Synergy between powder diffraction and density functional theory. Dilithium (citrate) crystals and their relatives

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The new compounds $LiMHC_6H_5O_7$ (M = Li, Na, K, Rb) have been prepared from the metal carbonates and citric acid in solution. The crystal structures have been solved and refined using laboratory (Mo K_α) X-ray powder diffraction data, and optimized using density functional techniques. The compounds crystallize in triclinic space group *P-1*, and are nearly isostructural. The Na occupies a different lattice site than the other M. The structure is lamellar, with the layers in the *ab* plane. The boundaries of the layers consist of hydrophobic methylene groups and very strong intermolecular O-H...O hydrogen bonds between un-ionized terminal carboxylic acid and ionized terminal carboxylate groups. The O...O distances range from 2.666 Å for M = Li to 2.465 Å for M = Rb; the graph set is *R1,1(8)* and the ring includes M. The hydroxy group acts as a hydrogen bond donor, forming *R1,1(6)* hydrogen bonds; the ring includes the Li. The Li-O bonds exhibit significant covalent character (as indicated by the Mulliken overlap populations), while the heavier M-O bonds are ionic. The Li are 4, 5, or 6-coordinate, while the coordination numbers of the larger cations are higher: 8 for Na and 9 for K and Rb. For M = Na, K, and Rb, the hydroxyl group, the ionized terminal carboxylate, and the central ionized carboxylate triply chelate to M. For M = Li, the triple chelation involves the hydroxyl group, the ionized central carboxylate, and the terminal carboxylic acid. Other trends in chelation will also be discussed. For M = Li and Na, the terminal ionized carboxylate chelates to a Li. The citrate occurs in the *trans,trans* conformation, one of two low-energy conformations of an isolated citrate anion.