BONDING IN GROUP 1 CITRATE SALTS

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Computational (both density-functional and molecular mechanics) studies of > 15 new crystal structures and the 10 previously-reported structures of alkali metal citrates provide insight into why the atoms are where they are. Both atomic charges and Mulliken overlap populations indicate that the metal-citrate bonding is predominantly ionic, with very little covalent character. The covalent character decreases as the cation size increases. Bond valence calculations indicate that most cations are crowded, and that the crowding decreases as the cation size increases. Although most oxygen atoms coordinate to the metals, a few do not, and they tend to be the least-negative oxygens. Trends in the coordination are discussed. Both the citrate hydroxyl groups and water molecules tend to bridge two cations, and the carboxylate coordination is more varied. Molecular mechanics calculations demonstrate that the solid state energy differences are dominated by differences in van der Waals and electrostatic energy contributions. In the Li and Na salts, the citrate anion occurs predominantly in a higher-energy “kinked” conformation, rather than the extended lowest-energy conformation observed in salts of the larger cations. Detailed conformational analysis of the citrate anions (carried out in water rather than vacuum) enables quantification of the conformational energy costs in these solids. Hydrogen bonding is important to the stability of these salts. The Mulliken overlap population in the hydrogen bonds provides a quantitative measure of their strength, and permits identification of long (weak) interactions which are significant in some of these compounds. Some of the hydrogen bonds are very strong. Patterns in both the local environments of the hydrogen bonds and the more-extended features (graph sets) are noted. Polymorphs and sets of isostructural compounds permit more-detailed analysis of the structures and energetics in these compounds. The order of ionization of the three carboxylic acid groups is in general central/terminal/terminal, but there are two exceptions. While we have concentrated on salts containing a single alkali metal cation (and hydrogen), the structures of NaK$_2$C$_6$H$_5$O$_7$ and NaKHC$_6$H$_5$O$_7$ provide an exciting window on a larger universe of mixed salts.