metal-organic compounds

Supramolecular structure and second harmonic generation in strontium bis(hydrogen L-malate) hexahydrate

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The title compound, tetraaquabis(hydrogen L-malato)strontium(II) dihydrate, $[Sr(C_4H_5O_5)_2(H_2O)_4]\cdot 2H_2O$, is a new non-linear optical semi-organic material with a second harmonic generation efficiency approximately 3.5 times greater than that of potassium dihydrogen phosphate. The malate anions are interconnected through directional O—H⋯O hydrogen bonding, in a head-to-tail arrangement, creating extended anionic chains along [001]. Neighbouring parallel chains are crosslinked by water molecules, resulting in a three-dimensional architecture. The Sr^{2+} ion is coordinated by eight O atoms. This material is a new candidate for non-linear optical applications since the crystals are stable and easy to grow.

Comment

Previous studies on organic and semi-organic crystals have shown that L-malic acid is a suitable anionic building block since it is a chiral dicarboxylic acid with two hydrogen-bond donors and five hydrogen-bond acceptors providing structural consistency and rigidity in crystalline solids. Hydrogen malate anions tend to create infinite chains through head-to-tail hydrogen-bond interactions and are able to generate supramolecular aggregates with unique chemical and physical properties (Aakeroy & Nieuwenhuyzen, 1996); an exception has, however, been found in L-histidinium hydrogen malate (de Matos Gomes et al., 2005). Moreover, its chirality ensures the absence of a center of symmetry, essential for optical non-linear second harmonic generation. The synthesis and X-ray crystalline structure of some organic (Trivedi et al., 2003; Farrell et al., 2002; Aakeroy & Nieuwenhuyzen, 1996) and inorganic (Fleck et al., 2004) salts of L-malic acid have been reported previously, but their physical properties have not been fully studied. Optical second harmonic generation has been reported in racemic potassium malate (Schuler et al.,

1982), ammonium malate (Betzler et al., 1977), zinc malate 1,10-phenanthroline (He et al., 2004) and recently caesium hydrogen malate (de Matos Gomes et al., 2005).

Strontium bis(hydrogen L-malate) hexahydrate, hereafter SrLM, is isostructural with its calcium analogue (Lenstra & Van Havere, 1980), having an orthorhombic unit cell and space group $P2_12_12_1$. The unit-cell volume of SrLM is only a few percent larger than that of the calcium compound. Although the ionic radius of an eight-coordinate Sr^{2+} ion is about 10% larger than Ca^{2+}, steric effects due to the minimization of intermolecular repulsions should have a smoothing effect in the volume increase of the unit cell. The asymmetric unit cell contains two singly-ionized L-malate anions, one strontium(II) cation and six water molecules (Fig. 1).

SrLM
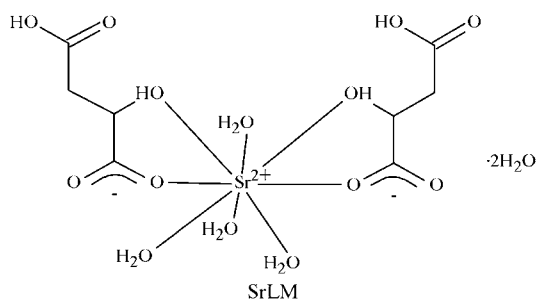
The conformation of the anions is staggered, as can be concluded from the Cn1—Cn2—Cn3—Cn4 (n = 1 and 2) torsion angles (Table 1). Comparison of the C—O bond distances in the two carboxyl groups of each anion shows that only one of them is ionized, as usually found in L-malic acid salts.

The cations are coordinated to eight O atoms forming irregular polyhedra; four of these O atoms belong to the anions, whereas the remaining four, viz. O1–O4, belong to
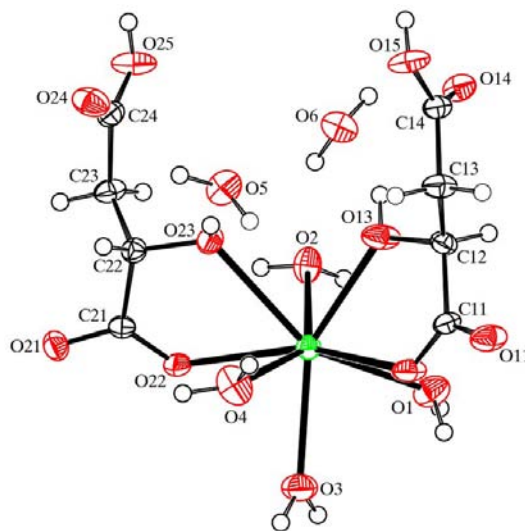

Figure 1
ORTEPII (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

water molecules. The O atoms of the anions involved are O13 and O23 of the hydroxy groups and O12 and O22 of the ionized carboxylate groups. The coordination distances range from 2.541 (2) to 2.693 (3) Å. Nearest coordination polyhedra do not share any O atoms, the shortest distance between adjacent Sr^{2+} cations being 7.983 (2) Å. The bonding of nearest cations is established *via* hydrogen bonds between the coordination O atoms and non-coordinated water molecules, as well as *via* carboxylate and carboxyl groups of the anions; Table 2 allows the comparison of their relative strengths. In fact, there are a large number of very strong hydrogen bonds, those between hydrogen L-malate anions connected in a head-to-tail arrangement being amongst the strongest.

