Strontium D-glutamate hexahydrate and strontium di(hydrogen L-glutamate) pentahydrate

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$[Sr(C_5H_7NO_4)] \cdot 6H_2O$, (I), and $[Sr(C_5H_8NO_4)_2] \cdot 5H_2O$, (II), both crystallize with similar strontium–glutamate–water layers. In (I), the neutral layers are connected through hydrogen bonds by water molecules, while in (II), the positively charged layers are connected through hydrogen bonds and electrostatic interactions by interleaving layers of hydrogen glutamate anions and water molecules.

Comment

In recent years, it has been found that strontium has a significant influence on the development and growth of bone, and the effect of dose on bone structure has been investigated in great detail (Schrooten *et al.*, 2003). These investigations have led to a growing interest in strontium(II) salts and in synthetic methods that may provide products of high yield and purity. The present paper presents the structural investigations of two new strontium(II) salts, *viz.* the title compounds, $[Sr(C_5H_7NO_4)] \cdot 6H_2O$, (I), and $[Sr(C_5H_8NO_4)_2] \cdot 5H_2O$, (II) (Figs. 1 and 2).

The crystal structure of (I) is in full agreement with the structure of strontium(II) L-glutamate hexahydrate (Schmidbaur *et al.*, 1989). Compounds (I) and (II) are built from the same type of layers; the strontium ions are nine-coordinated to three water and six carboxyl O atoms to form distorted monocapped quadratic antiprisms. The α-carboxylate groups bridge two adjacent Sr coordination complexes, with the polyhedra sharing edges to form zigzag polyhedral chains in the *a* and *b* directions in (I) and (II), respectively. The chelating α- and γ-carboxylate groups are connected to different strontium polyhedral chains, thus crosslinking them to form layers in the *ab* planes (*cf.* Figs. 3 and 4). Despite the difference in charge due to the protonated glutamate in (II), these layers are very similar, as reflected in the unit-cell dimensions $[a_{(I)} = 7.3244 (4)$ Å and $b_{(II)} = 7.2450 (4)$ Å, and $a_{(II)} = 8.7097 (5)$ Å and $b_{(I)} = 8.7417 (5)$ Å]. The difference between the structures

lies in the stacking of the layers. The neutral strontium–glutamate–water layers in (I) are linked by hydrogen bonding to the three water molecules not involved in strontium coordination (Fig. 3 and Table 2). In (II), the positively charged strontium–hydrogen glutamate–water layers are interleaved
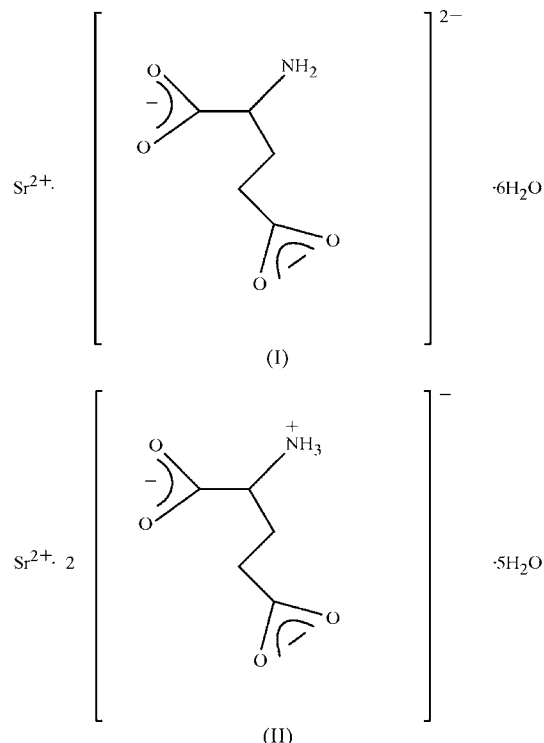

