Structural landscape of lanthanide coordinated polyoxometalates

Shailabh Tewari and Arunachalam Ramanan

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi, 110016

aramanan@iitd.ac.in

What should be investigated to comprehend a journey, life, or any dynamic phenomenon? Apart from the input and outcome, the observable steps in-between are pivotal in understanding the whole process and getting perspectives for further utilization. The struggle in rationalizing crystallization, a supramolecular reaction, for the targeted design of functional materials is to recognize the underlined possible pathways. The task is significantly challenging due to the obscurity of well-defined links between synthesis, structure, and property. However, Polyoxometalates (POM), the intermediate soluble molecular analogues of the bulk oxides, may provide some insights. These anionic oxo-clusters, typically of V, Mo, and W, have been of interest to researchers in the field of solid-state and materials chemistry not only due to their promising potential in near-future applications but also for the fundamental acumens they can provide into surface properties of bulk oxides. Out of many possible POM architectures, our choice of the Anderson Evans archetype was based on its structural versatility tunable at the molecular level. Our interest further strengthened upon noticing the ruby-like emission from the Cr-analogue of the archetype $\{Cr(OH)_6Mo_6O_{18}\}^3$, even when other luminescent species were present. We then ventured on the quest of incorporating luminescent lanthanide counter cations into $\{Cr(OH)_6Mo_6O_{18}\}^3$ as well as the photophysically silent $\{Al(OH)_6Mo_6O_{18}\}^3$ for understanding the variations in properties of the landscape of structures associated with changes in synthetic parameters. The poster presents a multidimensional structural landscape of lanthanide coordinated solids based on the Anderson-Evans cluster and the investigation of its photoluminescent properties.



Figure 1. Structural landscape of lanthanide-Anderson-Evans cluster-based solids isolated on variation of synthetic parameters (concentration, temperature, and lanthanide cation), leading to variation in dimensionality with similar stoichiometry. Similar analogies can be observed in the metal-sulphate-hydrate system.

 [1] Tewari, S. et al. Photoluminescence Properties of Two Closely Related Isostructural Series Based on Anderson-Evans Cluster Coordinated With Lanthanides [Ln(H2O)7{X(OH)6Mo6O18}]•yH2O, X = Al, Cr. Front. Chem. 6, (2019).

Keywords: Polyoxometalates; Lanthanides; Structural Landscape; Synthesis-structure-property correlations

Acta Cryst. (2021), A77, C1170