The crystal packing can be described as malate anion chains running parallel to the [001] direction. Along these chains, the anions show a head-to-tail arrangement; the carboxyl group (COOH) of each anion is hydrogen bonded to the carboxylate group (COO−) of the next anion in the chain, as shown in Fig. 2. There are four chains in the unit cell, two running up and two running down the *b* axis. Parallel chains along the [001] direction are crosslinked by water molecules *via* hydrogen bonds forming infinite layers of equivalent malate anions parallel to the *bc* plane. Consecutive layers along the *a* direction, generated by screw axis symmetry operations, are further linked *via* hydrogen bonds, giving rise to a three-dimensional packing network.

To investigate the linear and non-linear optical properties of the title compound, the transmission curve of a 1 mm-thick

SrLM plate was measured in the range 200–1200 nm using a Shimadzu spectrophotometer and showed a broad transparency, with a transmission greater than 80%. Preliminary measurements were undertaken to characterize the second-order non-linear optical response of the SrLM crystals. Using crystals ranging in thickness from 1.4 to 2.0 mm, the second harmonic of a multi-mode Q-switched Nd:YAG laser was generated. The Nd:YAG laser emitted 8 ns pulses with roughly 5 mJ of energy that were weakly focused on to the crystal, which was oriented to provide a maximum second harmonic signal (angle phase-matched). Simultaneously, in order to account for the large shot-to-shot fluctuations due to the random correlation between modes, the signal generated by a 2 mm-thick *z*-cut quartz plate was monitored. Subsequently, using the same experimental setup, the signal generated by a reference potassium dihydrogen phosphate (KDP) crystal orientated at its phase-matching angle was also measured. Taking into account the difference in crystal thickness, SrLM crystals were 3.5 times more efficient than the KDP reference crystal. We plan, in the near future, to characterize further the second order non-linear susceptibility using the Maker fringe technique.

The crystal stability and high optical second harmonic generation signal observed in SrLM make it a promising material for non-linear optics.

Experimental

An aqueous solution of analytical grade reagent, strontium hydroxide and L-malic acid (Aldrich) in a 1:2 molar ratio was stirred at 333 K for several hours and then allowed to cool to room temperature. Crystals were obtained after one week of evaporation of the solution and were stable in air. A suitable crystal was selected and checked by photographic methods before data collection.

Crystal data

$[Sr(C_4H_5O_5)_2(H_2O)_4]\cdot2H_2O$	$Z = 4$
$M_r = 461.88$	$D_x = 1.762$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 7.166\ (3)$ Å	$\mu = 3.18$ mm^{-1}
$b = 15.365\ (5)$ Å	$T = 292\ (2)$ K
$c = 15.818\ (5)$ Å	Block, clear colorless
$V = 1741.5\ (10)$ Å^3	$0.2 \times 0.2 \times 0.1$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2302 independent reflections
Profile data from ω–2θ scans	1970 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North *et al.*, 1968)	$R_{int} = 0.011$
$T_{min} = 0.541$, $T_{max} = 0.728$	$\theta_{max} = 27.5°$
2335 measured reflections	3 standard reflections
	frequency: 180 min
	intensity decay: 10%

Refinement

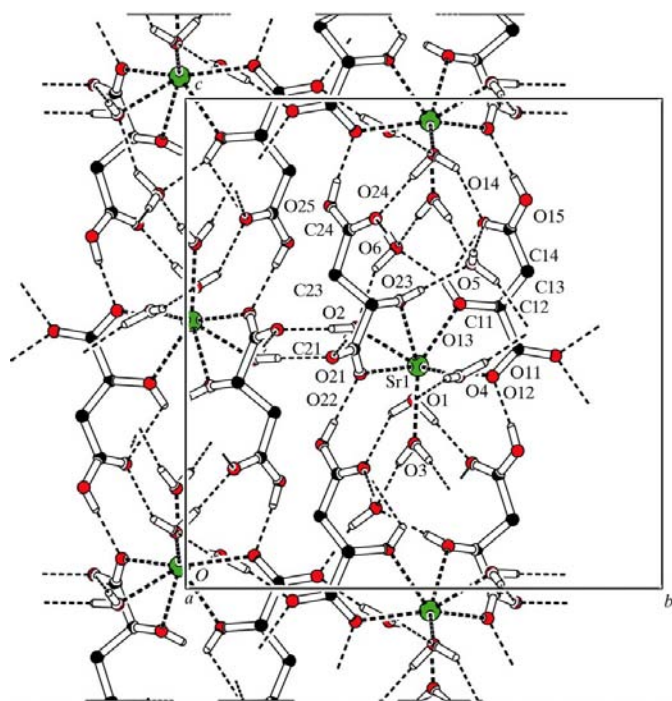|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 0.2880P]$
$R[F^2 > 2\sigma(F^2)] = 0.021$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.055$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
2302 reflections	$\Delta\rho_{min} = -0.31$ e Å^{-3}
267 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0064 (6)
	Absolute structure: Flack (1983)
	Flack parameter: −0.006 (7)

Figure 2
The packing, viewed along the *a* axis, showing the hydrogen-bonding network. All H atoms not involved in intermolecular hydrogen bonds have been omitted.