by negatively charged layers of hydrogen glutamate and the two water molecules not involved in strontium coordination. These layers are then linked by hydrogen-bonding and electrostatic interactions (Fig. 4 and Table 4). The conformations of the three glutamate ions, *viz.* (I), (II:1) and (II:2), are very similar, as seen from their torsion angles (Table 5). The difference between the strontium-coordinated glutamates (I) and (II:1) is due to the difference in absolute configuration, and the difference between the two L-glutamates (II:1) and
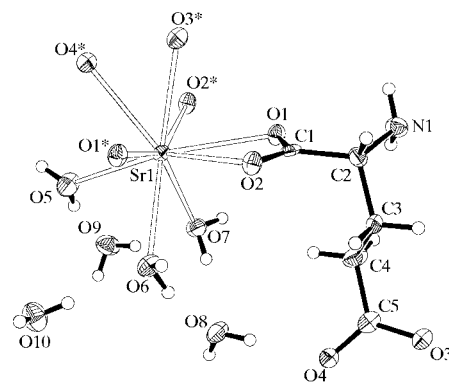
Figure 1
The asymmetric unit of (I), showing 75% probability displacement ellipsoids and the atomic numbering. H atoms are represented by circles of arbitrary size. [Atoms labelled with an asterisk (*) are at the symmetry positions indicated in Table 1.]

(II:2) is essentially in the rotation of the carboxyl groups in order to optimize hydrogen bonding.

A zigzag chain of strontium polyhedra is a common structural element in Sr^{II} dicarboxylic acid structures, seen in, for example, Sr^{II} maleate (Diaz de Delgade *et al.*, 1995), Sr^{II} oxalate (Sterling, 1965), Sr^{II} phthalate (Bats *et al.*, 1978) and Sr^{II} aspartate (Derrisen *et al.*, 1968). In contrast, the two forms of Sr^{II} tartrate, *viz.* the tri- (Ambady, 1968) and tetrahydrates (Starynowicz & Meyer, 2000), form isolated Sr^{II} polyhedra. The crosslinking of the Sr chains into layers as in the glutamates is also seen in Sr^{II} aspartate and Sr^{II} maleate. In Sr^{II}
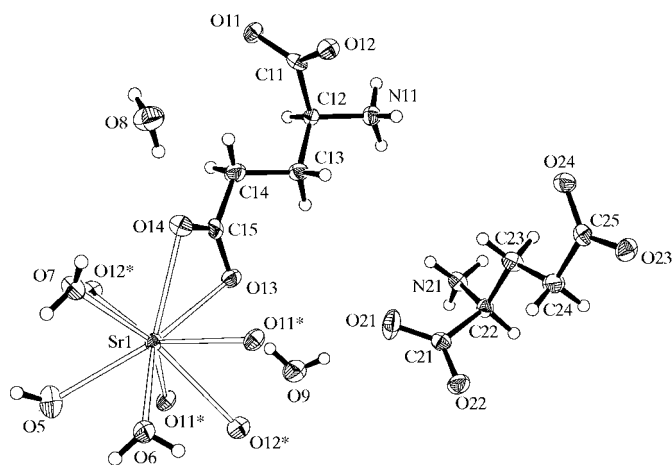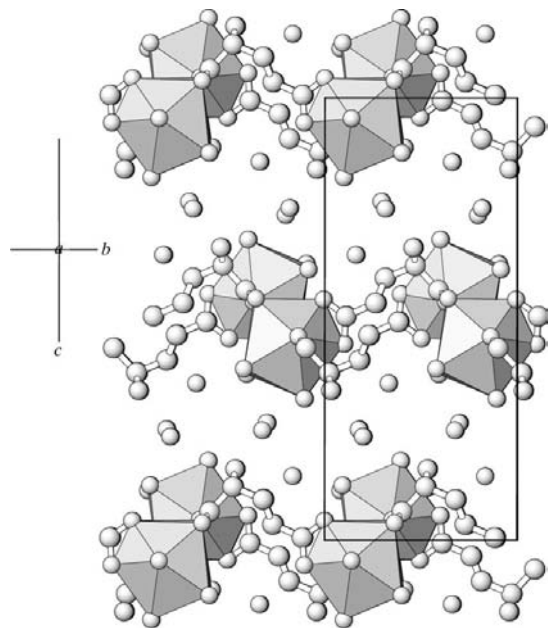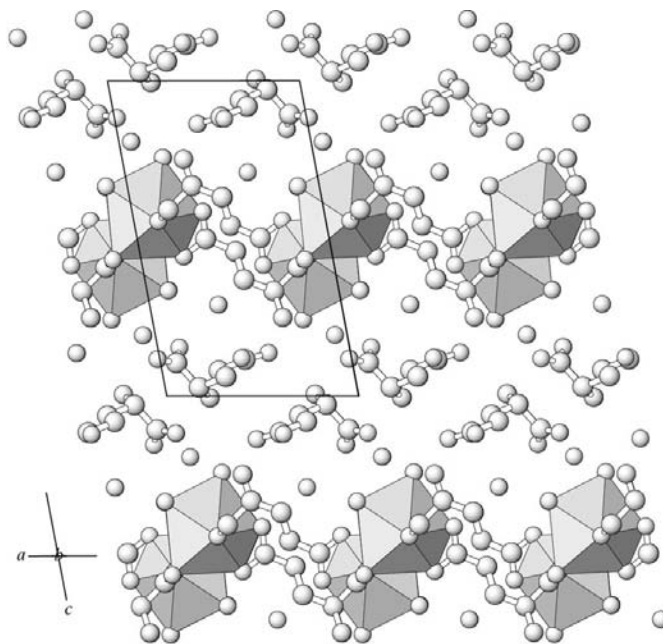

