

## $\{[\text{Ca}_5(\text{C}_8\text{H}_4\text{O}_4)_5(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}\}_n$ : the first crystallographically characterized non-transition metal salt of isophthalic acid

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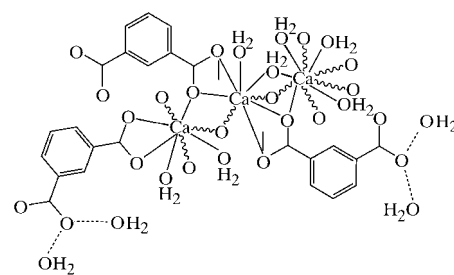
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The reaction of  $\text{CaCO}_3$  with isophthalic acid in water yields nonaqua-penta- $\mu$ -isophthalato-pentacalcium octahydrate,  $\{[\text{Ca}_5(\text{C}_8\text{H}_4\text{O}_4)_5(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}\}_n$ , a complex polymeric one-dimensional column structure bearing metal-carboxylate bonds and Ca-bound terminal and bridging water molecules, in addition to hydrogen-bonded water molecules of crystallization. The asymmetric unit comprises half of the formula unit, with one  $\text{Ca}^{2+}$  ion located on a twofold axis, and contains 16 unique strong  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds, some of which link the columns together.

### Comment

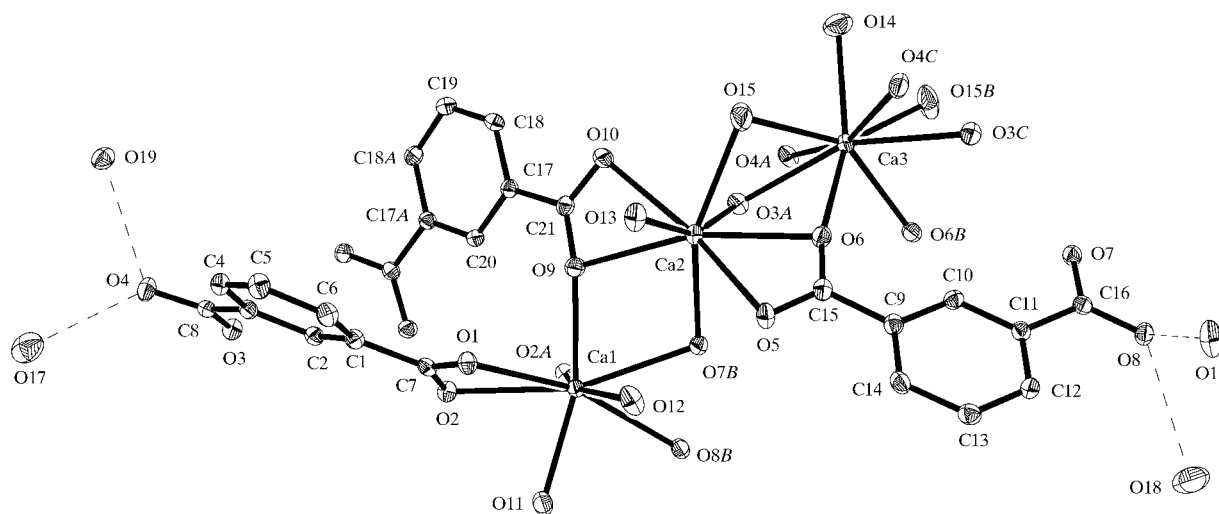
The benzenepolycarboxylic acid family has been extensively exploited in the challenge of creating functional porous

