

DILITHIUM (CITRATE) CRYSTALS AND THEIR RELATIVES

James A. Kaduk, kaduk@polycrystallography.com and Andrew J. Cigler
North Central College, Naperville IL 60540 USA

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 $\text{O-H}\cdots\text{O}$ hydrogen bonds between un-ionized terminal carboxylic acid and ionized terminal carboxylate groups. The $\text{O}\cdots\text{O}$ distances range from 2.666 Å for $M = \text{Li}$ to 2.465 Å for $M = \text{Rb}$; 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 $M\text{-O}$ 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 $\text{COOH}\cdots\text{O}_2\text{C}$ hydrogen bonds in these compounds are even shorter, with $\text{O}\cdots\text{O}$ distances ranging from 2.426 to as low as 2.347 Å, making these some of the shortest hydrogen bonds observed.