

Poster Presentation

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Bonding in Group 1 Citrate Salts

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Computational 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. The metal-citrate bonding is predominantly ionic, with very little covalent character, which 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. Both the citrate hydroxyl groups and water molecules tend to bridge two cations, and the carboxylate coordination is more varied. 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 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. 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 NaK₂C₆H₅O₇ and NaKHC₆H₅O₇ provide an exciting window on a larger universe of mixed salts.

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