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A new layered Ca–succinate coordination polymer

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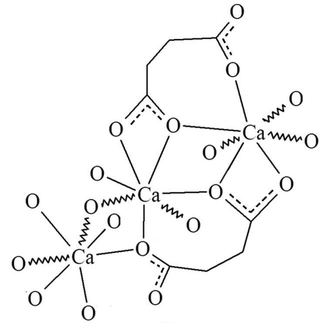
A new layered Ca–succinate coordination polymer, poly[μ_3-succinato-calcium(II)], $[Ca(C_4H_5O_4)]_n$, was synthesized by reaction of $CaCl_2\cdot 2H_2O$ and succinic acid in an aqueous medium under hydrothermal microwave conditions. The structure contains infinite layers of edge-sharing calcium pentagonal–bipyramidal polyhedra forming six-membered rings connected through succinate ligands. Such an assembly of inorganic building units is unique for calcium metal–organic framework-type structures. Adjacent layers are packed into a final pseudo-three-dimensional structure through weak C—H$\cdots$O hydrogen bonds.

Comment

The design of new metal–organic framework (MOF) materials with useful structural properties by combining various metal cations with heteropolyfunctional organic linkers such as polycarboxylates, polyphosphonates or polyamines has become a great challenge over the last decade (Yaghi, 2004; Eddaoudi, 2007; Kuppler *et al.*, 2009; Farrusseng *et al.*, 2009). Calcium-based polycarboxylates can be used in bioapplications due to the nontoxic nature and biocompatability of calcium cations. However, the number of known Ca-based polycarboxylate structures is relatively low compared with more frequently investigated MOFs based on transition metal cations. Several structures are known to date with aromatic polycarboxylic ligands (Platers *et al.*, 1997; Groeneman & Atwood, 1999; Zhu *et al.*, 2005; Volkringer *et al.*, 2007; Dale & Elsegood, 2003) and some with alkyl polycarboxylates (De Lill *et al.*, 2005; Mathew & Takagi, 1995; Mathew *et al.*, 1994). We report here the synthesis and structural characterization of a new layered Ca–succinate compound, the title compound, (I).

The crystal structure of (I) is built from infinite layers of edge-sharing calcium polyhedra. Each polyhedron shares three of its edges with neighbouring polyhedra, generating inorganic layers with six-membered rings (Fig. 1). Fig. 2 shows a view of adjacent inorganic layers connected *via* weak C—H$\cdots$O hydrogen bonds along the *a* axis. The Ca atoms at the centres of these polyhedra occupy two different crystallographic sites (Ca1 and Ca2) in general positions and both are coordinated to seven different O atoms, all from dicarboxylate groups. This sevenfold coordination defines slightly distorted pentagonal–bipyramidal polyhedra with Ca—O distances in the range 2.3027 (13)–2.5162 (12) Å (Table 1), which is similar to the coordination environment in some other known seven-coordinate Ca carboxylates (Williams *et al.*, 2008; Mathew & Takagi, 1995; Mathew *et al.*, 1994). The Ca1 atoms are coordinated by four O atoms in a monodentate bridging mode from three different succinate dianions ($O1^{ii}$, $O3^{ii}$, O4 and $O6^{iii}$) and by atom $O2^{i}$ in a monodentate manner (symmetry codes are as in Table 1). The remaining two O atoms (O7 and O8) are connected to Ca1 in chelating and bridging modes. The Ca2 atoms have similar O atom coordination modes. Four O atoms from three different succinate dianions are coordinated to Ca2 in a monodentate bridging mode ($O1^{v}$, O6, $O7^{i}$ and O8). Atom O5 coordinates in a monodentate fashion and the remaining two O atoms ($O3^{ii}$ and $O4^{ii}$) in a chelating mode. Edge-sharing CaO_7 polyhedra



(I)

