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Influence of Reactant Stoichiometry on the Composition of Nanojar Product Mixtures

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Abstract

Nanojars are large metal-organic complexes comprised of 26–36 repeating units of [Cu(OH)(R-pz)] (R-pz = pyrazolate anion, where R is either H or a substituent), which strongly and selectively incarcerate highly hydrophilic anions. Nanojars are prepared by the reaction of a copper salt, pyrazole, a base and an anion source (which could be the copper salt itself or a different salt). Usually, a mixture of nanojars of different sizes is obtained: {anion⊂[Cu(OH)(pz)]$_n$} (n = 26–36; anion = carbonate, sulfate, etc.). The value of n depends on the incarcerated anion and the substituents on the pyrazole moiety. It has become apparent that the outcome of nanojar-forming reactions is influenced by the ratio between the reaction ingredients shown above. For example, larger amounts of copper salt in the reaction mixture lead to larger amounts of nanojars with larger n (n = 31) and smaller amounts of nanojars with smaller n (n = 27 and 29). Therefore, it is possible that the relative amount of the other ingredients (such as pyrazole and base) also has an effect on the reaction outcome. The diameter of nanojars is about 2 nm, and they have the ability to bind to di-negative and tri-negative anions including PO_4^{-3}, HPO_4^{-2}, and AsO_4^{-3} [1].
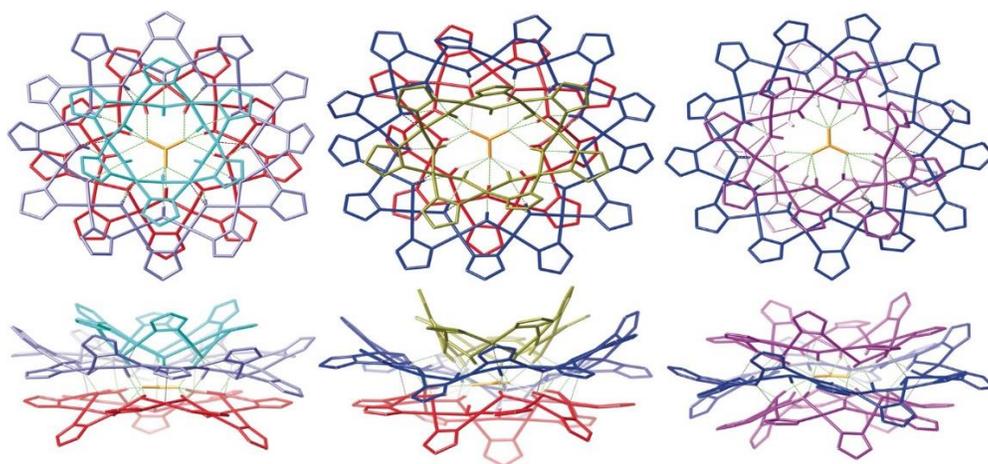
Figure I. Different views of the crystal structure of nanojars.[2]