Figure 2
The asymmetric unit of (II), showing 75% probability displacement ellipsoids and the atomic numbering. H atoms are represented by circles of arbitrary size. [Atoms labelled with an asterisk (*) are at the symmetry positions indicated in Table 3.]

Figure 3
The crystal packing of (I), viewed down the *a* axis. The nine-coordination of the Sr atoms is shown as polyhedra. H atoms have been omitted for clarity.

Figure 4
The crystal packing of (II), viewed along the *b* axis. The nine-coordination of the Sr atoms is shown as polyhedra. H atoms have been omitted for clarity.

oxalate, on the other hand, the oxalate groups form three-dimensional connections through strontium coordination, and in Sr^{II} phthalate, the Sr polyhedra chains are connected through hydrogen bonds into layers and by van der Waals bonds between layers. Obviously, the layer formations as in the glutamate, aspartate and maleate salts require a certain carbon chain length to allow for the layer formation.

Experimental

The synthesis of strontium(II) compounds was performed according to a novel method of high-temperature synthesis, which readily provided high-quality crystals that were well suited for analysis by single-crystal X-ray analysis (Price *et al.*, 1999). Briefly, crystals were obtained by synthesis in an autoclave at temperatures between 393 and 413 K over a period of 15 min. Crystals of strontium(II) D-glutamate were obtained by reacting strontium(II) hydroxide octahydrate with D-glutamic acid in a molar ratio of 1:1.2, while crystals of strontium(II) di(hydrogen L-glutamate) were obtained by reacting equimolar amounts of strontium(II) chloride hexahydrate with disodium L-glutamate (Price *et al.*, 1999).

Compound (I)

Crystal data

$[Sr(C_5H_7NO_4)]\cdot6H_2O$	Mo $K\alpha$ radiation
$M_r = 340.83$	Cell parameters from 3509
Orthorhombic, $P2_12_12_1$	reflections
$a = 7.3244\ (4)$ Å	$\theta = 2.5–28.0°$
$b = 8.7417\ (5)$ Å	$\mu = 4.23$ mm^{-1}
$c = 20.0952\ (12)$ Å	$T = 120\ (2)$ K
$V = 1286.65\ (13)$ Å^3	Plate, colourless
$Z = 4$	$0.30 \times 0.10 \times 0.03$ mm
$D_x = 1.760$ Mg m^{-3}	

Data collection

Bruker SMART APEX diffractometer	3098 independent reflections
ω scans, frame data integration	2812 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.039$
($SADABS$; Sheldrick, 2002)	$\theta_{max} = 28.0°$
$T_{min} = 0.64$, $T_{max} = 0.88$	$h = -9 \rightarrow 9$
9203 measured reflections	$k = -11 \rightarrow 11$
	$l = -26 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.028$	$(\Delta/\sigma)_{max} = 0.002$
$wR(F^2) = 0.051$	$\Delta\rho_{max} = 0.83$ e Å^{-3}
$S = 0.89$	$\Delta\rho_{min} = -0.44$ e Å^{-3}
3098 reflections	Absolute structure: Flack (1983),
196 parameters	1293 Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: 0.003 (6)

Table 1
Selected interatomic distances (Å) for (I).

