Assembly Process of the Supramolecular Nanojar
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Introduction

31Cu²⁺+31Pz+31OH⁻+CO₃²⁻→→[CO₃²⁻C(CuPzOH)₃]⁻ Nanojars are 94-piece supramolecular structures [CO₃²⁻C(CuPzOH)₃] 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 [Cu₃PzOH]³⁻ 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?

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.

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.

Spectrophotometric Titrations

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.

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.

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