

Calcium(II) *meso*-2,3-diphenylsuccinate heptahydrate

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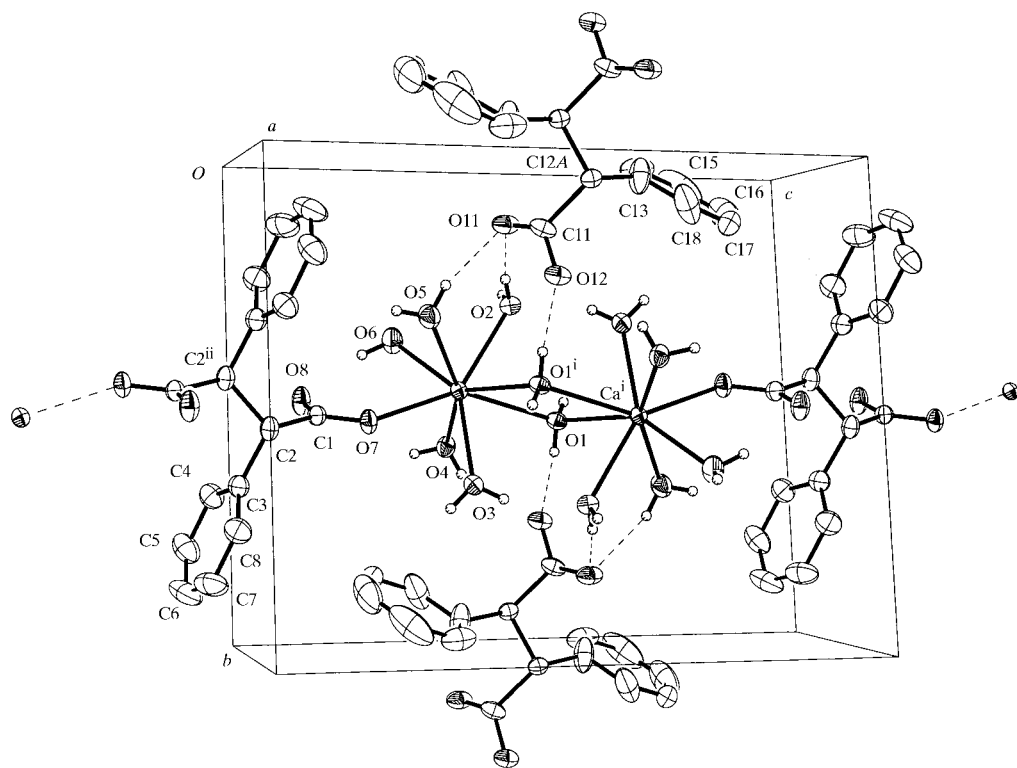
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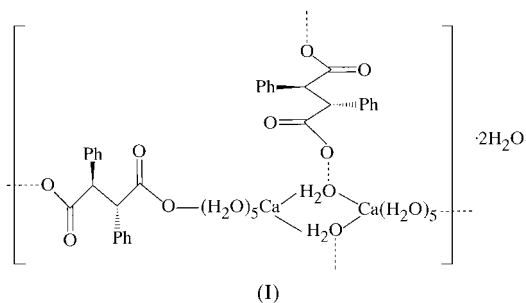
The title compound, $[\text{Ca}(\text{C}_{16}\text{H}_{12}\text{O}_4)(\text{H}_2\text{O})_6]\cdot\text{H}_2\text{O}$, adopts a conformation about the central C—C bond that places the two carboxylate groups in an *anti* orientation. The crystal consists of layers of two-dimensional arrays of 2,3-diphenylsuccinate dianions which are linked by bridging Ca^{2+} cations. The unit cell contains two Ca^{2+} cations in an unusual four-membered Ca—O—Ca—O ring in which the bridging O atoms belong to water molecules rather than carboxylates, *i.e.* poly[[[di- μ -aqua-bis[pentaaquacalcium(II)]]- μ -(*meso*-2,3-diphenylsuccinato-*O*:*O'*)] succinate dihydrate].


Figure 1

Representation of the unit cell of (I), drawn with 40% probability displacement ellipsoids. The uncoordinated water molecules and non-aqueous H atoms are not shown [symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$].

