The pseudo-orthorhombic crystal structure of monoclinic trilithium citrate tetrahydrate, $Li_3HOC(COO)(CH_2COO)_2 \cdot 4H_2O$

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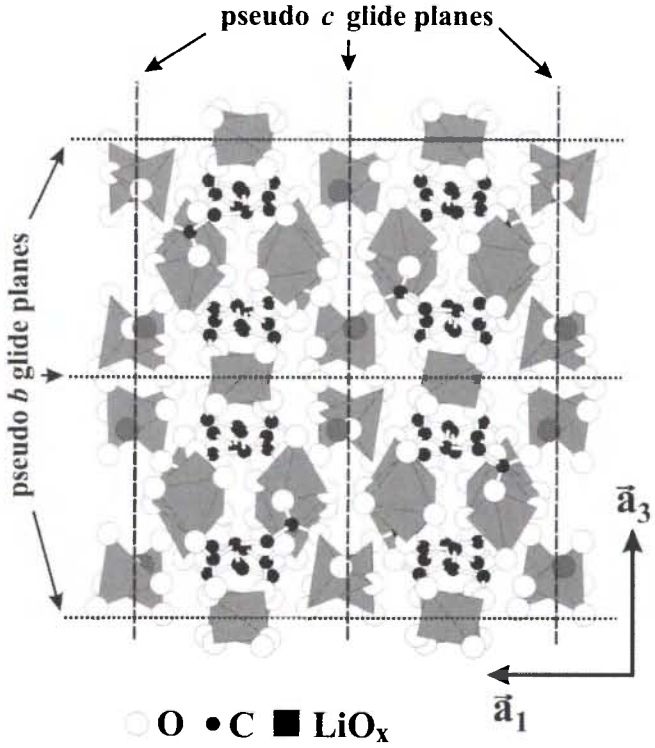

Abstract

$C_6H_{13}Li_3O_{11}$, monoclinic, *I*12/*a*1 (No. 15), $a = 18.177(4)$ Å, $b = 12.304(2)$ Å, $c = 20.595(4)$ Å, $\beta = 90.31(3)°$, $V = 4606.0$ Å^3, $Z = 16$, $\rho_m = 1.627$ g · cm^{-3}, $R_{gt}(F) = 0.031$, $wR_{ref}(F^2) = 0.085$, $T = 293$ K.

Source of material

Large single crystals were obtained from aqueous solutions of the title compound by controlled evaporation at about 315 K.

