A series of single-crystal to single-crystal transformations involving physical changes or chemical reactions or both, serve to illustrate the widely varied types of transitions that can occur in molecular crystals and the structural characteristics that can enable them. A non-exhaustive review of older work in this area underscores the important role that modern instrumentation and software have played in studying the dynamic behavior of molecular crystals. In a slightly more recent example, a nickel cyanurate complex was found to change shape as its single-component crystal undergoes a continuous (second order) phase transition.[1] Solid-state spectroscopy coupled with this transition opens the possibility of using this system as a molecular thermometer. In a second series of results, polymers based on transition-metal citrate cubanes have been found to exhibit a diversity of SC-SC behavior. This includes reversible polymer crosslinking in a cobalt-based system, in a solid-state chemical reaction that produces an unusual coordination environment about a Co(II) center.[2] Another cobalt citrate cubane system, based on discrete molecules which have single-molecule-magnet behavior, exhibits reversible metal-atom transfer between neighboring molecules. In a result of yet a different character, a non-porous crystal formed by a one-dimensional polymer whose basic link is a manganese citrate cubane was found to conduct protons by the Grotthuss mechanism.[3] In addition to the diverse behavior of the citrate systems, complexes of orotate have been found to display a rich phase-change behavior. The tetra-n-butylammonium salt of a Co(III) orotate complex (orotate = dianion of uracil-6-carboxylic acid) can be cycled through a conservative monoclinic-triclinic transition; but when a second cycle is attempted the transition occurs only partially, giving a two-phase sample whose components were simultaneously analyzed structurally using single-crystal techniques. A copolymer based on a combination of the same Co(III) orotate complex with a Cu(bipy) (H2O) (bipy = 2,2'-bipyridyl) fragment undergoes a substitution reaction in the solid state, and snapshots of intermediate structures in this transformation suggest an unexpected mechanism for the substitution. A final experimental example involves tracking the dehydration of a molecular crystal that possesses no pores. Both the dehydration and rehydration were followed photographically, giving a qualitative view of the changes occurring in the sample. These changes appear to be consistent with theoretical mechanisms proposed for the motion of small molecules through non-porous crystalline solids. Based on all of the experimental examples presented, possible enabling factors for transformations in molecular solids are identified and possibilities for further studies are briefly discussed.

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