CRYSTAL STRUCTURES OF GROUP 2 CITRATE SALTS

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Continuing a systematic examination of the crystal structures of citrate salts, the structures of several Group 2 salts have been solved and refined using X-ray powder data, combined with density-functional calculations. Several of the patterns were measured using the mail-in program at beam line 11-BM at the Advanced Photon Source at Argonne National Laboratory. New compounds to be presented include: Mg(H$_2$C$_6$H$_5$O$_7$)$_2$, which crystallizes in $P2_1/c$ with $a = 23.24984(8)$, $b = 10.97778(3)$, $c = 5.92449(1)$ Å, $\beta = 97.1860(2)^\circ$, $V = 1500.241(8)$ Å$^3$, and $Z = 4$. The structure was solved using direct methods as implemented in EXPO2009. Mg(HC$_6$H$_5$O$_7$(H$_2$O)$_2$ crystallizes in $Pn\overline{2}_1$ with $a = 26.91159(14)$, $b = 5.92442(2)$, $c = 6.15170(2)$ Å, $V = 980.800(7)$ Å$^3$, and $Z = 4$. The structure was solved using Monte Carlo simulated annealing techniques as implemented in Endeavour 1.7. [Ca(H$_2$C$_6$H$_5$O$_7$)$_2$(H$_2$O)](H$_2$O) crystallizes in $P\overline{1}$ with $a = 8.37261(3)$, $b = 10.90306(4)$, $c = 11.06287(4)$ Å, $\alpha = 105.2026(4)$, $\beta = 100.6846(4)$, $\gamma = 110.7096(3)^\circ$, $V = 867.2026(4)$ Å$^3$, and $Z = 2$. This structure was also solved with direct methods in EXPO2009. Several more calcium citrates have been prepared. But as yet only in mixtures. A compound with the apparent stoichiometry Ba$_3$(C$_6$H$_5$O$_7$)$_2$(H$_2$O)$_6$ crystallizes in $P2_1/a$ with $a = 11.4739(8)$, $b = 13.7361(9)$, $c = 15.0793(11)$ Å, $\beta = 107.994(5)^\circ$, $V = 2260.38(34)$ Å$^3$, and $Z = 4$. The Ba positions are well-defined, but it is proving difficult to refine the light atoms using only laboratory data.

Known structures include Mg$_3$(C$_6$H$_5$O$_7$)$_2$(H$_2$O)$_{10}$ and Sr$_3$(C$_6$H$_5$O$_7$)$_2$(H$_2$O)$_5$. The crystal structure of the mineral earlandite, Ca$_3$(C$_6$H$_5$O$_7$)$_2$(H$_2$O)$_4$, has been reported recently, but its powder pattern does not correspond to that of commercial calcium citrate tetrahydrate sold as a calcium supplement.

A pattern has been collected for Ba$_3$(C$_6$H$_5$O$_7$)$_2$(H$_2$O)$_7$, PDF entry 00-001-0009; this entry is the only reference in the crystallographic literature to this compound. Only amorphous beryllium citrates have been prepared so far. SrCO$_3$ does not react with citric acid at ambient or near-ambient conditions, so more-extreme reaction conditions will have to be used to prepare new strontium citrates.