



WESTERN MICHIGAN UNIVERSITY

Graduate College

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
Dr. Ekkhard Sinn
Dr. Andre Venter
Dr. Todd Barkman

Time/Place: **Friday, March 15, 2024
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 $(\text{TBA})_2[\text{XO}_{3/4}^{2-} \text{C}\{\text{Cu}^{\text{II}}(\mu\text{-OH})(\mu\text{-pyrazolate})\}_n]$ (TBA = tetrabutylammonium cation; $\text{XO}_{3/4}^{2-}$ = anion; X = Se, Te, Cr, Mo, W, HP, HAs, HV; n = 26 – 36) are synthesized from Cu^{2+} , OH^- , 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 SeO_4^{2-} , CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} , HPO_4^{2-} , HAsO_4^{2-} , HVO_4^{2-} , SeO_3^{2-} and TeO_3^{2-} . One of the challenges in the study of nanojars is the competitive formation of CO_3^{2-} -incarcerating nanojars due to the carbonate impurities. Using the polymer $[\text{Cu}(\text{OH})(\text{pyrazolate})]_\infty$, which

(over)

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 $[\textit{trans}\text{-Cu(OH)(pyrazolate)}]_\infty$ polymer into $[\textit{cis}\text{-Cu(OH)(pyrazolate)}]_n$ ($n = 27\text{--}32$) 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 ^1H 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.