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L-Argininium(+) maleate(−) dihydrate

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The title complex, $C_6H_{15}N_4O_2^+\cdot C_4H_3O_4^-\cdot 2H_2O$, contains a planar ring formed by sharing one H atom between the O atoms in the carboxyl groups of the maleate anion. This hydrogen bond is slightly asymmetric. In the L-argininium(+) cation, both the α-amino and the guanidyl groups are protonated. The nonlinear optical response of the compound is derived from the intrinsic hyperpolarizabilities of the L-argininium cations, maleate anions and intermolecular hydrogen bonds.

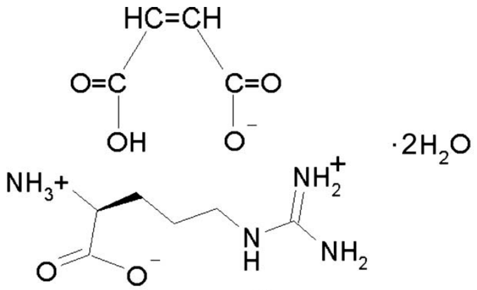
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.070
Data-to-parameter ratio = 8.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Over the past two decades, the discovery of promising optical properties in L-arginine phosphate monohydrate (LAP) has stimulated strong interest in crystals of this family of compounds. It has a large effective nonlinear optical coefficient and a high optical damage threshold. Its significant advantage in frequency conversion will give benefits to high-power laser devices and contemporary photonic devices. Recently, attention has been focused on analogues of LAP, *e.g.* salts of L-Arg with inorganic acids, such as HCl, HBr, HF, HNO_3, $HClO_4$, HBF_4 and H_3AsO_4 (Xu *et al.*, 1983; Monaco *et al.*, 1987; Tanusri & Tanusree, 2002; Terzyan *et al.*, 2004). In slightly different conditions, crystalline salts of L-Arg with organic acids were synthesized (Bhat & Vijayan, 1977; Suresh *et al.*, 1986; Soman & Vijayan, 1989; Xu *et al.*,2003; Marchewka *et al.*, 2003). The crystal cell parameters of L-Arg malate (Monaco *et al.*, 1987) and the crystal structure of L-Arg maleic acid (Ravishankar *et al.*, 1998) were reported previously.



(I)

In the structure of the title compound, (I) (Fig. 1), both the α-amino and guanidyl groups in the L-Arg$^+$ cations are protonated. The C—N bond lengths (Table 1) in the guanidyl group clearly indicate that the C—N bonds are conjugated, which also makes the guanidyl group planar.

The packing of the components of (I) is shown in Fig. 2. A typical characteristic feature of (I) is the intermolecular hydrogen bonds. It contains several kinds of hydrogen bonds

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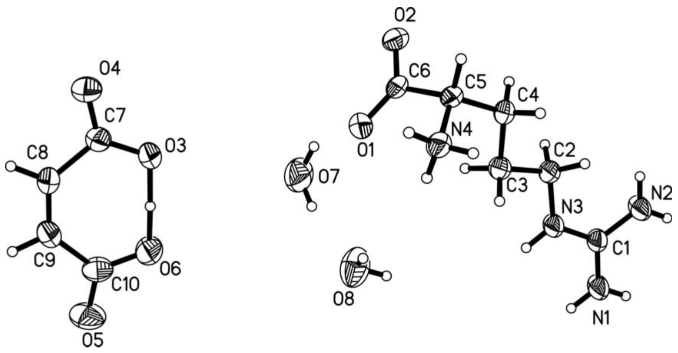

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

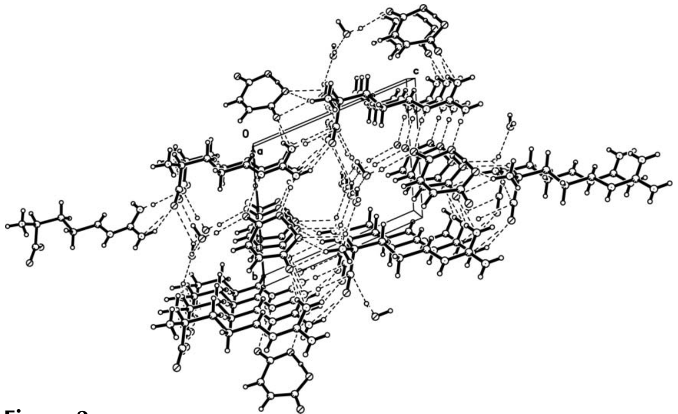

Figure 2
The crystal packing of (I), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines.

among the negatively charged carboxylate groups, positively charged protonated guanidyl groups and α-amino groups. The torsion angles of the maleate ion indicate that it forms a planar ring through sharing one H atom between O3 and O6. Similar results have been observed in many other complexes containing this anion (James & Williams, 1974; Barnes & Weakly, 1997; Pratap *et al.*, 2000).

