CRYSTAL STRUCTURE PREDICTION:
SYNERGY BETWEEN THEORY AND EXPERIMENT

James A. Kaduk, Kaduk@PolyCrystallography.com
Illinois Institute of Technology, Chicago IL 60616

There *has* been progress over the last 25 years in predicting crystal structures. This progress, and the current techniques for prediction, will be summarized. Any experimental data, especially powder diffraction data and/or a unit cell, provide strong constraints on a potential structure model, and so are very useful. Many potential crystal structure have very similar energies, and thus correct predictions are stringent tests of methodologies.

An example of successful structure prediction is trimellitic anhydride TMA), 1,2,4-benzenetricarboxylic acid 1,2-anhydride. The second lowest energy structure in a force-field-based library of potential structures had lattice parameters very similar to the observed ones - $P2_12_12_1$, with a = 21.7024(4), b = 5.36879(9), c = 6.86300(14) Å, V = 799.64(2) Å^3 - and led to a successful Rietveld refinement using synchrotron data.

With over 800,000 crystal structures determined, we have a good idea of normal molecular geometries. Statistical analysis in the crystallographic databases can yield insight into what is chemically reasonable. This knowledge can be built into a solution/refinement using powder diffraction data, and be useful in post-refinement interpretation of the model.

Refinements using X-ray powder data are often relatively insensitive to the hydrogen positions, but the hydrogen bonding is often the most interesting aspect of a crystal structure. I have found that density-function quantum chemical calculations are useful for determining the hydrogen atom positions, and quantifying the hydrogen bonding.

Examples of the combined application of computational and experimental tools are the crystal structures of several new Group 1 citrate salts, determined using X-ray powder and/or single crystal techniques. Comparing these structures to those of known citrates provides insight into the conformational flexibility of the citrate anion, the order of ionization of the three carboxyl groups, its coordination preferences, and the hydrogen bonding in the structures. Since citrate is a common pharmaceutical counter-ion, these insights may have practical utility. New compounds to be discussed will include $Na_2HC_6H_5O_7$. This structure corresponds to PDF entry 00-016-1182, and is different that the reported polymorph NAHCIT/02-063-5032. $KH_2C_6H_5O_7$ corresponds to 00-020-1687, and crystallizes in $P\bar{1}$ with Z = 8. $KH_2C_6H_5O_7(H_2O)_2$ also crystallizes in $P\bar{1}$, with Z = 2. In $Rb_2HC_6H_5O_7$ there is a very short hydrogen bond, with O···O = 2.441 Å, between citrates. $Rb_3C_6H_5O_7(H_2O)$ crystallizes in $P2_1/n$, with a = 7.4477(1), b = 11.8755(2), c = 13.4167(2) Å, β = 97.882(1)°, V = 1175.44(3) Å^3, and Z = 4. $CsH_2C_6H_5O_7$ crystallizes in $Pna2_1$, with a = 8.7362(2), b = 20.5351(2), c = 5.1682(5) Å, V = 927.17(9) Å^3, and Z = 4. These structures will be compared to each other, and to those of known citrate salts. Other new Group 1 and Group 2 citrates have been prepared, and will be discussed if their structures have been solved and refined. Density functional calculations permit quantitative analysis of the hydrogen bonds in these compounds, the atomic charges, and relative energetics of polymorphs and related compounds.