Introduction

Research on nanojars shows inconsistencies in product composition and purity if slightly different reaction conditions are employed. In other words, the results of nanojar synthesis have not always been reproducible. We will study the effect of varying amounts of reactants on the composition of the final nanojar product mixture. Thus, varying amounts of a copper salt, pyrazole ligand and a base (components of the nanojar products) were employed for the synthesis of nanojars, in series of experiments where the amount of one component is varied at a time. The composition of the nanojar product mixture, including small-nuclearity impurities, was assessed using mass spectrometry and nuclear magnetic resonance spectroscopy. It has become apparent that the outcome of nanojar-forming reactions is influenced by the ratio between the reaction ingredients shown above. For example, larger amounts of copper salt in the reaction mixture lead to larger amounts of nanojars with larger n ($n = 31$) and smaller amounts of nanojars with smaller n ($n = 27$ and 29). Therefore, it is possible that the relative amount of the other ingredients (such as pyrazole and base) also has an effect on the reaction outcome. We studied the effect of varying amounts of copper salt, pyrazole and base on the composition of resultant nanojar reaction mixtures.
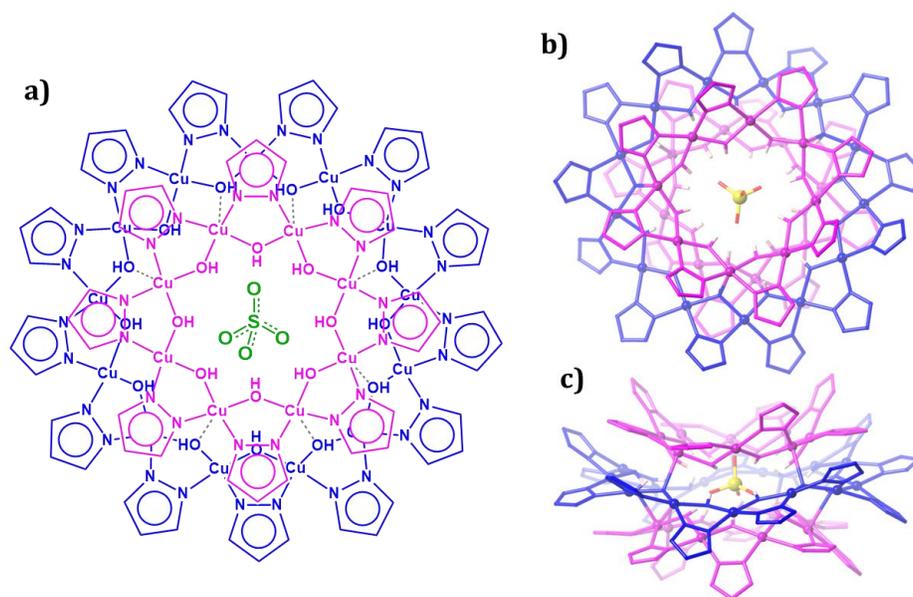
Figure II. a) Schematic representation of the Cu_{29}-nanojar $[SO_4 \subset \{Cu(\mu\text{-}OH)(\mu\text{-}pz)\}_{8+13+8}]^{2-}$ (only one of the two Cu_8-rings is shown for clarity); b) top-view and c) side-view of the crystal structure of the Cu_{29}-nanojar. Color scheme: Cu_8-ring – magenta, Cu_{13}-ring – blue; S – yellow; O – red. C−H hydrogen atoms, counterions and solvent molecules are not shown.[6]

Significance of the Study

This study has multiple significances. First, they will reveal the effect of acidic compounds (such as the copper salt employed) and alkaline compounds (such as sodium hydroxide, the base employed) on nanojars. Second, they will provide the ideal ratio of ingredients needed to maximize the formation of nanojars and minimize the formation of side-products in the reaction mixture. Third, they will unveil appropriate conditions for the synthesis of less complex mixtures of nanojars, and possibly allow for the synthesis of pure nanojars with a desired value of n. Ultimately, the results of this project will enhance our understanding of nanojar stability and reactivity, and will allow for improved designs of nanojar structure and reaction conditions for more efficient and selective extraction of harmful anions from contaminated environments.

