# Assembly Process of the Supramolecular Nanojar

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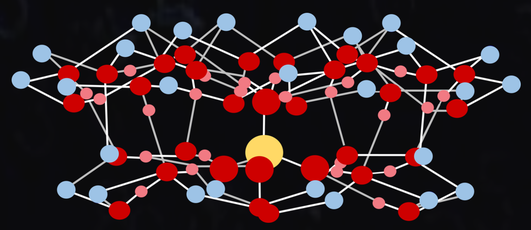
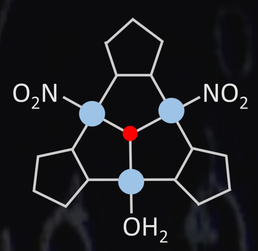
## Introduction

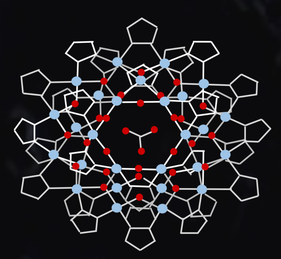
$$31Cu^{2+}+31Pz^{-}+31OH^{-}+CO_3^{2-}\xrightarrow{?}\xrightarrow{?}[CO_3^{2-}\subset(CuPzOH)_{31}]$$

Nanojars are 94-piece supramolecular structures $[CO_3^{2-}\subset(CuPzOH)_{31}]$ that self-assemble around a center dianion, sequestering the dianion from further reactions. We aim to study this assembly process and the intermediates that form in solution.



There is mass spectrometry evidence for the existence of a trimer species $[Cu_3Pz_3OH]^{2+}$ as a key intermediate. Is there evidence for this species in solution as well? How many intermediates are involved in the assembly process? What are the identities and corresponding absorptivity curves of those species?



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## Methods

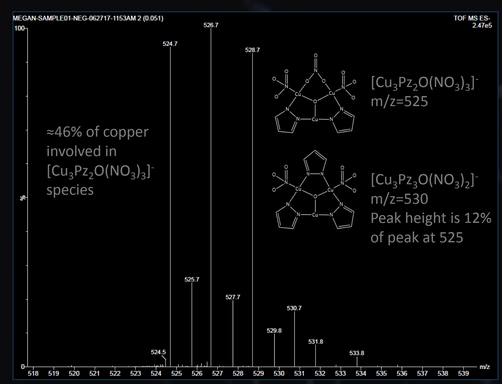
The absorbance of a solution depends on the molar absorptivity and concentration of each species in solution. Spectrophotometric titrations measure the changes in a solution's absorbance as the ratio of the components changes, giving insight into the reactions taking place.

1. Titrations of copper and ligand solutions
2. Unrestricted factor analysis by Sivvu™ to determine the number of absorbing species
3. Equilibrium restricted factor analysis to test chemical models
4. Calculations of molar absorptivity curves and binding constants

Mass spectrometry was used on solutions of various copper-pyrazole-hydroxide ratios for comparison.

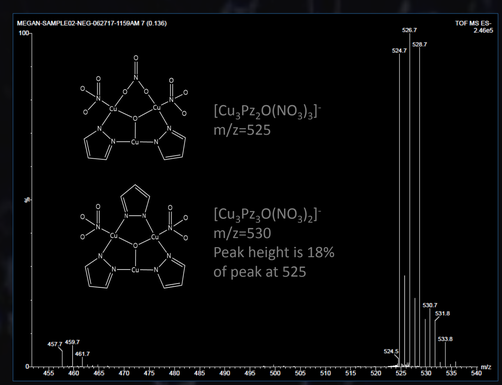
## Mass Spectrometry

Mass spectrometry was performed on 1:1 copper:pyrazole solutions with various amounts of hydroxide. Observed species could be used in Sivvu™ testing of chemical models.



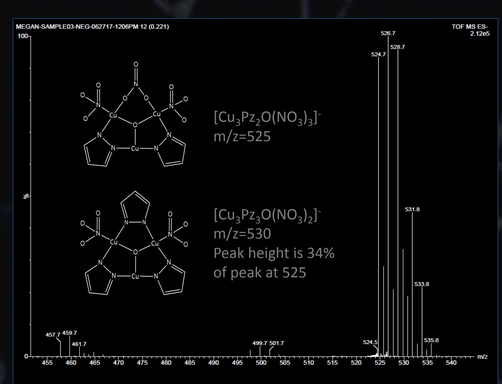

1 Equivalent $Cu^{2+}$
1 Equivalent Pz
0 Equivalents $OH^-$

Even without the addition of base, approximately half of the copper is involved in a trimer species (m/z=525).



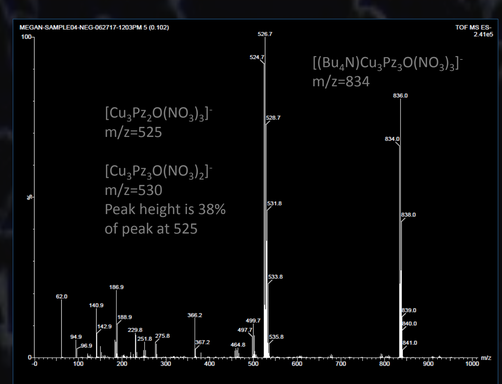

1 Equivalent $Cu^{2+}$
1 Equivalent Pz
0.5 Equivalents $OH^-$

Two forms of the trimer exist. One with 2 pyrazoles and 3 nitrates (m/z=525), one with 3 pyrazoles and 2 nitrates (m/z=530).