Comment

As part of our ongoing study of shape-switchable molecules (Monahan *et al.*, 1998), we have examined some of the structural and environmental factors that control the conformation of *meso*-2,3-succinate derivatives ($^-\text{O}_2\text{CCHXCHXCO}_2^-$). In the case of $X = \text{OH}$ (*meso*-tartrate), previous NMR evidence indicates that in aqueous solution, the dianion adopts a conformation with the carboxylate groups in a *gauche* arrangement when the molecule is viewed along the central C2—C3 bond (Ascenso & Gil, 1980). It was of interest to know if other derivatives adopted, or could be forced to adopt,



the same unusual conformation. The conformations in alkaline solution were assigned from vicinal H—H coupling constants ($^3J_{\text{HH}}$). In the case of $X = \text{OCH}_3$, $^3J_{\text{HH}} = 5.5$ Hz, which indicates that a *gauche* conformation is predominant (Ascenso & Gil, 1980). In the case of $X = \text{Br}$ and $X = \text{Ph}$, the $^3J_{\text{HH}}$ values of 11.4 and 12.5 Hz, respectively, suggest conformations with the carboxylate groups in an *anti* orientation.

In the case of $X = \text{Ph}$, attempts were made to induce a conformational change to *gauche* by adding CaCl_2 or MgCl_2 to the basic aqueous solutions. In both cases, there were only minor changes in $^3J_{\text{HH}}$ values (<0.5 Hz), indicating that even in the presence of chelating dications, *meso*-2,3-diphenylsuccinate remains in an *anti* conformation. Since this result is counter to that obtained with a related system (Monahan *et al.*, 1998), we decided to confirm our structural assignments with an X-ray analysis of the title crystalline calcium *meso*-2,3-diphenylsuccinate, (I).

The crystal structures of a number of succinate salts are known, including the mono- and trihydrates of calcium

succinate (Karipides & Reed, 1980; Mathew *et al.*, 1994). However, this is the first reported structure of a 2,3-diphenylsuccinate salt. X-ray analysis of (I) shows that the molecule adopts an *anti* conformation about the C2—C3 bond (Fig. 1). The crystal consists of layers of a two-dimensional array of succinate dianions that are linked by bridging Ca²⁺ ions. Along one axis, the carboxylates are directly bonded to the Ca²⁺ ions, whereas along the other axis they are hydrogen bonded to bridging water molecules. The phenyl rings pack in face-to-face and edge-to-face orientations to form square-shaped nanotubes with aromatic walls, and the interiors of the tubes contain the hydrated calcium-carboxylate ion pairs.

The literature structures of calcium succinate show the Ca and the carboxylate O atoms in two types of four-membered rings (Karipides & Reed, 1980; Mathew *et al.*, 1994). Either a carboxylate group forms a bidentate Ca—O—C—O ring or it provides a bridging monodentate O atom which is part of a four-membered Ca—O—Ca—O ring. As shown in Fig. 1, compound (I) forms a different type of Ca—O—Ca—O ring in which the bridging O atoms belong to water molecules rather than to carboxylates. The internuclear Ca···Ca distance is 4.3110 (7) Å, which is longer than the range 3.98–4.01 Å found in the literature succinate Ca—O—Ca—O rings (Karipides & Reed, 1980; Mathew *et al.*, 1994).

Experimental

meso-2,3-Diphenylsuccinic acid (182 mg, 0.673 mmol), synthesized according to the method of Wawzonek (1940), was added to a solution of Ca(OH)₂ (50 mg, 0.673 mmol) in water (100 ml). Slow evaporation of the water produced crystals of (I) suitable for analysis.