Experimental

I.   General Method for the Synthesis of Nanojars

All chemicals and solvents are commercially available and are used as received. Metal nitrate of the general formula $M(NO_3)y \cdot xH_2O$ ($M = Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Cr^{3+}, Zn^{2+}, Cd^{2+}$; x = 2.5, 4, 6 or 9; y = 2 or 3) is dissolved in 20 mL of tetrahydrofuran[4] . Pyrazole is added to the mixture under stirring and tetrabutylammonium hydroxide (TBAOH, 55% in water) is added and the mixture is stirred for 10 min in the air[4]. The solution is washed directly into deionized water under stirring; precipitate A is washed with THF and is dried in vacuum (Scheme 1). [4]
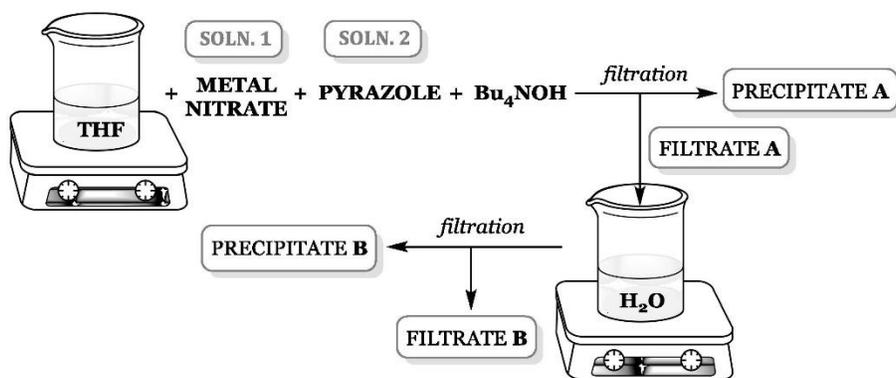
Scheme 1. Experimental scheme for the general synthesis of nanojars. [4]

Three series of reactions were conducted, where the relative amounts of one of the reaction ingredients (copper salt, pyrazole or base) will be varied (Figure III). Standard reaction protocols [4] were followed to provide consistency and to ensure that there is only one variable in each series.
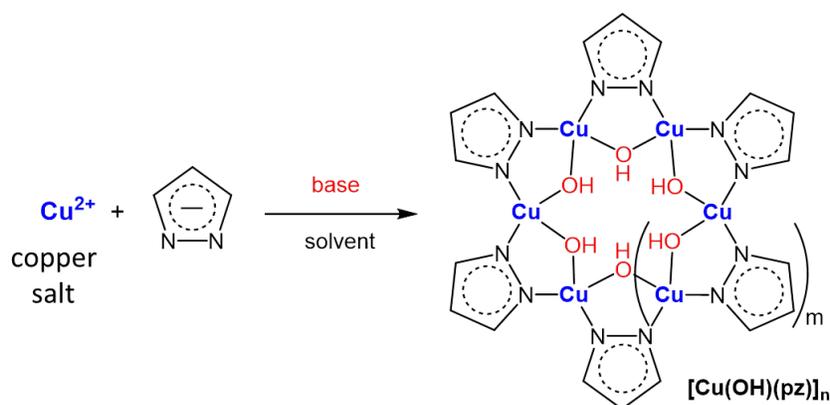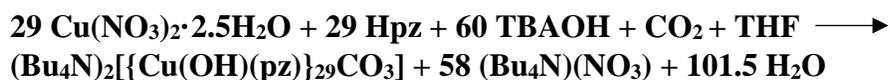
Figure III. Schematic representation of the synthesis of nanojars, using a copper salt, pyrazole and base (n = 26–36; m = 1–13).

The balanced reaction of nanojar synthesis is illustrated below for n = 29:

29 Cu(NO₃)₂·2.5H₂O + 29 Hpz + 60 TBAOH + CO₂ + THF ⟶
(Bu₄N)₂[{Cu(OH)(pz)}₂₉CO₃] + 58 (Bu₄N)(NO₃) + 101.5 H₂O

The main goal of this work is getting the larger and purer amount of nanojars by changing the ratio of reactants. For each reactant, we used an excess of +40%, +20%, -20%, and -40%. In every experiment, we changed only one reactant and kept the other two constants. The amounts of Copper (II) Nitrate and pyrazole were measured and put in 50 mL beaker. Then, 25 mL THF was added and the solution was stirred for 10 mins. Then, the stirrer was turned off. The solution color from the previous step was light and shiny blue. Then, TBAOH was added to the previous solution. Once the TBAOH was added, the solution color turned dark blue and it became darker as we added more TBAOH till we reached the desired amount. After stirring for two hours, the solution was filtered and added drop wise to 250 mL deionized water in 500 mL beaker under vigorous stirring. The solution was kept under stirring for approximately 12 hours to let THF evaporate. The solution

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was filtered and washed with 250 mL DI water. The filter paper and its contents were kept in the desiccator for it least 24 hours before taking the mass to calculate the yield. The final product was collected and stored in small vials for further studying.

