

*Dilithium (citrate) crystals and their relatives*James Albert Kaduk¹, Andrew Cigler¹¹Chemistry, North Central College, Naperville, United States

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The new compounds LiMHC₆H₅O₇ (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 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. 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 NaMHC₆H₅O₇ (M = K, Rb, Cs) the M = K and Rb compounds are isostructural (P-1), and contain chains of metal-oxygen polyhedra. The M = 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.

Keywords: [citrate](#), [powder diffraction](#), [hydrogen bonding](#)