Sr1—O1^i	2.623 (2)	Sr1—O3^{iii}	2.6639 (17)
Sr1—O5	2.625 (2)	Sr1—O2	2.6687 (18)
Sr1—O2^{ii}	2.635 (2)	Sr1—O6	2.693 (2)
Sr1—O7	2.637 (2)	Sr1—O1	2.7083 (19)
Sr1—O4^{iii}	2.6501 (17)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H3$\cdots$O4^{iv}	0.90 (2)	2.40 (2)	3.283 (3)	169 (3)
O5—H8$\cdots$O9^v	0.84 (2)	1.95 (2)	2.768 (3)	163 (3)
O5—H9$\cdots$O10^{vi}	0.81 (2)	2.14 (2)	2.939 (3)	168 (3)
O6—H10$\cdots$O8^v	0.80 (2)	1.97 (2)	2.740 (3)	160 (4)
O6—H11$\cdots$O3^{vii}	0.78 (2)	2.01 (2)	2.783 (3)	170 (4)
O7—H12$\cdots$O3^{iv}	0.81 (2)	1.90 (2)	2.713 (3)	177 (3)
O7—H13$\cdots$O8^v	0.83 (2)	1.90 (2)	2.719 (3)	170 (3)
O8—H14$\cdots$O10^{viii}	0.78 (2)	1.94 (2)	2.711 (3)	171 (3)
O8—H15$\cdots$O4^v	0.80 (2)	1.91 (2)	2.708 (3)	176 (4)
O9—H16$\cdots$O7^v	0.80 (2)	2.00 (2)	2.766 (3)	163 (3)
O9—H17$\cdots$N1^{ix}	0.81 (2)	1.93 (2)	2.735 (3)	176 (3)
O10—H18$\cdots$O9^x	0.81 (2)	1.97 (2)	2.775 (3)	172 (4)
O10—H19$\cdots$O6^v	0.80 (2)	2.00 (2)	2.796 (3)	178 (4)

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

Compound (II)

Crystal data

[Sr(C$_5$H$_8$NO$_4$)$_2$]·5H$_2$O	$D_x = 1.725$ Mg m^{-3}
$M_r = 469.95$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 4782
$a = 8.7097$ (5) Å	reflections
$b = 7.2450$ (4) Å	$\theta = 2.4$–$30.0°$
$c = 14.5854$ (8) Å	$\mu = 3.05$ mm^{-1}
$\beta = 100.521$ (1)°	$T = 117$ (2) K
$V = 904.89$ (9) Å^3	Plate, colourless
$Z = 2$	$0.46 \times 0.15 \times 0.04$ mm

Data collection

Bruker SMART APEX diffractometer	4586 independent reflections
	4179 reflections with $I > 2\sigma(I)$
ω scans, frame data integration	$R_{int} = 0.021$
Absorption correction: multi-scan	$\theta_{max} = 30.0°$
($SADABS$; Sheldrick, 2002)	$h = -11 \rightarrow 12$
$T_{min} = 0.633$, $T_{max} = 0.883$	$k = -9 \rightarrow 10$
7102 measured reflections	$l = -20 \rightarrow 18$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2)]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.054$	$\Delta\rho_{max} = 0.74$ e Å^{-3}
$S = 0.79$	$\Delta\rho_{min} = -0.33$ e Å^{-3}
4586 reflections	Absolute structure: Flack (1983),
283 parameters	1850 Friedel pairs
H atoms treated by a mixture of independent and constrained refinement	Flack parameter: 0.010 (5)

Table 3
Selected interatomic distances (Å) for (II).

Sr1—O11^{xi}	2.603 (2)	Sr1—O11^{xii}	2.636 (2)
Sr1—O5	2.605 (2)	Sr1—O12^{xiii}	2.639 (2)
Sr1—O14	2.6130 (13)	Sr1—O13	2.6478 (12)
Sr1—O6	2.619 (2)	Sr1—O12^{xii}	2.816 (2)
Sr1—O7	2.6326 (16)		

Symmetry codes: (xi) $-x + 1, y - \frac{1}{2}, -z + 1$; (xii) $x + 1, y, z$; (xiii) $-x + 1, y + \frac{1}{2}, -z + 1$.

