Synthesis and Characterization of Group 13 Polynuclear Metal Clusters

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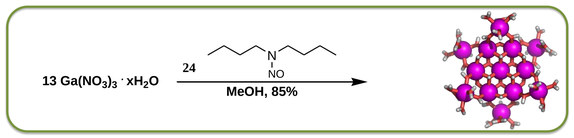
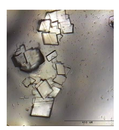
Introduction

We have examined the synthesis and use of Group 13 metal hydroxide clusters as single-source precursors for thin film transistors. Using a solution-based synthetic strategy for the preparation of these discrete clusters, we have prepared both homo- and heterometallic clusters which are described herein. An alternative synthetic approach has been developed that utilizes redox chemistry to slowly raise the pH of the precursor solution and generate the hydroxide cluster. This new synthesis has been used to synthesize an Al_{13} cluster. Solid-state ^{27}Al NMR indicates three distinct sites in the cluster.

Ga_{13} Synthesis

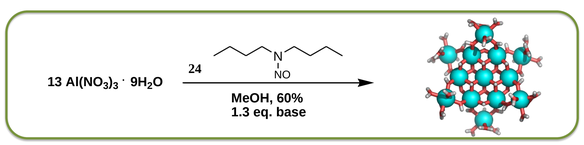
$[Ga_{13}(\mu_3\text{-}OH)_6(\mu_2\text{-}OH)_{18}(H_2O)_{24}](NO_3)_{15} \cdot 6H_2O$ and mixed Ga/In tridecameric clusters are obtained from the slow evaporation of a methanolic solution of hydrated $Ga(NO_3)_3$ in the presence of N-nitrosodibutylamine, within one to two weeks.



