

Two Jahn-Teller systems involved in different kinds of crystal-to-crystal transformations

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Two molecular-crystal solids with Jahn-Teller active Cu(II) centers undergo crystal-to-crystal transformations by different routes.

The first example is a coordination copolymer with alternating Co and Cu centers along the polymer chain, and with a charge of (+1) for each link in the chain. Charge is balanced by an anion whose composition is identical to the Co-centered link of the copolymer. The overall composition can be described as $\{[\text{Co}(\text{orot})_2(\text{bpy})][\mu\text{-Cu}(\text{bpy})(\text{H}_2\text{O})]\}_n[\text{Co}(\text{orot})_2(\text{bpy})]_n \cdot 5n\text{H}_2\text{O}$, 1, in which H₂orot is otrotic acid, C₅H₄N₂O₄. With gentle heating in dry nitrogen gas, crystals of this compound undergo a chemical reaction in which the anion is incorporated into the polymer as a metalloligand with one oxygen atom of the original anion substituting an aqua ligand on the Cu center of the polymer. Structure analysis at intermediate stages of the process indicate that substitution occurs by an associative mechanism.

The second example involves a Jahn-Teller intermediate, formed in solution and isolable as a crystalline precipitate, which when left in contact with the reaction mixture undergoes a solvent mediated crystal-to-crystal transformation in which the two axial ligands involved in Jahn-Teller elongation are lost. The intermediate Cs₂[trans-Cu(orot)₂(H₂O)₂]₂·4H₂O, 2, proceeds to the simple square-planar final product, Cs₂[trans-Cu(orot)₂]₂·3H₂O, 3. It is noted that the nickel-centered analogue of compound 2 does not undergo further transformation to a square-planar product.

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