Crystal structure of potassium rubidium bis(L-malate) L-malic acid, $K(K_{0.67}Rb_{0.33})(C_4H_5O_5)_2 \cdot C_4H_6O_5$

V. H. Rodrigues^{*I}, M. M. R. Costa^I, E. Matos Gomes^{II} and A. Criado^{III}

^I Universidade de Coimbra, Faculdade de Ciências e Tecnologia, Departamento de Física, CEMDRX, 3004-516 Coimbra, Portugal

^{II} Universidade do Minho, Departamento de Física, Campus de Gualtar, 4710-057 Braga, Portugal

^{III} Universidad de Sevilla, Departamento de Física de la Materia Condensada, Apartado, 423566 Sevilla, Spain

Received March 8, 2006, accepted and available on-line April 6, 2006; CCDC no. 1267/1747

Abstract

$C_{12}H_{16}K_{1.67}O_{15}Rb_{0.33}$, orthorhombic, $P2_12_12_1$ (no. 19), $a = 7.721(1) \text{ \AA}$, $b = 7.895(2) \text{ \AA}$, $c = 29.914(3) \text{ \AA}$, $V = 1823.6 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.061$, $wR_{\text{ref}}(F^2) = 0.147$, $T = 293 \text{ K}$.

Source of material

Single crystals of the title compound have been grown from a saturated equimolar aqueous solution of potassium and rubidium hydroxide and L-malic acid by a controlled solvent evaporation method. A small single crystal of fair quality was selected and used for X-ray data collection.

Experimental details

All hydrogen atoms were refined as riding with isotropic displacement parameters constrained to those of the parent atoms. Appropriate AFIX instructions with SHELXL-97 [1] defaults were used to implement the latter restraints. The final structure was examined with PLATON [2] showing that there are no solvent-accessible voids in the crystal structure.

Discussion

L-malic acid ($C_4H_6O_5$), one of the simplest dicarboxylic acids, is a suitable building block in crystal engineering, being used to create two dimensional anionic networks held together by hydrogen bonds [3,4]. Metal dicarboxylates are also known to form structures with varying dimensionalities, e.g., chains or layers, linked by the dicarboxylate ions [5]. This work is part of a project aiming at synthesizing and investigating the structure and physical properties of new L-malate salts. A thermal analysis of the title compound was performed on a differential scanning calorimeter in the temperature range 270 K – 470 K. No phase transitions were observed up to the fusion temperature (appr. 425 K). The title compound shows a second harmonic generation with an effective second order susceptibility estimated to be 0.50 that of potassium dihydrogen phosphate [6]. The present compound is isostructural with the reported bis(potassium hydrogen L-malate) · malic acid [7]; however, the space group attributed to that structure is incompatible with preliminary measurements of the pyroelectric effect in the compound [6]. Attempts are underway to grow good quality crystals of the material in order to clarify the true symmetry of its crystal structure.

The main carbon skeletons of the independent hydrogen-L-malate anions and L-malic acid molecules are in *anti* conformation (figure, top). The cations show an eightfold coordination to oxygen atoms of the organic molecules and form zig-zag chains along the *a* axis. Two neighboring cations along each chain are coordinated to sets of three oxygen atoms. The remaining two coordination O atoms connect each cation to neighboring chains of organic molecules. The crystal structure can be seen as an almost layered 3D network in which ac slabs are bridged by organic molecules through hydrogen bonding and coordination to the cations lying in the slabs (figure, bottom). In these ac planes chains of head-to-tail hydrogen-L-malate anions alternate with neutral L-malic acid molecules and zigzag chains of cations. The present material can be described as having an open framework structure with channels parallel to [100]. The rubidium cations substitute randomly the K1 potassium cations. According to the X-ray data there are 0.337(7) % of Rb occupying K1. An elemental preliminary analysis of the carbon and hydrogen content using caffeine as a standard showed 28.8(4) % of carbon, yielding an amount of substitutional Rb of 49(15) % which is not in disagreement with the X-ray result.

* Correspondence author (e-mail: vhugo@pollux.fis.uc.pt)

Table 1. Data collection and handling.

Crystal:	translucent colorless square pyramid, size 0.10 × 0.15 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	14.06 cm ⁻¹
Diffraction, scan mode:	Enraf-Nonius CAD4, ω -2 θ , profile data
2 $\theta_{\max}$:	55.02°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8928, 4181
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1954
$N(\text{param})_{\text{refined}}$:	279
Programs:	SHELXL-97 [1], PLATON [2], SHELXS-97 [8], ORTEP-II [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U_{iso}
H(11)	4a	0.8143	0.6671	0.3888	0.060
H(12)	4a	0.5802	0.8581	0.4139	0.035
H(13)	4a	0.7232	1.0799	0.4273	0.049
H(13A)	4a	0.4906	1.0356	0.3339	0.034
H(13B)	4a	0.4219	0.8534	0.3448	0.034
H(14)	4a	0.1345	0.9723	0.4173	0.066
H(22)	4a	0.7032	0.2157	0.2634	0.037
H(23)	4a	0.8027	0.1893	0.3280	0.052
H(23A)	4a	0.7242	0.5674	0.2861	0.033
H(23B)	4a	0.6838	0.5131	0.2366	0.033
H(24)	4a	0.2938	0.3764	0.2561	0.076
H(32)	4a	0.2013	0.6518	0.4986	0.050
H(33)	4a	0.2621	0.6948	0.4306	0.089
H(33A)	4a	0.2150	0.3211	0.4599	0.047
H(33B)	4a	0.1715	0.3409	0.5110	0.047
H(34)	4a	-0.2059	0.5187	0.4974	0.106