supramolecular architectures (Yaghi *et al.*, 1998; Janiak, 1997). While numerous examples of polymeric metal-organic frameworks (MOFs) exist in the literature, containing the more commonly used terephthalic (*e.g.* Groeneman *et al.*, 1999) and trimesic (*e.g.* Yaghi *et al.*, 1995) acids, a search of the Cambridge Structural Database (Version 5.24, July 2003 update; Allen, 2002) has highlighted the use of isophthalic acid ( $\text{H}_2\text{IPA}$ , benzene-1,3-dicarboxylic acid), predominantly in mixed-ligand metal complexes, for example, in combination with derivatives of 4,4'-bipyridine (Bourne *et al.*, 2001; Tao *et al.*, 2000, 2002). Only two examples exist of solely hydrated salts of  $\text{H}_2\text{IPA}$ , namely those of  $\text{Zn}^{2+}$  (Otto & Wheeler, 2001) and  $\text{La}^{3+}$  (Kim *et al.*, 2001), and this led us to investigate the synthesis of other hydrated metal salts of  $\text{H}_2\text{IPA}$ , including the title  $\text{Ca}^{2+}$  salt, (I), presented here.

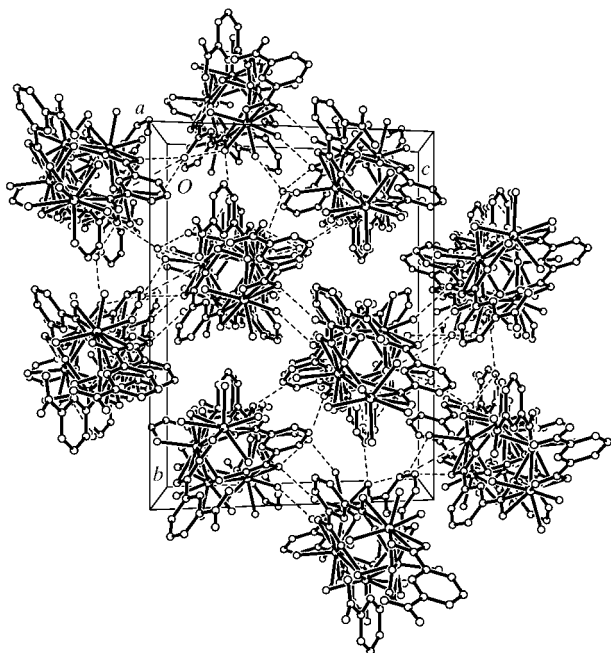


(I)

The asymmetric unit of (I),  $\{[\text{Ca}_5(\text{C}_8\text{H}_4\text{O}_4)_5(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}\}_n$ , contains half a formula unit, with 2.5  $\text{Ca}^{2+}$  cations, 2.5  $\text{IPA}^{2-}$  anionic ligands and 8.5 water molecules. Two  $\text{Ca}^{2+}$  ions (Ca1 and Ca2) in general positions both have a coordination number of eight, with the coordination sphere of atom Ca1 comprising six metal-carboxylate bonds and two terminal metal- $\text{OH}_2$  bonds, while atom Ca2 has six metal-carboxylate bonds, one terminal metal- $\text{OH}_2$  bond and one bridging metal-


**Figure 1**

A view of (I), showing the atom-labelling scheme and the completed  $\text{Ca}^{2+}$  coordination spheres. Displacement ellipsoids are drawn at the 50% probability level and all H atoms have been omitted for clarity. Atoms with the suffix *A* are at the symmetry position  $(-x, y, \frac{1}{2} - z)$ , *B* at  $(1 - x, y, \frac{1}{2} - z)$  and *C* at  $(x + 1, y, z)$ .



**Figure 2**

A packing plot of (I), showing the one-dimensional coordination polymer columns extending parallel to the crystallographic *a* axis. H atoms have been omitted for clarity and hydrogen-bond  $O \cdots O$  contacts are indicated by dashed lines.

$\text{OH}_2$  bond, with the water molecule (atom O15) bridging atoms Ca2 and Ca3, which lies on a twofold axis. In contrast, atom Ca3 has a coordination number of nine and forms six metal–carboxylate bonds, in addition to one terminal and two bridging metal– $\text{OH}_2$  bonds (Fig. 1 and Table 1). The Ca–O bond lengths are in the range 2.3252 (12)–2.7746 (13) Å for metal–carboxylate bonds and 2.3568 (13)–2.5800 (16) Å for metal– $\text{OH}_2$  bonds, which compare well with bond lengths observed in the literature, for example, in calcium terephthalate trihydrate (Dale & Elsegood, 2003).