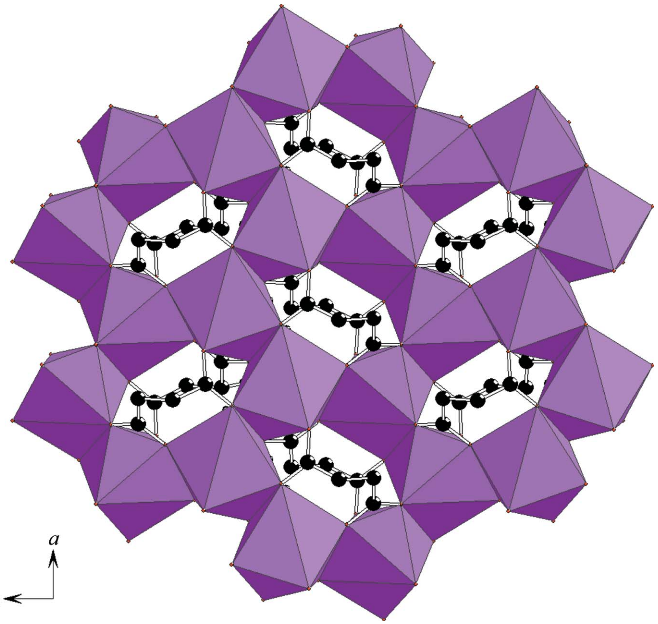


Figure 1
A layer of edge-shared Ca pentagonal–bipyramidal polyhedra forming six-membered rings, viewed along the *c* axis, with succinate ligands shown in ball-and-stick representation.

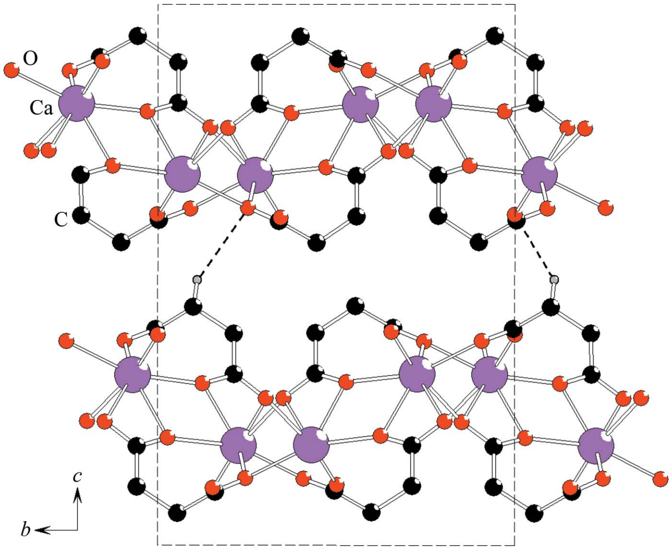


Figure 2
A view of the Ca–succinate structure along the *a* axis, with the cell edges, showing two adjacent layers of edge-sharing calcium polyhedra connected through succinate anions. Adjacent layers are connected through C—H···O hydrogen bonds (dotted lines). Generic atom labels are shown. (In the electronic version of the paper, purple spheres are Ca atoms, red spheres are O atoms and black spheres are C atoms.)

forming six-membered rings are further connected to succinate species from both sides of the inorganic layers (Fig. 1). Structures with edge-sharing metal-based polyhedra forming layers of multi-membered rings are already known in manganese and magnesium glutarates (Vaidhyanathan *et al.*, 2003; Hulvey & Cheetham, 2007) and cobalt succinate (Livage *et al.*, 1998). Ca-based polyhedra in MOF-type structures show a low degree of crystal structure flexibility and are usually arranged through common edges or faces into one-dimensional chain-like inorganic units. The assembly of Ca-based polyhedral units into layers forming six-membered rings in the structure of (I) is, to our knowledge, unique and described in this contribution for the first time.

There are two symmetry-independent succinate ligands which are fully deprotonated, with C—O distances in the range 1.245 (2)–1.272 (2) Å. C—C bonds in the succinate chain are in the range 1.509 (3)–1.524 (2) Å, typical for distances between C atoms in aliphatic chains (Livage *et al.*, 1998; Hulvey & Cheetham, 2007). The succinate ligands connect to the inorganic layers from both sides. Two dicarboxylate groups from two different succinate ligands chelate one Ca^{2+} centre and also bridge a second Ca^{2+} centre. The remaining two dicarboxylate anions bridge three Ca^{2+} centres in a monodentate manner with one O atom and in a bidentate manner with the second O atom. The coordination geometries of the Ca^{2+} centres and succinate ligands are shown in Fig. 3.