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	4a	0.663(7)	0.087(1)	0.495(1)	0.3559(3)	0.016(5)	0.121(7)	0.056(6)	0.000(6)	0.009(4)	-0.016(5)
Rb(1)	4a	0.337	0.0882(9)	0.4972(8)	0.3553(2)	0.019(4)	0.036(2)	0.017(2)	0.010(3)	0.000(3)	0.006(3)
K(2)	4a		0.5868(2)	0.4234(2)	0.39495(4)	0.0178(7)	0.037(1)	0.0266(7)	-0.0010(9)	-0.0007(7)	-0.0003(7)
O(11)	4a		0.7761(7)	0.6926(7)	0.3641(2)	0.028(3)	0.038(3)	0.053(3)	0.003(3)	0.006(3)	-0.005(3)
O(12)	4a		0.8459(7)	0.9436(7)	0.3366(1)	0.024(3)	0.043(4)	0.043(3)	0.002(3)	0.015(2)	0.009(2)
C(11)	4a		0.7535(9)	0.846(1)	0.3623(2)	0.018(4)	0.030(5)	0.032(4)	0.000(4)	-0.003(3)	0.001(4)
C(12)	4a		0.6139(8)	0.930(1)	0.3886(2)	0.014(4)	0.036(4)	0.035(4)	0.003(4)	0.003(3)	-0.004(4)
O(13)	4a		0.6665(7)	1.0913(7)	0.4044(1)	0.028(3)	0.042(3)	0.028(3)	0.001(3)	-0.005(2)	-0.009(2)
C(13)	4a		0.4570(8)	0.9603(9)	0.3580(2)	0.018(3)	0.046(5)	0.022(3)	-0.001(3)	0.000(3)	0.006(3)
C(14)	4a		0.306(1)	1.036(1)	0.3826(2)	0.023(4)	0.050(7)	0.036(4)	0.002(4)	0.001(3)	0.004(4)
O(14)	4a		0.2164(7)	0.9252(8)	0.4051(2)	0.026(3)	0.050(4)	0.057(4)	0.004(3)	0.012(3)	0.001(3)
O(15)	4a		0.2764(9)	1.1883(9)	0.3822(2)	0.046(4)	0.055(4)	0.080(4)	0.020(4)	0.022(4)	0.017(4)
O(21)	4a		0.9308(8)	0.3056(7)	0.2084(1)	0.026(3)	0.085(4)	0.028(3)	-0.017(4)	0.011(3)	-0.013(3)
O(22)	4a		1.0780(8)	0.3469(9)	0.2710(2)	0.008(3)	0.102(5)	0.046(3)	-0.002(4)	-0.002(3)	-0.020(3)
C(21)	4a		0.941(1)	0.321(1)	0.2498(2)	0.017(4)	0.053(5)	0.033(4)	0.005(4)	0.009(4)	-0.006(4)
C(22)	4a		0.772(1)	0.310(1)	0.2753(2)	0.021(4)	0.044(5)	0.028(4)	-0.006(4)	0.002(3)	-0.001(4)
O(23)	4a		0.7908(8)	0.2900(6)	0.3220(2)	0.032(3)	0.038(3)	0.034(3)	0.009(3)	0.013(3)	0.005(2)
C(23)	4a		0.6737(8)	0.479(1)	0.2677(2)	0.014(3)	0.044(5)	0.026(3)	-0.009(4)	0.004(3)	0.008(4)
C(24)	4a		0.486(1)	0.457(1)	0.2797(2)	0.025(4)	0.040(6)	0.029(4)	-0.006(4)	0.000(3)	0.000(3)
O(24)	4a		0.3962(7)	0.3785(9)	0.2489(2)	0.015(3)	0.079(4)	0.058(3)	-0.009(4)	0.002(3)	-0.026(3)
O(25)	4a		0.4230(7)	0.5084(8)	0.3143(1)	0.016(2)	0.086(4)	0.031(2)	0.008(4)	0.000(2)	-0.010(3)
O(31)	4a		0.5769(7)	0.5466(9)	0.4807(2)	0.016(2)	0.119(6)	0.035(3)	0.009(5)	0.008(3)	0.000(3)
O(32)	4a		0.4491(6)	0.5041(8)	0.5457(2)	0.013(3)	0.077(4)	0.036(3)	-0.009(3)	0.004(2)	0.007(3)
C(31)	4a		0.4461(9)	0.534(1)	0.5048(2)	0.024(4)	0.039(5)	0.040(4)	-0.008(4)	0.001(3)	0.011(3)
C(32)	4a		0.266(1)	0.562(1)	0.4834(3)	0.017(4)	0.055(7)	0.052(5)	0.003(5)	0.004(4)	0.024(5)
O(33)	4a		0.2826(9)	0.5947(9)	0.4356(2)	0.042(4)	0.075(5)	0.061(4)	-0.003(5)	-0.006(3)	0.029(3)
C(33)	4a		0.1648(9)	0.396(1)	0.4821(3)	0.015(4)	0.064(7)	0.038(4)	0.006(5)	-0.006(3)	-0.008(4)
C(34)	4a		-0.0226(9)	0.431(1)	0.4705(3)	0.009(3)	0.065(6)	0.043(5)	-0.006(4)	0.001(4)	0.007(5)
O(34)	4a		-0.1055(7)	0.499(1)	0.5046(2)	0.022(3)	0.157(7)	0.034(3)	-0.001(5)	0.003(2)	-0.022(4)
O(35)	4a		-0.0872(8)	0.3999(7)	0.4350(1)	0.029(3)	0.067(4)	0.031(3)	0.003(4)	-0.011(3)	-0.006(2)

Acknowledgment. This work was financially supported by the Programme FEDER/POCTI (project no. 33657/2000, Fundação para a Ciência e Tecnologia).

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