The carboxylate groups of the  $\text{IPA}^{2-}$  anions and their respective benzene rings lie close to coplanarity, with the greatest twist angle being 10.0 (3)°, while the aromatic rings of the anions lie at angles of roughly 60° to each other [dihedral angles with respect to the C1–C6 ring: carboxyl groups C7/O1/O2 = 6.5 (2)° and C8/O3/O4 = 4.8 (2)°, and rings C9–C14 = 63.45 (6)° and C17–C20 = 62.84 (6)°; dihedral angles with respect to the C9–C14 ring: carboxyl groups C15/O5/O6 = 6.3 (2)° and C16/O7/O8 = 1.0 (2)°, and ring C17–C20 = 62.15 (5)°; dihedral angle with respect to the C17–C20 ring: carboxyl group C21/O9/O10 = 10.0 (3)°].

Each unique carboxylate group in (I) chelates one  $\text{Ca}^{2+}$  centre, with one of its O atoms also bridging a second  $\text{Ca}^{2+}$  centre, producing a  $\eta^2:\eta^1:\mu_2$  motif. This creates an infinite one-dimensional coordination polymer which, viewed end on, approximates to a five-pointed star in cross-section. An extensive array of 16 unique strong  $\text{O} \cdots \text{H} \cdots \text{O}$  hydrogen bonds (Table 2) between metal-coordinated water molecules, water molecules of crystallization and carboxyl O atoms produces an extensive hydrogen-bonding network, too

complex to describe here in detail. Packing plots reveal that each column (propagating parallel to the crystallographic *a* axis) is connected, either *via* direct or water-bridged hydrogen-bond paths, to five neighbouring columns (Fig. 2).

## Experimental

Isophthalic acid (1 equivalent) was refluxed with  $\text{CaCO}_3$  (1 equivalent) in  $\text{H}_2\text{O}$  for 24 h, producing X-ray quality colourless crystals of (I) in quantitative yield upon slow evaporation of the cooled filtered solution. The crystals were observed to desolvate at 318–323 K. Spectroscopic analysis, IR (KBr,  $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ): 3442 (*br*, OH), 3136 and 3118 (aromatic C–H), 1603 and 1533 (asymmetric  $\text{CO}_2^-$ ), 1479, 1448, 1394 (symmetric  $\text{CO}_2^-$ ), 1280, 1163, 1107, 1080 (C–O), 942, 916, 840, 833, 745, 725 (aromatic C–H). Analysis calculated for  $\text{C}_{40}\text{H}_{54}\text{Ca}_5\text{O}_{37}$ : C 36.20, H 4.10%; found: C 36.39, H 3.63%.

### Crystal data

$[\text{Ca}_5(\text{C}_8\text{H}_4\text{O}_4)_5(\text{H}_2\text{O})_9] \cdot 8\text{H}_2\text{O}$   
 $M_r = 1327.24$   
 Monoclinic,  $C2/c$   
 $a = 15.6289$  (8) Å  
 $b = 21.2640$  (11) Å  
 $c = 17.1852$  (9) Å  
 $\beta = 112.134$  (2)°  
 $V = 5290.3$  (5) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.666$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 Cell parameters from 9880 reflections  
 $\theta = 2.4$ – $28.9^\circ$   
 $\mu = 0.62$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Block, colourless  
 $0.38 \times 0.20 \times 0.10$  mm

### Data collection

Bruker SMART 1000 CCD area-detector diffractometer  
 $\omega$  rotation scans with narrow frames  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
 $T_{\text{min}} = 0.836$ ,  $T_{\text{max}} = 0.941$   
 23 336 measured reflections  
 6434 independent reflections

5100 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\text{max}} = 29.0^\circ$   
 $h = -20 \rightarrow 21$   
 $k = -27 \rightarrow 28$   
 $l = -23 \rightarrow 22$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.033$   
 $wR(F^2) = 0.083$   
 $S = 1.08$   
 6434 reflections  
 428 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 4.8388P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.46$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.33$  e Å<sup>-3</sup>

**Table 1**

Selected interatomic distances (Å).