II.   Mass spectrometry

Waters SynaptG1 HDMS instrument was used for analysis. The reaction products were isolated and analyzed by electrospray-ionization mass spectrometry (ESI) in acetonitrile solutions. The resultant mass spectra were analyzed and interpreted, which will provide the relative amounts of nanojars obtained in each particular reaction. The actual spectra (Figure 1 – Figure 13) are in the Supplementary part. The mass spectrum of the control trial (Figure 13) shows a mixture of nanojars is obtained. Within this mixture, Cu_{27} *(m/z 2020),* Cu_{29} *(m/z 2170),* Cu_{30} *(m/z 2250)*, and Cu_{31} *(m/z 2320)* are identified as major components of the spectrum (Figure 13). The spectrum of the -20% copper (II) nitrate (Figure 2) and the spectrum of the -40% copper (II) nitrate (Figure 4), both show that Cu_{27}, Cu_{29}, Cu_{30}, and Cu_{31} are present in the spectrum. While the spectrum of the +20% copper (II) nitrate (Figure 1) shows that Cu_{27} and Cu_{31} are present, it shows very small peaks for the Cu_{29}, Cu_{30} and shows a peak at *m/z 992* which corresponds to hexanuclear copper complex and shows a tri-nuclear species peak at around *m/z 528.* The spectrum of the +40% copper (II) nitrate (Figure 3) does not show the presence Cu_{29} and Cu_{30}. Also, it shows the hexanuclear copper complex peak at around *m/z 992* and a peak for the tri-nuclear species at around *m/z 528* in the spectrum. In all spectra of the pyrazole experiments (Figure 5 – Figure 8), we are able to obtain Cu_{27}, Cu_{29}, Cu_{30}, and Cu_{31}. The spectrum of the -20% TBAOH (Figure 10) and the spectrum of the -40% TBAOH (Figure 12) show the hexanuclear copper complex peak at around *m/z 992*, tri-

nuclear species peak at around *m/z 528,* Cu_{27}, Cu_{29}, and Cu_{31} are formed. The spectrum of the +20% TBAOH (Figure 9) and the spectrum of the +40% TBAOH (Figure 11) show that Cu_{27}, Cu_{29}, Cu_{30}, and Cu_{31} are formed.

Observations

The filtered aqueous phase after pouring the reaction mixture in water was dark blue when we used +40% copper (II) nitrate and -40% TBAOH, and the filtration process took long time (more than two hours). The filtered water was colorless when we used -40% copper (II) nitrate and +40% TBAOH, and the filtration process took short time (around 45 mins). In all experiments, we washed the final product with 250 mL DI water to keep the reaction conditions consistent. Table 1 summarizes the observations.

Reactant axcess	Solution A	Solution B	Filtrate A	Precipitate A	Filtrate B	Precipitate B
Copper II Nitrate +40%	Blue	Dark Blue	Blue	n/a	Dark Blue	Blue
Copper II Nitrate +20%	Blue	Dark Blue	Blue	n/a	Blue	Blue
Copper II Nitrate -20%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
Copper II Nitrate -40%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
Pyrazole +40%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
Pyrazole +20%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
Pyrazole -20%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
Pyrazole -40%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
TBAOH +40%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
TBAOH +20%	Blue	Dark Blue	Blue	n/a	Colorless	Blue
TBAOH -20%	Blue	Dark Blue	Blue	n/a	Blue	Blue
TBAOH -40%	Blue	Dark Blue	Blue	n/a	Dark Blue	Blue

Table 1. Color of the different solutions and precipitates obtained during the syntheses described in Section I of the experimental.

