MONOPOTASSIUM DIHYDROGEN CITRATES

James A. Kaduk, BP Chemicals, Naperville IL 60566

Monopotassium dihydrogen citrate ($KH_2C_6H_5O_7$, CASRN 866-83-1) is a commercially-available material. Although powder data has been reported (PDF entry 20-1867), the crystal structure is not in the Cambridge Structural Database. Attempts to index the pattern were not (initially) successful, but did yield a high-quality (ITO figure of merit = 79) triclinic cell which indexed 15 of the first 20 peaks; the unindexed peaks included some strong ones. The high quality of this lattice suggested that it contained some truth, so the NIST Crystal Data Identification File was searched for supercells having # 4× the volume of this cell. The unit cell of $K^+C_6H_7O_7^-$ was reported in 1960 by Love and Patterson, but the structure was not determined - the triclinic cell has $Z = 8$!

Attempts to grow single crystals yielded another material, which bulk analysis demonstrated was the dihydrate. Attempts to solve the structure using the powder data were plagued by severe preferred orientation. Crystals of the anhydrous material could be grown at 42EC. Both structures were solved by applying standard single crystal techniques to data collected from fragments of the badly-twinned crystals at -110EC. The room-temperature structures were refined using powder data.

At ambient conditions, $KH_2C_6H_5O_7$ crystallizes in $P\bar{1}$, with a = 9.4537(2), b = 13.0068(2), c = 14.9400(3) Å, α = 109.882(1), β = 91.555(2), γ = 93.394(2)E, V = 1722.34(6) Å^3, and Z = 8; the calculated density is 1.776 gm/cm^3. The structure contains isolated 8-coordinate K cations. There is a 3-dimensional hydrogen bonding network. The central carboxyl group of each citrate is ionized. The conformations of the four independent citrates are very similar, and differ in energy by < 12 kJ/mole.

$KH_2C_6H_5O_7(H_2O)_2$ crystallizes in $P\bar{1}$, with a = 6.1572(3), b = 8.8430(2), c = 10.1249(3) Å, α = 100.614(1), β = 102.254(2), γ = 90.148(3)E, V = 529.00(3) Å^3, and Z = 2; the calculated density is 1.671 gm/cm^3. The structure contains chains of edge-sharing 8-coordinate K cations parallel to b. The coordination and hydrogen bond network result in formation of layers parallel to ab, consistent with the extreme needle morphology of the crystals. A small hydrophobic pocket exists between the layers, consistent with the lower density. One of the terminal carboxyl groups is ionized, and the citrate anion has a different (and higher-energy) conformation than in the anhydrous material.

Quantum calculations were carried out to understand the hydrogen bonding in each structure. The dihydrate is the lower-energy compound, by 132.7 kJ/mole, and forms at lower temperatures; the anhydrous compound has higher entropy. The dihydrate is less-dense because of the formation of stronger (but fewer!) hydrogen bonds. Water is a better ligand than COOH. The thermal expansion of each material between -110 and 25EC is approximately isotropic.