

DILITHIUM (CITRATE) CRYSTALS AND THEIR RELATIVES

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The new compounds $\text{LiMHC}_6\text{H}_5\text{O}_7$ ($M = \text{Li, Na, K, Rb}$) 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 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 $M = \text{Li}$ to 2.465 Å for $M = \text{Rb}$; the graph set is $R1, I(8)$ and the ring includes M. The hydroxy group acts as a hydrogen bond donor, forming $R1, I(6)$ 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. Trends in chelation will also be discussed. The citrate occurs in the *trans,trans* conformation, one of two low-energy conformations of an isolated citrate anion. In the series $\text{NaMHC}_6\text{H}_5\text{O}_7$ ($M = \text{K, Rb, Cs}$) the $M = \text{K}$ and Rb compounds are isostructural ($P-1$), and contain chains of metal-oxygen polyhedra. The $M = \text{Cs}$ compound is monoclinic ($I2$), and is also lamellar. The COOH...O2C hydrogen bonds in these compounds are even shorter, with O...O distances ranging from 2.426 to as low as 2.347 Å, making these some of the shortest hydrogen bonds observed.