Results

After completing twelve different reactions, the following results were obtained. When we used +20% TBAOH, the yield was 91.3%, 63.5% when we used -20% of TBAOH, 21.1% when we used -40% TBAOH, and 95.6% when we used +40% of TBAOH. When we used -40% copper (II) nitrate, the yield was 91.5%, 93.6% when we used -20% of copper (II) nitrate, 63.6% when we used +20% of copper (II) nitrate, and 15.2% when +40% of copper (II) nitrate was used. When we used -40% Hpz, the yield was 7.5%, 67.0% when -20% Hpz was used, 77.9% when +20 Hpz was used, and 77.5% when +40% Hpz. Figure IV summarizes the yields of $(Bu_4N)_2[\{Cu(OH)(pz)\}_nCO_3]$ (with average n = 29) for all experiments conducted.
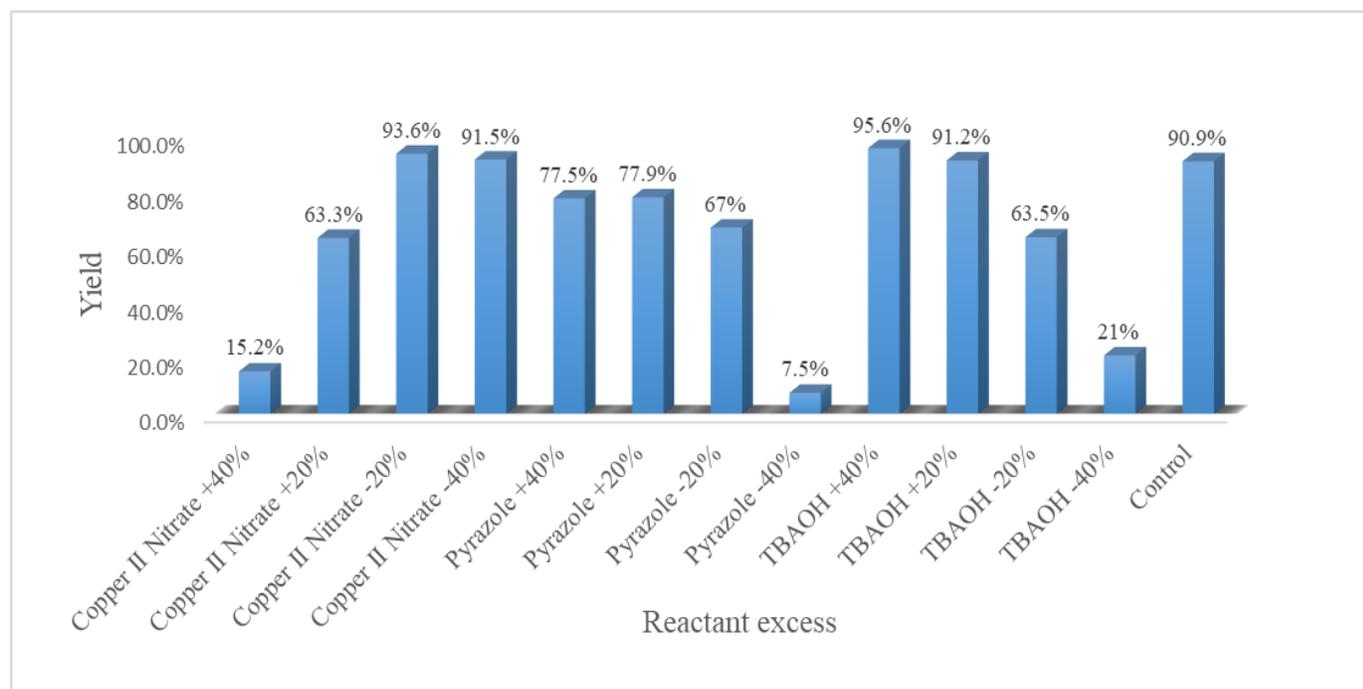
Figure IV. Yields of $(Bu_4N)_2[\{Cu(OH)(pz)\}_nCO_3]$ (average n = 29).