There are no classical hydrogen-bond donors (O—H···O) in (I) and consequently no such hydrogen bonds in the structure. However, two potential weak C—H···O contacts (C2—H21···O2^{vi} and C2—H21···O6^{iii}; Table 2) between metal-coordinated carboxylate O atoms from one layer and C-chain-bonded H atoms from a neighbouring layer connect the Ca–succinate units into a hydrogen-bonded network. Despite the relatively long C—H···O contacts between these layers, the C—H···O angles tend towards linearity, which indicates the existence of weak hydrogen-bonding interactions between neighbouring layers (Desiraju, 1991). There are also two weak intra-layer C—H···O interactions between coordinated O atoms and the H atoms bonded to atoms C3 and C7 (Table 2).

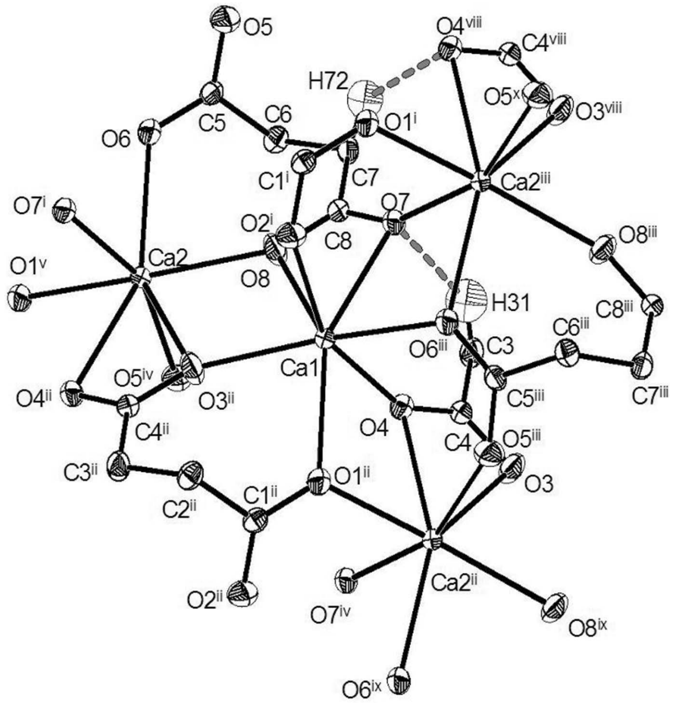


Figure 3
The coordination of the Ca^{2+} ions in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines represent possible intra-layer C—H···O interactions. [Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x-1, y, z$; (v) $x, y-1, z$; (viii) $x+1, y, z$; (x) $-x+2, y+\frac{1}{2}, -z+\frac{1}{2}$.]

Experimental

$CaCl_2 \cdot 2H_2O$ (0.68 g, 4.6 mmol) and succinic acid (0.82 g, 6.9 mmol) were dissolved in demineralized water (10 ml) prior to the addition of KOH (1.04 g, 18.5 mmol). The reaction mixture was placed in a Teflon-lined autoclave and hydrothermally treated by microwave heating (600 W) at 453 K for 3 h. The colourless X-ray quality crystals of (I) obtained were filtered off and washed repeatedly with distilled water. Elemental composition obtained by energy-dispersive X-ray analysis (EDAX) was found to be 25.3 wt% Ca, 31.5 wt% C and 43.2 wt% O, which corresponds to the theoretical composition for $Ca[O_2C(CH_2)_2CO_2]$ (25.7 wt% Ca, 30.8 wt% C and 41.0 wt% O).

Crystal data

$[Ca(C_4H_4O_4)]$
$M_r = 156.15$
Monoclinic, $P2_1/c$
$a = 5.8860$ (1) Å
$b = 11.2117$ (3) Å
$c = 17.0754$ (4) Å
$\beta = 95.9450$ (15)°
$V = 1120.78$ (4) $Å^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 1.05$ mm^{-1}
$T = 293$ K
0.30 × 0.30 × 0.02 mm

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Table 1
Selected bond lengths (Å).

