

Force Conversion from Thermal Linear Expansion to Circular Rotation by Kinematic Movement in the Molecular Crystal

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Molecules in the crystals are packed to maximize their contacting surface to gain the greater intermolecular dispersion forces, while they also show dynamic molecular motions in the case that lattice includes space. Dynamic molecular motions in the crystal often become an origin of wide range of interests involving structural phase transition, ferroelectrics (including dielectric property), dipole glass, mechanical work and solid-state molecular machine. Herein, correlation between molecular motions in the amphidynamic molecular crystals are still in the early stage. This is because of the difficulty to design sufficient vacancy for amphidynamic behaviour and intermolecular interaction for correlated movement. However, these correlated motions realize mechanical movement by which the transformation of motion and/or the transmission of force.

Herein, we studied correlated molecular motion in the quaternary molecular ionic crystal of $\text{Co}(\text{dabco})\text{K}(\text{OCN})_3$ (**1**, dabco=1,4-diazabicyclo[2.2.2]octane). In the crystal **1**, the Co^{2+} centre employs trigonal bipyramidal $\{\text{Co}(\text{N}(\text{OCN})_3(\text{N}_{\text{dabco}})_2)\}$ where dabco molecules bridges Co^{2+} with forming one-dimensional chains $-\text{Co}-\text{dabco}-\text{Co}-$. Additionally, these chains are linked by $\text{Co}^{2+} \cdots \text{NCO}^- \cdots \text{K}^+$ through $\{\text{K}(\text{O}(\text{OCN})_6)\}$ units. Both structural sub-units of $\{\text{Co}(\text{N}(\text{OCN})_3(\text{N}_{\text{dabco}})_2)\}$ and $\{\text{K}(\text{O}(\text{OCN})_6)\}$ were packed by hexagonal closed-packing manner. Temperature dependent crystallographic study revealed that orientation angles of dabco and NCO^- were temperature dependent such as thermal expansion of lattice. We study the temperature evolution of the structure by mechanical kinematic of slider-crank type movement. This is mechanical motion which convert force between liner sliding of piston and circular rotation of crank. We revealed that structural temperature evolution observed for crystal **1** was well-agreed with the relationship of the slider-crank movement, where linear thermal sliding of the K^+ ions by 0.0119 Å between 135 K and 390 K was converted to circular rotation of the dabco molecule by 8.3° at this temperature range.

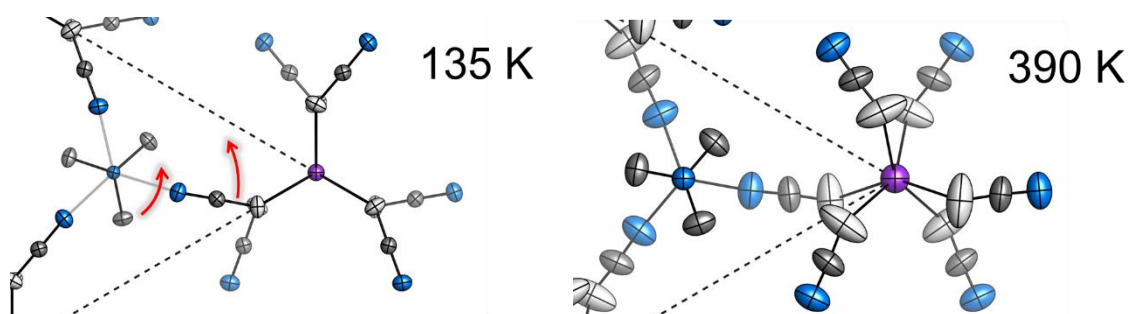


Fig. 1. Crystal structure at 135 K and 390 K.