Crystal data

[Ca(C ₁₆ H ₁₂ O ₄)(H ₂ O) ₆].H ₂ O	Z = 2
<i>M_r</i> = 434.45	<i>D_x</i> = 1.420 Mg m ⁻³
Triclinic, P1̄	Mo Kα radiation
<i>a</i> = 6.2394 (8) Å	Cell parameters from 25 reflections
<i>b</i> = 11.6342 (8) Å	<i>θ</i> = 15–16°
<i>c</i> = 14.1648 (12) Å	<i>μ</i> = 0.364 mm ⁻¹
<i>α</i> = 89.697 (7)°	<i>T</i> = 293 (2) K
<i>β</i> = 88.440 (9)°	Plate-like, colorless
<i>γ</i> = 81.320 (8)°	0.42 × 0.40 × 0.15 mm
<i>V</i> = 1016.1 (2) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.010
<i>θ</i> / <i>2θ</i> scans	<i>θ</i> _{max} = 24.97°
Absorption correction: <i>ψ</i> scan (North <i>et al.</i> , 1968)	<i>h</i> = -7 → 0
<i>T</i> _{min} = 0.922, <i>T</i> _{max} = 0.947	<i>k</i> = -13 → 13
3939 measured reflections	<i>l</i> = -16 → 16
3580 independent reflections	3 standard reflections
3307 reflections with <i>I</i> > 2σ(<i>I</i>)	every 200 reflections
	frequency: 120 min
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F_o</i> ²) + (0.0345 <i>P</i>) ² + 0.5761 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.032	where <i>P</i> = (<i>F_o</i> ² + 2 <i>F_c</i> ²)/3
<i>wR</i> (<i>F</i> ²) = 0.083	(Δ/ <i>σ</i>) _{max} = -0.001
<i>S</i> = 1.057	Δ <i>ρ</i> _{max} = 0.32 e Å ⁻³
3580 reflections	Δ <i>ρ</i> _{min} = -0.21 e Å ⁻³
305 parameters	
H atoms: see below	

Table 1

Selected geometric parameters (Å, °).

Ca—O3	2.3799 (13)	Ca—O2	2.4822 (13)
Ca—O7	2.4093 (12)	Ca—O5	2.5017 (15)
Ca—O6	2.4237 (14)	Ca···Ca ⁱ	4.3110 (7)
Ca—O4	2.4728 (13)	C2—C3	1.528 (3)
O3—Ca—O7	73.03 (5)	O7—Ca—O1	146.65 (4)
O3—Ca—O6	138.96 (5)	O6—Ca—O1	121.18 (5)
O7—Ca—O6	78.01 (5)	O5—Ca—O1	133.04 (4)
O3—Ca—O4	78.32 (5)	O3—Ca—Ca ⁱ	70.89 (4)
O3—Ca—O2	142.01 (5)	C1—O7—Ca	136.09 (11)
O7—Ca—O2	141.86 (4)	C2 ⁱⁱ —C2—C3	111.3 (2)
O4—Ca—O2	106.93 (5)	C2 ⁱⁱ —C2—C1	110.1 (2)
O4—Ca—O5	154.35 (5)		
O6—Ca—O7—C1	7.2 (2)	C1—C2—C3—C4	-58.3 (2)

Symmetry codes: (i) 1 - *x*, 1 - *y*, 1 - *z*; (ii) 1 - *x*, 1 - *y*, -*z*.

Phenyl H atoms were refined with a riding model. All other H atoms were refined with a free variable to restrain H—O and H···H distances.

Data collection: CAD-4 ARGUS (Enraf–Nonius, 1994); cell refinement: CAD-4 ARGUS; data reduction: CHI90S (Boyle, 1997); program(s) used to solve structure: SHELXS86 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXTL (Siemens, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1102). Services for accessing these data are described at the back of the journal.

References

- Ascenso, J. & Gil, V. M. S. (1980). *Can. J. Chem.* **58**, 1376–1379.
 Boyle, P. D. (1997). CHI90S. North Carolina State University, USA.
 Enraf–Nonius (1994). CAD-4 ARGUS. Version of 1994. Enraf–Nonius, Delft, The Netherlands.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Karipides, A. & Reed, A. T. (1980). *Acta Cryst.* **B36**, 1377–1381.
 Mathew, M., Takagi, S., Fowler, B. O. & Markovic, M. (1994). *J. Chem. Crystallogr.* **24**, 437–440.
 Monahan, C., Bien, J. T. & Smith, B. D. (1998). *J. Chem. Soc. Chem. Commun.* pp. 431–432.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). SHELXL97. University of Göttingen, Germany.
 Siemens (1994). SHELXTL. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Wawzonek, S. (1940). *J. Am. Chem. Soc.* **62**, 745–749.