Ca1—O2^{i}	2.3027 (13)	Ca2—O5^{iv}	2.3144 (13)
Ca1—O4	2.3215 (12)	Ca2—O7^{i}	2.3300 (12)
Ca1—O3^{ii}	2.3646 (13)	Ca2—O8	2.3774 (13)
Ca1—O1^{ii}	2.4171 (13)	Ca2—O1^{v}	2.4197 (13)
Ca1—O6^{iii}	2.4312 (13)	Ca2—O6	2.4387 (13)
Ca1—O8	2.4876 (13)	Ca2—O3^{ii}	2.4855 (13)
Ca1—O7	2.5162 (12)	Ca2—O4^{ii}	2.5126 (13)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H31$\cdots$O7	0.91 (4)	2.63 (3)	3.370 (3)	139 (3)
C2—H21$\cdots$O2^{vi}	0.97 (2)	2.59 (2)	3.424 (2)	144 (2)
C2—H21$\cdots$O6^{vii}	0.97 (2)	2.79 (2)	3.584 (2)	140 (2)
C7—H72$\cdots$O4^{viii}	0.92 (3)	2.67 (3)	3.376 (3)	135 (2)

Symmetry codes: (vi) $-x+1, -y+2, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $x+1, y, z$.

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)
$T_{\min} = 0.744$, $T_{\max} = 0.979$

4997 measured reflections
2567 independent reflections
2096 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.109$
$S = 0.99$
2567 reflections

195 parameters
All H-atom parameters refined
$\Delta\rho_{\max} = 0.95$ e Å^{-3}
$\Delta\rho_{\min} = -0.56$ e Å^{-3}

All H atoms were located from a difference Fourier map and refined isotropically.

Data collection: *COLLECT* (Bruker–Nonius, 2000); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2010); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3053). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. (2010). *DIAMOND*. Version 3. Crystal Impact GbR, Bonn, Germany.
Bruker–Nonius (2000). *COLLECT*. Bruker–Nonius, Delft, The Netherlands.
Dale, S. H. & Elsegood, M. R. J. (2003). *Acta Cryst.* C**59**, m540–m542.
De Lill, D. T., Bozzuto, D. J. & Cahill, C. L. (2005). *Dalton Trans.* pp. 2111–2115.
Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
Eddaoudi, M. (2007). *Nat. Mater.* **6**, 718–719.
Farrusseng, D., Aguado, S. & Pinel, C. (2009). *Angew. Chem. Int. Ed.* **48**, 7502–7513.
Groeneman, R. H. & Atwood, J. L. (1999). *Cryst. Eng.* **2**, 241–249.
Hulvey, Z. & Cheetham, A. K. (2007). *Solid State Sci.* **9**, 137–143.
Kuppler, R. J., Timmons, D. J., Fang, Q.-R., Li, J.-R., Makal, T. A., Young, M. D., Yuan, D., Zhao, D., Zhuang, W. & Zhou, H.-C. (2009). *Coord. Chem. Rev.* **253**, 3042–3066.
Livage, C., Egger, C., Nogues, M. & Ferey, G. (1998). *J. Mater. Chem.* **8**, 2743–2747.
Mathew, M. & Takagi, S. (1995). *Z. Kristallogr.* **210**, 199–201.
Mathew, M., Takagi, S., Fowler, B. O. & Markovic, M. (1994). *J. Chem. Crystallogr.* **24**, 437–440.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Platers, M. J., Howie, R. A. & Roberts, A. J. (1997). *Chem. Commun.* pp. 893–894.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Vaidhyanathan, R., Natarajan, S. & Rao, C. N. R. (2003). *Dalton Trans.* pp. 1459–1464.
Volkringer, C., Loiseau, T., Ferey, G., Warren, J. E., Wragg, D. S. & Morris, R. E. (2007). *Solid State Sci.* **9**, 455–458.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Williams, C. A., Blake, A. J., Wilson, C., Hubberstey, P. & Schroeder, M. (2008). *Cryst. Growth Des.* **8**, 911–922.
Yaghi, O. (2004). *Microporous Mesoporous Mater.* **73**, 3–14.
Zhu, H.-F., Zhang, Z.-H., Sun, W.-Y., Okamura, T. & Ueyama, N. (2005). *Cryst. Growth Des.* **5**, 177–182.

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