CRYSTAL STRUCTURES OF AMMONIUM CITRATES

Austin M. Wheatley and James A. Kaduk
North Central College, Naperville IL 60540

The crystal structures of $(NH_4)H_2C_6H_5O_7$ and $(NH_4)_3C_6H_5O_7$ have been determined using a combination of powder and single crystal techniques. The structure of $(NH_4)_2HC_6H_5O_7$ has been determined previously by single crystal diffraction. All three structures were optimized using density functional techniques. The crystal structures are dominated by N-H···O hydrogen bonds, though O-H···O hydrogen bonds are also important. In $(NH_4)H_2C_6H_5O_7$ very strong centrosymmetric charge-assisted O13-H21-O13 and O14-H22-O14 hydrogen bonds link one end of the citrate into chains along the *b*-axis. A more-normal O12-H20···O15 links the other end of the citrate to the central ionized carboxyl group. In $(NH_4)_2HC_6H_5O_7$, the very strong centrosymmetric O1-H8-O1 hydrogen bonds link the citrates into zig-zag chains along the *b*-axis. The citrates occupy layers parallel to the *bc* plane, and the ammonium ions link the layers through N-H···O hydrogen bonds. In $(NH_4)_3C_6H_5O_7$, the hydroxyl group forms a hydrogen bond to a terminal carboxylate, and there is an extensive array of N-H···O hydrogen bonds. The energies of the strutcures lead to a correlation between the energy of an N-H···O hydrogen bond and the Mulliken overlap population: E(N-H···O) (kcal/mole) = 23.1(overlap)^{½}. Powder patterns of $(NH_4)H_2C_6H_5O_7$ and $(NH_4)_3C_6H_5O_7$ have been submitted to ICDD for inclusion in the Powder Diffraction File.