

Poster Presentations

[MS23-P03] Phase Behaviour of Lithium Tartrate Framework Isomers: Kinetic and Thermodynamic Effects.

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Inorganic-organic frameworks have been the subject of great interest for several decades, including much recent research into metal-organic frameworks, coordination polymers and other similar materials. Composed of inorganic moieties connected by organic linkers, they form 1-, 2- and 3-D architectures with intriguing properties that arise from the combination of their constituent parts.[1] Perhaps the most diverse group of inorganic-organic frameworks is based on the tartaric acid ligand, (C₄H₆O₆), due to its conformational and binding flexibility. Individual tartrate structures exhibit many different architectures and physical properties, such as chirality, porosity, magnetism, luminescence and dielectricity. Indeed, the first known ferroelectric material, Rochelle's Salt, whose crystal structure was first determined in 1940, is a potassium sodium tartrate framework: KNa(C₄H₄O₆)·4H₂O. [2]

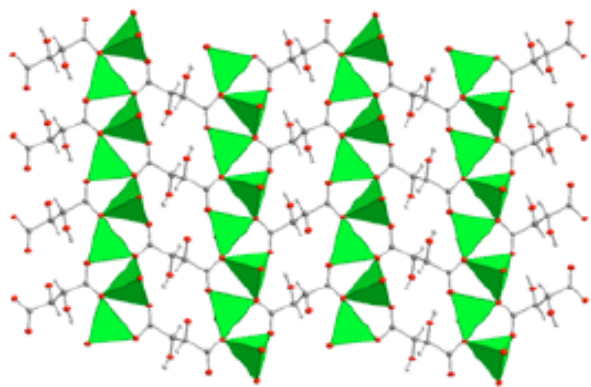


Figure 1: Structure of Li₂(meso-C₄H₄O₆).

Despite their many potential applications, the design and structure prediction of inorganic-organic frameworks that contain flexible ligands such as tartaric acid are poorly developed compared to those containing rigid ligands (e.g. benzene dicarboxylates and imidazolates). Phase behaviour has previously been attributed to both kinetic and thermodynamic effects (e.g. initial formation of low density phases, and lower hydration at higher synthesis temperatures, respectively), but more specific structural details, such as ligand conformation effects, have been lacking. We are therefore studying the fundamental structural properties and factors that affect phase behaviour, in order to gain a wider understanding of such systems.

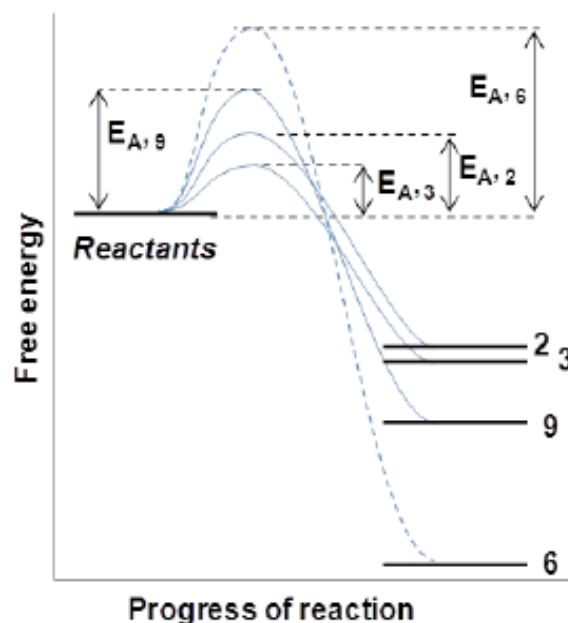


Figure 2: Qualitative energy profiles for the formation of lithium tartrates 2, 3, 6 and 9 from L-tartaric acid.

Combined experimental (synthetic and single crystal X-ray diffraction) and computational (DFT) investigations have given insight into the structure-energy relationships of nine new lithium tartrate frameworks (e.g. Figure 1).[3,4] Analysis of the framework architectures - including features such as ligand conformation,

that framework isomer enthalpies correlate with only density and hydrogen bond strength. [4] Furthermore, our recent study of lithium tartrate phase behaviour have enabled us to make fundamental observations about kinetic and thermodynamic phase formation (see Figure 2), which relate closely to the crystal structures of both products and precursors.[5] Such unparalleled insight is only possible due to the diversity of the lithium tartrate family, which contains 14 known crystal structures to date, including eight dilithium tartrate isomers, $\text{Li}_2(\text{C}_4\text{H}_4\text{O}_6)$. Our findings lend themselves well to development of synthetic strategies and structure prediction, particularly for inorganic-organic frameworks containing flexible, multifunctional ligands like tartaric acid.

[1] Rao, C. N. R.; Cheetham, A. K.; Thirumurugan, A. *J. Phys.-Condens. Matter* **2008**, 20, (8), 083202.

[2] Beevers, C. A.; Hughes, W. *Nature* **1940**, 146, 96.

[3] Yeung, H. H.-M.; Kosa, M.; Parrinello, M.; Forster, P. M.; Cheetham, A. K. *Cryst. Growth Des.* **2011**, 11, (1), 221-230.

[4] Yeung, H. H.-M.; Kosa, M.; Parrinello, M.; Cheetham, A. K. *Cryst. Growth Des.*, manuscript submitted.

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