The second harmonic generation (SHG) of crystals of (I) was studied by the powder SHG method (Kurtz & Perry, 1968). A green light beam was observed and its intensity was less than that from a urea crystal.

Experimental

High-quality crystals used for X-ray analysis were obtained from an aqueous solution of L-Arg acid and maleic acid, mixed in 1:2 molar ratio, after several days at 313 K.

Crystal data

$C_6H_{15}N_4O_2^+ \cdot C_4H_3O_4^- \cdot 2H_2O$
$M_r = 326.32$
Triclinic, $P1$
$a = 5.2710$ (1) Å
$b = 8.0481$ (2) Å
$c = 9.7942$ (2) Å
$\alpha = 106.155$ (1)°
$\beta = 97.265$ (1)°
$\gamma = 101.649$ (2)°
$V = 383.42$ (2) Å^3
$Z = 1$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 293$ (2) K
0.25 × 0.23 × 0.19 mm

Data collection

Bruker APEX II CCD detector diffractometer
Absorption correction: multi-scan (*APEX2*; Bruker, 2005)
$T_{\min} = 0.971$, $T_{\max} = 0.977$
3711 measured reflections
1762 independent reflections
1697 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.011$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.070$
$S = 1.01$
1762 reflections
220 parameters
7 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N2	1.324 (3)	C6—O2	1.262 (2)
C1—N1	1.321 (3)	C10—O5	1.222 (3)
C1—N3	1.330 (2)	C10—O6	1.288 (3)
C6—O1	1.235 (2)	C10—C9	1.485 (3)
N2—C1—N1	119.20 (18)	O1—C6—O2	126.16 (19)
N2—C1—N3	120.33 (18)	O1—C6—C5	118.50 (17)
N1—C1—N3	120.46 (18)	O2—C6—C5	115.34 (17)
O5—C10—C9—C8	179.8 (3)	C9—C8—C7—O4	179.9 (2)
O6—C10—C9—C8	1.2 (4)	C9—C8—C7—O3	−1.0 (4)
C10—C9—C8—C7	−0.4 (4)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N4—H4*AA*$\cdots$O2$^{\rm i}$	0.89	1.98	2.843 (2)	162
N1—H1*A*$\cdots$O1$^{\rm ii}$	0.86	2.18	2.935 (2)	147
N1—H1*B*$\cdots$O3$^{\rm ii}$	0.86	1.98	2.843 (2)	176
N4—H4*BB*$\cdots$O5$^{\rm iii}$	0.89	2.23	3.079 (3)	160
N2—H2*A*$\cdots$O2$^{\rm ii}$	0.86	2.10	2.948 (2)	171
N2—H2*B*$\cdots$O5$^{\rm iv}$	0.86	2.08	2.862 (3)	152
N3—H3$\cdots$O4$^{\rm ii}$	0.86	2.10	2.955 (2)	172
N4—H4*CC*$\cdots$O7$^{\rm v}$	0.89	1.92	2.801 (2)	173
O3—H6*A*$\cdots$O6	1.28 (4)	1.13 (4)	2.407 (2)	173 (3)
O7—H7*A*$\cdots$O8	0.90 (2)	1.91 (2)	2.791 (3)	165 (5)
O7—H7*B*$\cdots$O1	0.87 (2)	2.35 (4)	3.081 (3)	142 (5)
O7—H7*B*$\cdots$O8$^{\rm vi}$	0.87 (2)	2.57 (5)	3.186 (4)	129 (5)
O8—H8*A*$\cdots$O4$^{\rm ii}$	0.87 (3)	2.01 (2)	2.873 (3)	170 (4)
O8—H8*B*$\cdots$O2$^{\rm i}$	0.88 (2)	1.97 (3)	2.770 (2)	152 (5)

Symmetry codes: (i) $x+1, y, z$; (ii) $x+1, y, z+1$; (iii) $x-1, y-1, z$; (iv) $x-1, y-1, z+1$; (v) $x, y-1, z$; (vi) $x-1, y, z$.

H atoms attached to C and N atoms were positioned geometrically and treated as riding, with C—H = 0.93–0.98 Å and N—H = 0.86 or 0.89 Å; $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,N) or $1.5U_{\rm eq}$(N) (for NH_3). The other H atoms were found from a difference Fourier map and refined isotropically. In the refinement, the distances between water H and O atoms were restrained to the range 0.87–0.90 Å. In the absence of significant anomalous scattering, Friedel pairs were averaged.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *APEX2*; data reduction: *APEX2*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*

(Sheldrick, 2000); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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