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Table 1
Selected geometric parameters (Å, °).

Sr1—O3	2.541 (2)	C12—C13	1.527 (4)
Sr1—O4	2.557 (3)	C13—C14	1.508 (4)
Sr1—O12	2.561 (2)	C14—O14	1.217 (4)
Sr1—O22	2.561 (2)	C14—O15	1.312 (4)
Sr1—O2	2.579 (2)	O21—C21	1.257 (4)
Sr1—O13	2.592 (2)	O22—C21	1.250 (4)
Sr1—O23	2.650 (2)	C21—C22	1.541 (4)
Sr1—O1	2.693 (3)	C22—O23	1.428 (4)
O11—C11	1.256 (4)	C22—C23	1.530 (4)
O12—C11	1.262 (4)	C23—C24	1.511 (4)
C11—C12	1.532 (4)	C24—O24	1.219 (4)
C12—O13	1.427 (4)	C24—O25	1.297 (4)
O11—C11—O12	124.6 (3)	O22—C21—O21	124.7 (3)
O13—C12—C11	107.7 (2)	O23—C22—C21	110.6 (2)
O14—C14—O15	123.9 (3)	O24—C24—O25	124.2 (3)
O11—C11—C12—O13	−166.2 (3)	O21—C21—C22—O23	172.0 (3)
O11—C11—C12—C13	−43.4 (5)	O21—C21—C22—C23	−67.5 (4)
C11—C12—C13—C14	179.1 (3)	C21—C22—C23—C24	173.2 (3)
C12—C13—C14—O14	−21.8 (5)	C22—C23—C24—O24	−39.3 (5)

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O13—H13$\cdots$O6	0.82	2.01	2.753 (3)	150
O13—H13$\cdots$O14	0.82	2.54	3.065 (3)	123
O15—H15$\cdots$O22[i]	0.82	1.82	2.607 (3)	162
O23—H23$\cdots$O5	0.82	1.93	2.749 (3)	177
O25—H25$\cdots$O12[i]	0.82	1.74	2.541 (3)	167
O1—H1$A\cdots$O24[ii]	0.95 (3)	1.83 (3)	2.782 (3)	172 (4)
O1—H1$B\cdots$O14[iii]	0.96 (3)	2.19 (2)	3.051 (3)	150 (3)
O2—H2$A\cdots$O21[iv]	0.95 (3)	1.875 (15)	2.805 (3)	164 (3)
O2—H2$B\cdots$O21[v]	0.953 (10)	1.729 (11)	2.681 (3)	179 (4)
O3—H3$A\cdots$O6[ii]	0.95 (3)	1.85 (3)	2.797 (4)	176 (4)
O3—H3$B\cdots$O5[ii]	0.96 (3)	1.97 (3)	2.919 (4)	170 (3)
O4—H4$A\cdots$O11[vi]	0.94 (3)	1.81 (3)	2.741 (4)	169 (4)
O4—H4$B\cdots$O1[vii]	0.945 (10)	2.105 (16)	3.016 (4)	161 (4)
O5—H5$A\cdots$O14[vii]	0.949 (10)	1.913 (14)	2.845 (4)	167 (4)
O5—H5$B\cdots$O11[vi]	0.95 (3)	1.985 (18)	2.899 (4)	160 (4)
O6—H6$A\cdots$O2	0.94 (3)	2.03 (2)	2.900 (4)	152 (4)
O6—H6$B\cdots$O24[v]	0.94 (3)	1.893 (16)	2.812 (4)	164 (4)

Symmetry codes: (i) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+1, z-\frac{1}{2}$; (iii) $-x-\frac{1}{2}, -y+1, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+1$; (v) $x-1, y, z$; (vi) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (vii) $x+1, y, z$.

All H atoms were located in a difference Fourier map; those bonded to C and hydroxyl and carboxyl O atoms were placed at idealized positions and refined as riding [C—H = 0.97 and 0.98 Å, O—H = 0.82 Å, and U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(O)]. The positions of the H atoms belonging to the water molecules were restrained so that the intramolecular O—H and H$\cdots$H distances would be 0.96 and 1.52 Å within 0.01 Å, respectively, thus enforcing the known average geometry of water molecules [U_{iso}(H) = $1.5U_{eq}$(O)]. Examination of the crystal structure with *PLATON* (Spek, 2003) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *PLATON* (Spek, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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