MS13-1-8 Phase transitions in flexible crystals of cocrystal solvate of caffeine
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Abstract
Single crystals of 1:1:1 cocrystal solvate of caffeine, 4-chloro-3-nitrobenzoic acid and methanol are reported to demonstrate reversible bending up to large elastic strain at ambient conditions [1]. The compound has orthorhombic space group symmetry *Fdd*2 [T = 100 K: a = 32.784(9) Å, b = 55.541(15) Å, c = 3.9564(12) Å, V = 7191(4) Å3]. Elastic bending in these crystals is governed by changing distances between molecules within stacks and molecular rotations [2]. While combination of weak dispersive interactions viz. weak C–H···O hydrogen bonds, π-stacking and van der Waals forces between pseudo spherical functional groups aids flexibility, permanent plastic deformation in these crystals has been argued to be prevented by “interlocking”/ steric barriers in the supramolecular architecture [1,2]. Upon heating at Tc1 = 333 K, the crystals lose flexibility and are mechanically brittle [1]. Further heating leads to partial desolvation of methanol from their structure at Tc2 = 388 K [1].
Using temperature dependent specific heat capacity and single crystal X-ray diffraction experiments, the phase transition at Tc1 is found to be continuous. Crystal structures above Tc1 suggest reorganization of the stacking arrangement between the caffeine-acid dimers with respect to the longest growth direction of the crystals.
High temperature *in situ* powder X-ray diffraction experiments suggest that the compound undergoes a phase transition at a significantly lower temperature. Additional peaks are observed in the diffraction pattern. These peaks violate the *F*-centred orthorhombic lattice. Alternatively, these peaks could be approximately described with an additional wave vector in (3+*d*) dimensions.

References
[1] Ghosh S, Reddy C. M. Elastic and bendable caffeine cocrystals: Implications for the design of flexible organic crystals. *Angew. Chem. Int. Ed*., **51**, 10319-10323 (2012)
[2] Thompson A. J., Price J. R., McMurtrie J. C., Clegg J. K. The mechanism of bending in co-crystals of caffeine and 4-chloro-3-nitrobenzoic acid. *Nat. Commun*., **12**, 5983 (2021)