Discussion

Nanojars have recently been developed in Dr. Mezei's laboratory as a novel class of anion binding and extraction agents of unprecedented efficiency. Ten publications in peer reviewed journals (references 1–10) and two patents (reference 11) describe the properties and reactivity of nanojars, and their application for the selective extraction of anions. Nanojars have several key advantages over other known anion extraction agents: a) they have unprecedentedly high binding affinity for highly hydrophilic anions; b) they are easy to synthesize and inexpensive; c) they are recyclable; d) they are easy to derivatize/functionalize; e) they are thermally robust; f) they resist extremely high pH conditions (pH > 14) and can be employed for anion extraction form highly alkaline solutions[3]. The results clearly show that when an excess of copper (II) nitrate was used in the reaction, the yield significantly decreased. This is because copper (II) nitrate is acidic and caused nanojars to break down. The blue was aqueous filtrate obtained from filtration of the reaction mixture poured in water and the spectrum of the +40% copper (II) nitrate (Figure 3) which does not show the presence Cu_{29} and Cu_{30} both support the notion that there was a breakdown of nanojars. In general, acids cause a breakdown of nanojars as they protonate the constituent hydroxide and pyrazolate ions[5]. This ability of breaking down nanojars increases by increasing the concentration of acid until no nanojars forms (for example, when 20 equivalents of formic acid are added).[5] Same reasoning applies to the case of -40% TBAOH, which is a base and its absence increases the acidity of the environment.
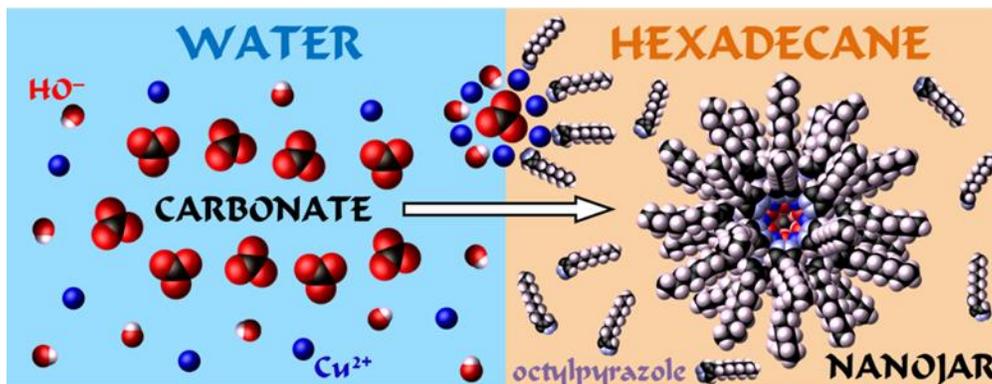
Figure V. A representation of anion extraction from aqueous solutions using nanojars. [3]

Conclusion

Based on a comprehensive synthetic study, we observed that under the given experimental conditions which lead to nanojars of the formula $(Bu_4N)_2[\{Cu(OH)(pz)\}_nCO_3]$ (n = 27–31), none of the reactants used in excess has shown a significant increase in the yield of the product compared to the control experiment (the stoichiometry of which is shown by the balanced reaction above). Increasing the ratio of copper (II) nitrate decreases the yield of formation of nanojars and vice versa. Decreasing the ratio of TBAOH also decreases the yield of produced nanojars. The amount of pyrazole ligand seems to have the least effect on nanojar yield, which is supported by spectra of the pyrazole experiments (Figure 5 – Figure 8), where we are able to obtain Cu_{27}, Cu_{29}, Cu_{30}, and Cu_{31} The spectrum of the +40% copper (II) nitrate (Figure 3) shows the presence of only Cu_{27} and Cu_{31}, which leads us to another finding that the Cu_{29} and Cu_{30} are less resistant to acidic environment than Cu_{27}, Cu_{31}. The most important finding of this study is that in order to maximize nanojar yield, a reactant molar ratio as close as possible to the stoichiometry of 29:29:60 for

$Cu(NO)_3$:pzH:TBAOH has to be used, as excess copper (II) nitrate or insufficient TBAOH (base) will lead to acidic reaction environments which lead to breakdown of nanojars.

Acknowledgements

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