Discussion

The crystal structure of trilithium citrate tetrahydrate, TLCT, is built up from lithium cations, citric anions and water molecules which are linked by ionic interactions and strong hydrogen bonds. Except of Li7, which is surrounded by 6 oxygen atoms forming a distorted LiO_6 octahedron with an average Li—O bond distance of about 2.165 Å, the independent lithium cations are tetrahedrally coordinated by oxygen atoms at distances between 1.859 Å and 2.057 Å. The anions and the hydrate molecules are arranged in layers parallel (100) whereas the cations are more homogenously distributed. All hydrogen atoms of the water molecules participate on a threedimensional network of strong hydrogen bonds characterized by O···O distances of about 2.85 Å and O–H···O angles of 165°. The H atoms of the hydroxyl groups of the anions are involved in intramolecular hydrogen bonds. The weak anisotropy of the longitudinal elastic stiffness of TLCT [1] corresponds to the lack of a direction of predominant bond chains. The lattice parameters of TLCT, the morphology of the crystals and the anisotropy of thermal expansion and elastic properties possess a distinct pseudo-orthorhombic character. A closer inspection of the monoclinic structure reveals that, for instance, the non-equivalent citric anions are approximately related by *c* and *b* glide planes parallel to (100) and (001), respectively. In accordance with the pseudosymmetry the average intensity of *(0kl)/(hk0)* reflections with *l/k* odd is more than 10/20 times smaller compared to the average intensity of those with *l/k* even. If one takes further into account the lamellar twinning observed by Haussühl and Wang [1], a phase transition of type $I2/a \leftrightarrow Icab$ close to room temperature appears very likely. However, the thermal expansion of TLCT, which was studied with the aid of an optical Fizeau interferometer, and the twinning pattern observed under the polarizing microscope did not show significant anomalies between 260K and the decomposition temperature of about 380 K.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 1.5 × 2.5 × 2.5 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.53 cm^{-1}
Diffractometer, scan mode:	Nonius CAD4, ω/2θ
$2\theta_{max}$:	55.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11077, 5543
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4558
$N(param)_{refined}$:	467
Programs:	SHELXS-97 [2], SHELXL-97 [3], ATOMS [4]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1C1)	8*f*	0.246(1)	0.358(2)	0.2619(9)	0.041(5)
H(2C1)	8*f*	0.3086(9)	0.525(1)	0.3161(8)	0.029(4)
H(3C1)	8*f*	0.3333(8)	0.479(1)	0.3851(8)	0.027(4)
H(4C1)	8*f*	0.2747(9)	0.316(1)	0.4291(8)	0.032(4)