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N11—H12$\cdots$O9^x	0.89 (2)	1.88 (2)	2.769 (3)	171 (3)
N11—H13$\cdots$O7^{xi}	0.87 (2)	2.19 (2)	3.004 (3)	155 (2)
N11—H14$\cdots$O23^{iii}	0.88 (2)	1.87 (2)	2.715 (3)	161 (2)
N21—H22$\cdots$O24^{xiv}	0.92 (2)	1.93 (2)	2.840 (3)	173 (3)
N21—H23$\cdots$O23^{iii}	0.88 (2)	1.96 (2)	2.805 (3)	162 (2)
N21—H24$\cdots$O22^{xv}	0.89 (2)	1.88 (2)	2.760 (3)	168 (2)
O5—H1$\cdots$O13^{xvi}	0.80 (2)	1.95 (2)	2.743 (3)	177 (4)
O5—H2$\cdots$O21^{xvi}	0.83 (2)	1.95 (2)	2.736 (3)	158 (3)
O6—H3$\cdots$O13^{xvii}	0.82 (2)	1.89 (2)	2.698 (3)	173 (4)
O6—H4$\cdots$O8^{xii}	0.83 (2)	1.93 (2)	2.738 (3)	167 (3)
O7—H5$\cdots$O22^{xvi}	0.81 (2)	1.96 (2)	2.763 (3)	170 (3)
O7—H6$\cdots$O24^{xiii}	0.80 (2)	2.08 (2)	2.852 (3)	163 (3)
O8—H7$\cdots$O14	0.81 (2)	1.91 (2)	2.722 (2)	178 (4)
O8—H8$\cdots$O5^x	0.83 (2)	2.11 (2)	2.866 (3)	150 (3)
O9—H9$\cdots$O21	0.83 (2)	1.92 (2)	2.745 (3)	176 (3)
O9—H10$\cdots$O6^{xvi}	0.81 (2)	1.99 (2)	2.765 (3)	161 (3)

Symmetry codes: (iii) $x, y + 1, z$; (x) $x - 1, y, z$; (xi) $-x + 1, y - \frac{1}{2}, -z + 1$; (xii) $x + 1, y, z$; (xiii) $-x + 1, y + \frac{1}{2}, -z + 1$; (xiv) $-x + 1, y + \frac{1}{2}, -z + 2$; (xv) $-x + 2, y + \frac{1}{2}, -z + 2$; (xvi) $-x + 2, y + \frac{1}{2}, -z + 1$; (xii) $-x + 2, y - \frac{1}{2}, -z + 1$.

Table 5
Torsion angles (°).

	(I)	(II:1)	(II:2)
O1—C1—C2—C3	−107.3 (3)	−109.8 (2)	91.3 (3)
C1—C2—C3—C4	54.5 (3)	55.1 (3)	70.7 (3)
C2—C3—C4—C5	−178.5 (2)	177.4 (2)	−179.6 (2)
C3—C4—C5—O3	−56.3 (4)	−43.5 (4)	−170.6 (2)
O1—C1—C2—N1	17.5 (3)	128.3 (2)	−28.3 (3)
N1—C2—C3—C4	−73.0 (3)	176.8 (2)	−169.4 (2)

All H-atom parameters were initially refined freely. In the final cycles, H atoms of CH$_2$ and CH groups were placed in calculated positions, with C—H distances of 0.97 and 0.98 Å, respectively, and refined as riding atoms. The water O—H distances were restrained to 0.84 (2) Å and the N—H distances were restrained to 0.89 (2) Å. The displacement parameters were set at 1.2 (CH and NH) or 1.5 (OH) times the equivalent isotropic displacement parameters of the corresponding C, N or O atoms.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*

metal-organic compounds

and *SADABS* (Sheldrick, 2002); structure solution: *SHELXTL* (Sheldrick, 2000); structure refinement: *SHELXTL*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ATOMS* (Dowty, 2000); software used to prepare material for publication: *SHELXTL*.

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