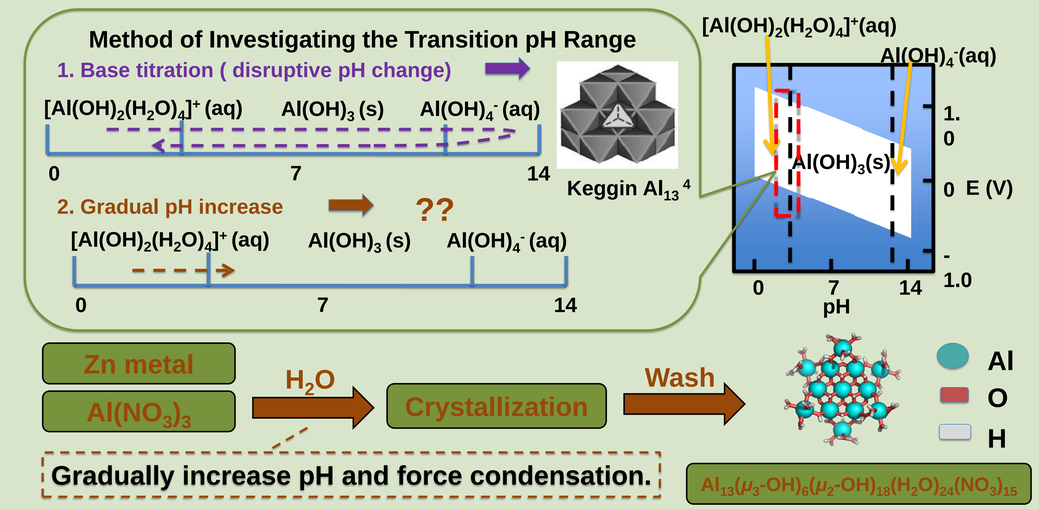


Group 13 Analogues

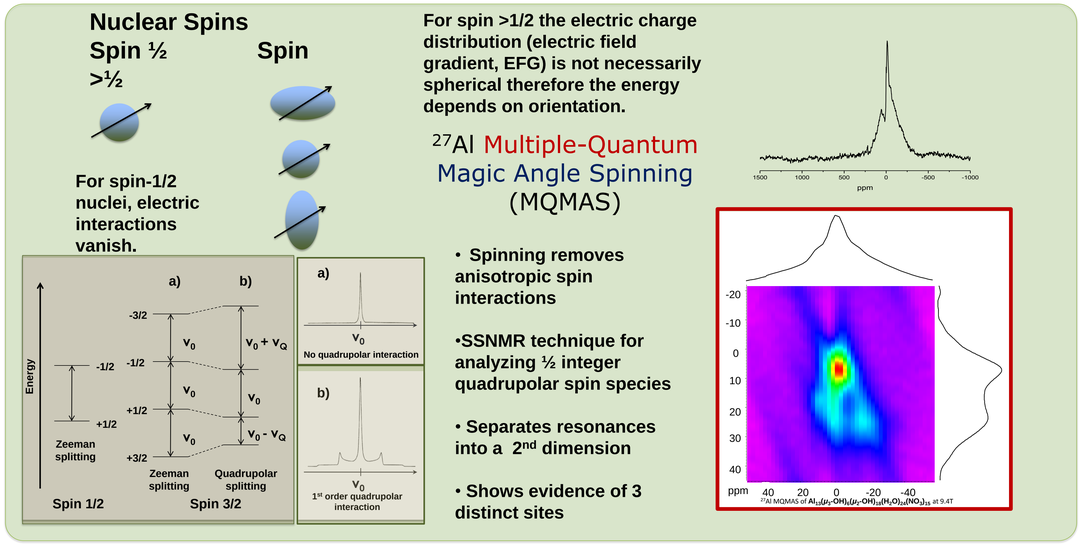
A similar synthetic method yields the analogous tridecameric aluminum complex. Due to the Lewis acidity of Al, a base is used to promote hydrolysis.



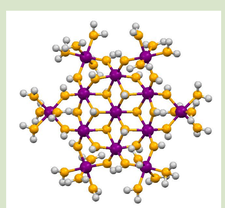
Alternative route to Al_{13}



Solid-state NMR

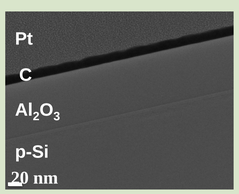


Thin Film Fabrication

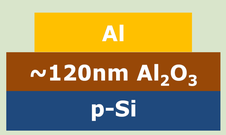


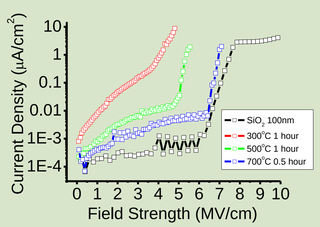
H_2O

Spin coating



All MIM (metal-insulator-metal) capacitors exhibit leakage current < 1 nA/cm² at 1 MV/cm and breakdown field > 5 MV/cm .





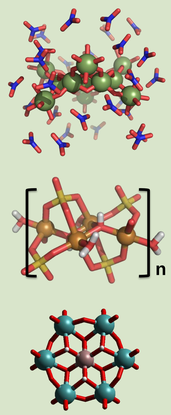
Current and Future Work

Research is currently in progress to produce new single-source precursors.

Anion exchange:
- Anionic polyoxometallates
  - Tungstate
  - Chromate
  - Cuprate

Metal exchange:
- Varying pH conditions

Nanocomposites:
- Anionic clusters
  - Anderson cluster
  - (NEW) tetrameric copper Sulfate cluster



Conclusions

- A solution-based synthetic strategy is used for the preparation of discrete Group 13 tridecameric hydroxo/aquo clusters.
- Gradual pH increase in aqueous solution is necessary for the synthesis of Al_{13} clusters from aqueous environment.
- Solid-State NMR is a powerful tool for structural characterization of quadrupolar nuclei (I>½) such as ^{27}Al and ^{69}Ga/ ^{71}Ga.

References

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Acknowledgments

•Dr. Darren W. Johnson
•Dr. Lev N. Zakharov
•Dr. Zachary L. Mensinger
•Dr. Douglas A. Keszler
•Dr. Sophia E. Hayes
•Dr. J. Scott McIndoe
•Anna Oliveri
•Wei Wang
•Katherine Wentz
•Laura Thompson
•Matthew Baseman
•NSF Center for Green Materials Chemistry (NSF-0847926)
•NSF IGERT (DGE-0549503)