

Polymorphic transformations of $[\text{Co}(\mu\text{-OOC}^t\text{Bu})_2\text{py}]_2$

Amelia M. Wheaton¹, Ilia A. Guzei¹, Caleb Harris¹, John F. Berry¹

¹ University of Wisconsin-Madison Chemistry Department, Madison, WI, USA

The dicobalt carboxylate paddlewheel complex $[\text{Co}(\mu\text{-OOC}^t\text{Bu})_2\text{py}]_2$ undergoes two distinct enantiotropic non-destructive phase transitions; to the best of our knowledge, these phase transitions are the first reported for this class of compounds. All three phases are triclinic, space group $P\bar{1}$. Variable temperature single-crystal X-ray diffraction (SCXRD) experiments were performed to determine both the regions of stability of the three phases (phase I, phase II, and phase III) and the physical characteristics of the phase transitions. Phase I is indefinitely stable in the 298–124 K region and corresponds to a small unit cell with $V = 1889.6(10)$, $Z = 2$, $Z' = 1$. Upon cooling to 124 K, phase I transforms into phase II, stable in the 124 – 116 K region. Phase II may be equally well described by a medium ($V = 3695.47(11) \text{ \AA}^3$, $Z = 4$, $Z' = 4$) or large unit cell ($V = 7392(4) \text{ \AA}^3$, $Z = 8$, $Z' = 4$); thus the transformation of phase I to phase II may be classified as a type k2 (small to medium) or k3 (small to large) transition. The II→III transition occurs over the 116–112 K temperature range. Phase III, stable in the 112 – 90 K range, is described by another medium-sized unit cell ($V = 3669(2) \text{ \AA}^3$, $Z = 4$, $Z' = 2$). The II→III transformation corresponds to a type k1 (medium to medium) or type k2 (medium to large) transition. The crystal structures of phases I–III were determined from SCXRD experiments at 200, 120, and 100 K, respectively. The overall complex connectivity and coordination environments about the cobalt centers is unaffected by the two phase transitions. However, the dicobalt complexes in the structures of phase I and phase III reside on inversion centers, whereas the dicobalt complexes in the phase II structures do not. This break and then subsequent restoration of symmetry is accompanied by partial order-disorder of the carboxylate ^tBu groups in the phase II (120 K) structures and then further ordering of those groups in the phase III (100 K).