Ca1–O11	2.3568 (13)	Ca2–O15	2.4457 (16)
Ca1–O2 <sup>i</sup>	2.3652 (12)	Ca2–O6	2.4555 (12)
Ca1–O9	2.3772 (12)	Ca2–O10	2.4575 (13)
Ca1–O12	2.4078 (13)	Ca2–O5	2.5473 (13)
Ca1–O1	2.5238 (12)	Ca2–O9	2.5682 (12)
Ca1–O8 <sup>ii</sup>	2.5377 (12)	Ca3–O14	2.376 (3)
Ca1–O7 <sup>ii</sup>	2.5600 (12)	Ca3–O6	2.4138 (13)
Ca1–O2	2.6610 (12)	Ca3–O3 <sup>i</sup>	2.5733 (12)
Ca2–O3 <sup>i</sup>	2.3252 (12)	Ca3–O15	2.5800 (16)
Ca2–O13	2.3824 (13)	Ca3–O4 <sup>i</sup>	2.7746 (13)
Ca2–O7 <sup>ii</sup>	2.4089 (12)		

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

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O11—H11A...O16 <sup>i</sup>	0.82 (2)	1.96 (2)	2.7670 (18)	169 (2)
O11—H11B...O19 <sup>ii</sup>	0.82 (2)	1.96 (2)	2.7656 (19)	167 (2)
O12—H12A...O1 <sup>iii</sup>	0.82 (2)	2.05 (2)	2.8535 (18)	169 (2)
O12—H12B...O5	0.82 (2)	2.20 (2)	2.9836 (18)	162 (2)
O13—H13A...O19 <sup>iv</sup>	0.82 (2)	1.90 (2)	2.7110 (19)	172 (2)
O13—H13B...O16 <sup>v</sup>	0.82 (2)	1.99 (2)	2.786 (2)	164 (2)
O14—H14B...O18 <sup>vi</sup>	0.82 (2)	1.81 (2)	2.606 (3)	164 (3)
O15—H15B...O17 <sup>vii</sup>	0.82 (2)	2.06 (2)	2.818 (3)	155 (2)
O16—H16A...O5 <sup>v</sup>	0.82 (2)	1.98 (2)	2.7185 (18)	150 (2)
O16—H16B...O8	0.82 (2)	1.91 (2)	2.7278 (18)	174 (2)
O17—H17A...O4	0.82 (2)	2.00 (2)	2.808 (2)	167 (3)
O17—H17B...O10 <sup>iv</sup>	0.82 (2)	2.02 (2)	2.839 (2)	177 (3)
O18—H18A...O8	0.82 (2)	2.07 (2)	2.876 (2)	168 (3)
O18—H18B...O10 <sup>ii</sup>	0.82 (2)	2.16 (2)	2.890 (2)	158 (3)
O19—H19A...O4	0.82 (2)	2.00 (2)	2.7747 (18)	159 (2)
O19—H19B...O1 <sup>iv</sup>	0.82 (2)	2.00 (2)	2.7639 (18)	156 (2)

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

In the refinement of the water molecules, 1,2- and 1,3-distances were refined with the *SHELXTL* commands SADI 0.005 and DFIX 1.33 0.005, respectively. Aromatic H atoms were placed in geometric positions (C—H = 0.95 Å) using a riding model, while the coordinates of the water H atoms were refined using geometric restraints on the O—H bond lengths and H—O—H bond angles.  $U_{\text{iso}}(\text{H})$  values were set at  $1.2U_{\text{eq}}$  for aryl H ( $1.5U_{\text{eq}}$  for water H). Atom O14 is disordered over two equally occupied sets of positions close to a twofold axis and restraints were applied to the anisotropic displacement parameters of this atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1070). Services for accessing these data are described at the back of the journal.

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