H(5C1)	8*f*	0.2778(9)	0.244(1)	0.3658(8)	0.032(4)
H(1C2)	8*f*	0.249(1)	0.853(2)	0.2715(9)	0.047(5)
H(2C2)	8*f*	0.1698(8)	0.965(1)	0.3981(7)	0.025(4)
H(3C2)	8*f*	0.1885(9)	1.016(1)	0.3285(8)	0.031(4)
H(4C2)	8*f*	0.2329(9)	0.811(1)	0.4387(8)	0.029(4)
H(5C2)	8*f*	0.2249(9)	0.739(1)	0.3749(8)	0.035(4)
H(1W1)	8*f*	0.094(1)	0.628(2)	0.399(1)	0.045(5)
H(2W1)	8*f*	0.089(1)	0.652(2)	0.464(1)	0.060(6)
H(1W2)	8*f*	0.012(1)	–0.374(2)	0.260(1)	0.054(6)
H(2W2)	8*f*	0.022(1)	–0.390(2)	0.192(1)	0.065(7)
H(1W3)	8*f*	0.010(1)	0.374(2)	0.230(1)	0.059(6)
H(2W3)	8*f*	0.019(1)	0.395(2)	0.296(1)	0.061(7)
H(1W4)	8*f*	–0.102(2)	0.844(2)	0.469(1)	0.092(9)
H(2W4)	8*f*	–0.096(1)	0.867(2)	0.402(1)	0.066(7)
H(1W5)	8*f*	0.528(2)	0.625(2)	0.409(1)	0.076(8)
H(2W5)	8*f*	0.454(1)	0.644(2)	0.395(1)	0.059(6)
H(1W6)	8*f*	0.053(1)	0.143(2)	0.395(1)	0.056(6)
H(2W6)	8*f*	0.041(2)	0.035(2)	0.394(1)	0.079(8)
H(1W7)	8*f*	0.398(2)	0.332(3)	0.478(2)	0.11(1)
H(2W7)	8*f*	0.379(1)	0.431(2)	0.505(1)	0.058(6)
H(1W8)	8*f*	0.111(1)	0.921(2)	0.507(1)	0.066(7)
H(2W8)	8*f*	0.041(2)	0.900(2)	0.527(1)	0.078(8)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1C1)	8*f*	0.21133(5)	0.37599(7)	0.28456(4)	0.0197(4)	0.0237(4)	0.0140(4)	–0.0011(3)	0.0001(3)	–0.0054(3)
O(2C1)	8*f*	0.14589(5)	0.53779(8)	0.34236(4)	0.0278(5)	0.0270(5)	0.0215(4)	0.0107(4)	–0.0009(4)	–0.0011(4)
O(3C1)	8*f*	0.19419(5)	0.49758(8)	0.43907(4)	0.0237(4)	0.0327(5)	0.0170(4)	0.0004(4)	0.0003(3)	–0.0077(4)
O(4C1)	8*f*	0.43791(5)	0.39227(9)	0.32652(5)	0.0175(4)	0.0500(6)	0.0284(5)	0.0035(4)	0.0015(4)	–0.0093(4)
O(5C1)	8*f*	0.35124(5)	0.34206(8)	0.25642(5)	0.0260(5)	0.0322(5)	0.0272(5)	0.0018(4)	0.0026(4)	–0.0136(4)
O(6C1)	8*f*	0.11816(5)	0.26696(8)	0.37867(4)	0.0178(4)	0.0309(5)	0.0217(4)	–0.0010(3)	–0.0016(3)	0.0040(4)
O(7C1)	8*f*	0.17814(5)	0.17756(8)	0.45534(5)	0.0268(5)	0.0365(6)	0.0343(5)	–0.0008(4)	–0.0004(4)	0.0189(4)
C(1C1)	8*f*	0.24036(6)	0.40159(9)	0.34798(5)	0.0158(5)	0.0173(5)	0.0126(5)	–0.0008(4)	–0.0005(4)	–0.0014(4)
C(2C1)	8*f*	0.18812(6)	0.48502(9)	0.37878(5)	0.0149(5)	0.0177(5)	0.0180(5)	–0.0027(4)	0.0016(4)	–0.0016(4)
C(3C1)	8*f*	0.31529(6)	0.4590(1)	0.34197(6)	0.0165(5)	0.0175(5)	0.0195(6)	–0.0018(4)	0.0018(4)	–0.0034(4)
C(4C1)	8*f*	0.24781(7)	0.2989(1)	0.38983(6)	0.0173(5)	0.0208(6)	0.0237(6)	0.0007(4)	–0.0017(4)	0.0046(5)
C(5C1)	8*f*	0.37312(6)	0.3921(1)	0.30660(6)	0.0191(5)	0.0201(6)	0.0206(6)	–0.0014(4)	0.0043(4)	–0.0001(4)
C(6C1)	8*f*	0.17632(6)	0.24381(9)	0.40957(6)	0.0204(5)	0.0173(5)	0.0175(5)	0.0015(4)	0.0013(4)	0.0000(4)
O(1C2)	8*f*	0.28753(5)	0.86923(7)	0.29221(4)	0.0197(4)	0.0239(4)	0.0145(4)	0.0017(3)	0.0018(3)	–0.0036(3)
O(2C2)	8*f*	0.35411(5)	1.03217(8)	0.34806(4)	0.0311(5)	0.0327(5)	0.0225(4)	–0.0127(4)	0.0043(4)	–0.0025(4)