1 Equivalent $Cu^{2+}$
1 Equivalent Pz
1 Equivalent $OH^-$

As the concentration of $OH^-$ increases, more copper is converted from hydrated copper nitrate into trimer species.

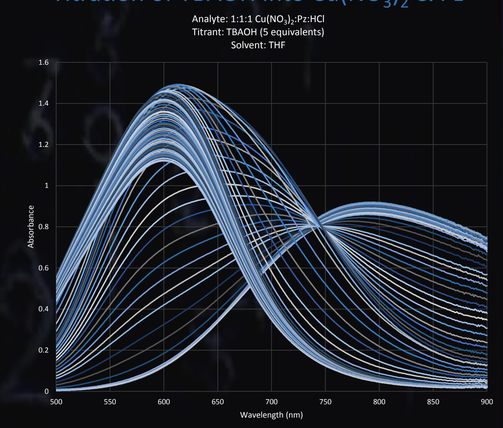



1 Equivalent $Cu^{2+}$
1 Equivalent Pz
1.5 Equivalents $OH^-$

As more TBAOH is added, the $TBA^+$ coordinates to the trimer, resulting in a peak at m/z=834.

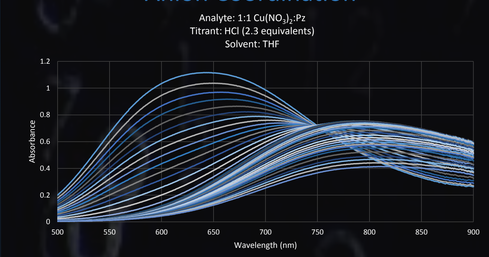
## Spectrophotometric Titrations

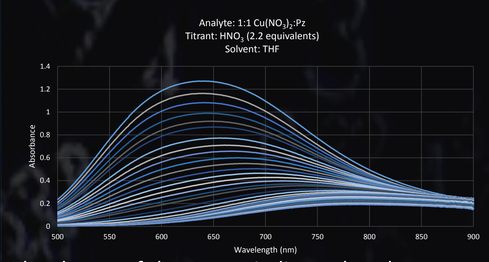
### Titration of TBAOH into $Cu(NO_3)_2$ & Pz




Acid was added to the analyte solution to prevent initial coordination of the copper and pyrazole. The addition of TBAOH should have counteracted the acid, deprotonated the pyrazole, and formed the nanojar. Unrestricted factor analysis shows five species contributing to the changes in the solution's absorbance.

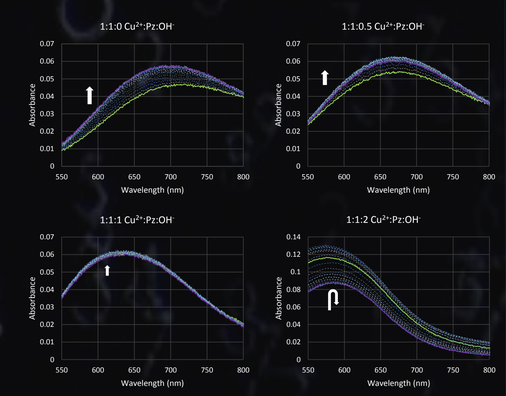
### Anion Coordination



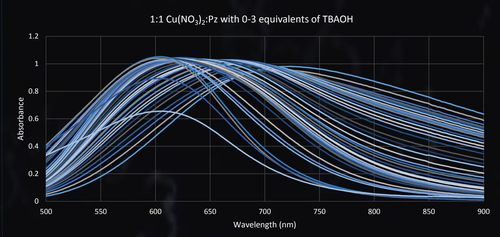

The shapes of the curves indicate that the copper coordinates differently with nitrate than with chloride. $CuCl_2$ absorbs more strongly and at a higher wavelength than $Cu(NO_3)_2$.

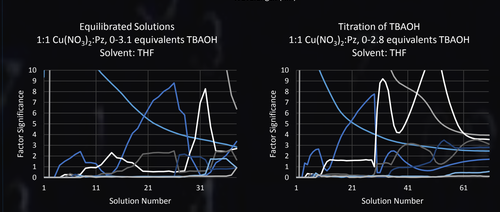
### Absorbance Changes over Time in Acetonitrile/THF mixture




Solutions were made in THF and diluted with acetonitrile. Over time, the acetonitrile reacted with the copper and the ligands, changing the absorbance of the solution. The resulting changes are dependent on the amount of base present in the solution.

### Absorbance Curves of Equilibrated Solutions




Solutions of 1:1 $Cu(NO_3)_2$:Pz and various amounts of TBAOH were prepared and given time to equilibrate. No acid was present so the $\lambda_{max}$ of the solution without base is at a lower wavelength than before. Factor analyses of this set of solutions and the corresponding titration look very similar.

## Conclusions

- Trimer forms without added base.
- Two forms of the trimer exist.
- Anions affect copper coordination.
- Acetonitrile results in changes in a solution's absorbance.

## Acknowledgements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