeO}_3^{2-}\). One of the challenges in the study of nanojars is the competitive formation of \(\text{CO}_3^{2-}\)-incarcerating nanojars due to the carbonate impurities. Using the polymer \([\text{Cu(OH)}(\text{pyrazolate})]_\infty\), which
already has a deprotonated pyrazolate as well as the OH\(^-\) molecule needed for the nanojar structure, eliminates the need for additional base during nanojar synthesis, thus reducing the CO\(_3^{2-}\) impurities. Depolymerization of the [trans-Cu(OH)(pyrazolate)]\(_\infty\) polymer into [cis-Cu(OH)(pyrazolate)]\(_n\) (n = 27–32) in the presence of the TBA salt of different anions generates nanojars with no or minimal amounts of CO\(_3^{2-}\) impurities.

In addition to inorganic anion pollutants, organic anions such as phosphonates are also ubiquitous in our environment, present in the form of various organophosphorus compounds. Nanojars were also synthesized by the two different methods described above to capture phosphonate anions. The phosphonate anions employed feature various small to long alkyl chains as well as aryl groups, including methyl, ethyl, n-propyl, n-butyl, dodecyl, phenyl and benzyl. Characterization was done by electrospray-ionization mass spectrometry, variable-temperature \(^1\)H and \(^{31}\)P NMR spectroscopy, UV-vis spectroscopy and X-ray crystallography. A number of X-ray crystal structures of these novel phosphonate nanojars confirm that the nanojars self-assemble and wrap around the hydrophilic anionic part of the phosphonate and leave the hydrophobic alkyl/aryl part of the anion to string outside the cavity of the nanojar. A novel motif in nanojar chemistry, in which a pair of nanojar molecules is tethered by two phosphonate ligands, termed nanojar clamshell, has also been discovered. Importantly, these clamshell structures double the phosphonate binding capacity of nanojars.

Exploration of the formation of nanojars from copper ions in the presence of various multinuclear metal pyrazolate clusters (with Ni, Fe, Mo, Ti, Sn, Mn) was performed to assess the stability of nanojars relative to other metal pyrazolate clusters. ESI-MS\(^-\) spectrometry confirmed the conversion of different metal clusters into nanojars.

This research also considered the potential of nanojars to capture singly-charged anions, which has not been observed yet. Enhanced hydrophobic interactions between the nanojar host and the anion guest might lead to the binding of singly-charged anions with aromatic substituents. 4-Phenylpyrazole and 4-benzylpyrazole were used for the formation of nanojars with increased aromatic outer surface. The crystal structure of a nanojar based on 4-phenylpyrazole reveals a novel Cu\(_{16}\) central ring, the largest nanojar ring observed so far, sandwiched between two Cu\(_{10}\) side rings.