O(3C2)	8*f*	0.30838(5)	0.99560(8)	0.44564(4)	0.0246(4)	0.0360(5)	0.0170(4)	0.0005(4)	0.0017(3)	–0.0076(4)
O(4C2)	8*f*	0.06366(5)	0.87481(9)	0.34089(5)	0.0182(4)	0.0442(6)	0.0263(5)	–0.0044(4)	–0.0002(3)	0.0022(4)
O(5C2)	8*f*	0.14697(5)	0.83625(8)	0.26588(5)	0.0272(5)	0.0354(5)	0.0285(5)	–0.0029(4)	–0.0006(4)	–0.0137(4)
O(6C2)	8*f*	0.38269(5)	0.74386(8)	0.37774(4)	0.0206(4)	0.0362(5)	0.0245(5)	0.0036(4)	0.0046(3)	0.0104(4)
O(7C2)	8*f*	0.32812(5)	0.66746(8)	0.46173(5)	0.0253(5)	0.0293(5)	0.0275(5)	0.0001(4)	0.0015(4)	0.0131(4)
C(1C2)	8*f*	0.26178(6)	0.89368(9)	0.35659(5)	0.0163(5)	0.0179(5)	0.0133(5)	0.0015(4)	0.0020(4)	–0.0011(4)
C(2C2)	8*f*	0.31354(6)	0.9799(1)	0.38568(6)	0.0150(5)	0.0197(6)	0.0183(5)	0.0027(4)	–0.0007(4)	–0.0018(4)
C(3C2)	8*f*	0.18517(6)	0.9480(1)	0.35318(6)	0.0165(5)	0.0202(6)	0.0187(5)	0.0022(4)	–0.0005(4)	–0.0038(5)
C(4C2)	8*f*	0.25689(7)	0.7906(1)	0.39859(6)	0.0187(5)	0.0223(6)	0.0231(6)	0.0011(5)	0.0038(5)	0.0054(5)
C(5C2)	8*f*	0.12736(6)	0.8802(1)	0.31814(6)	0.0196(5)	0.0187(6)	0.0190(5)	0.0014(4)	–0.0029(4)	0.0025(4)
C(6C2)	8*f*	0.32819(6)	0.73048(9)	0.41411(6)	0.0193(5)	0.0172(5)	0.0176(5)	–0.0021(4)	–0.0008(4)	0.0000(4)
O(1W1)	8*f*	0.06480(5)	0.65677(8)	0.42975(5)	0.0211(4)	0.0283(5)	0.0303(5)	0.0054(4)	–0.0002(4)	–0.0027(4)
O(1W2)	8*f*	0.04617(5)	–0.37911(8)	0.23001(5)	0.0236(5)	0.0347(5)	0.0280(5)	–0.0011(4)	0.0065(4)	0.0050(4)
O(1W3)	8*f*	0.04305(5)	0.38147(8)	0.26168(5)	0.0239(5)	0.0349(5)	0.0275(5)	0.0043(4)	–0.0037(4)	0.0011(4)
O(1W4)	8*f*	–0.07424(6)	0.82679(9)	0.43422(6)	0.0268(5)	0.0361(6)	0.0418(6)	0.0094(4)	0.0013(5)	0.0037(5)
O(1W5)	8*f*	0.49025(6)	0.59453(9)	0.39454(6)	0.0239(5)	0.0332(6)	0.0573(7)	0.0023(4)	–0.0037(5)	–0.0005(5)
O(1W6)	8*f*	0.01917(6)	0.0935(1)	0.39266(6)	0.0266(5)	0.0305(6)	0.0512(7)	–0.0007(5)	0.0009(5)	0.0013(5)
O(1W7)	8*f*	0.41118(7)	0.4011(1)	0.48101(6)	0.0386(6)	0.0469(7)	0.0374(6)	0.0037(5)	0.0117(5)	–0.0019(5)
O(1W8)	8*f*	0.06862(7)	0.8980(1)	0.49376(6)	0.0359(6)	0.0620(8)	0.0342(6)	–0.0087(6)	–0.0007(5)	–0.0132(6)
Li(1)	4*e*	1/4	0.0903(3)	1/2	0.023(1)	0.025(2)	0.020(1)	0	0.001(1)	0
Li(2)	4*e*	1/4	0.9147(2)	0	0.020(1)	0.024(2)	0.020(1)	0	–0.003(1)	0
Li(3)	8*f*	0.1210(1)	0.7223(2)	0.2112(1)	0.027(1)	0.025(1)	0.024(1)	–0.0013(9)	0.0025(8)	–0.0020(9)
Li(4)	8*f*	0.0315(1)	0.8124(2)	0.4231(1)	0.025(1)	0.028(1)	0.032(1)	0.0011(9)	0.0012(9)	0.0025(9)
Li(5)	8*f*	0.1199(1)	0.2837(2)	0.2867(1)	0.024(1)	0.025(1)	0.022(1)	0.0027(8)	–0.0020(8)	–0.0025(8)
Li(6)	8*f*	0.4755(1)	0.4411(2)	0.4108(1)	0.029(1)	0.038(1)	0.030(1)	0.005(1)	0.0019(9)	–0.000(1)
Li(7)	8*f*	0.1314(1)	0.5035(2)	0.2462(1)	0.034(1)	0.029(1)	0.025(1)	0.0026(9)	0.0025(9)	0.0026(9)

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