

catena-Poly[[aqua(benzoato- κ^2O,O')-(benzoic acid- κO)calcium]- μ_3 -benzoato- $\kappa^4O:O,O':O'$]

Olimjon Azizov,^a Zuhra Kadirova,^{b*} Tohir Azizov,^a Samat Tolipov^c and Bakhtiyar Ibragimov^c

^aInstitute of General and Inorganic Chemistry, Abdullaev St 32, Tashkent 100077, Uzbekistan, ^bTashkent Chemical–Technological Institute, Navoi St 32, Tashkent 100011, Uzbekistan, and ^cInstitute of Biorganic Chemistry, Mirzo-Ulugbek St 83, Tashkent 100125, Uzbekistan

Correspondence e-mail: zuhra_kadirova@yahoo.com

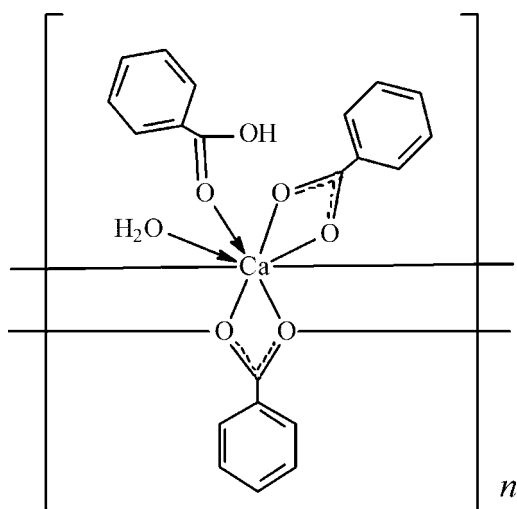
Received 22 February 2011; accepted 11 April 2011

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.041; wR factor = 0.121; data-to-parameter ratio = 14.0.

In title compound, $[Ca(C_7H_5O_2)_2(C_7H_6O_2)(H_2O)]_n$, the eight-fold-coordinated Ca^{II} ion is bonded to four carboxylate O atoms from two benzoate ions, an O atom from benzoic acid and a water O atom. One of the carboxylate groups bridges adjacent Ca^{2+} ions, forming a polymeric ribbon structure parallel to $[010]$. In the crystal, the benzoate anions and water molecule interact by way of inter- and intramolecular $O-H\cdots O$ hydrogen bonds.

Related literature

For background to the crystal structures and physical stability of calcium benzoate hydrates, mesophases and related compounds, see: Cherkezova *et al.* (1987); Zhang *et al.* (1999); Yano *et al.* (2001); Senkovska & Thewalt (2005); Terakita & Byrn (2006).



Experimental

Crystal data

$[Ca(C_7H_5O_2)_2(C_7H_6O_2)(H_2O)]$
 $M_r = 422.43$
 Monoclinic, $P2_1/n$
 $a = 15.5535$ (3) Å
 $b = 6.61183$ (16) Å
 $c = 20.1828$ (4) Å
 $\beta = 94.3750$ (18)°

$V = 2069.49$ (8) Å³
 $Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 2.96$ mm⁻¹
 $T = 293$ K
 $0.55 \times 0.45 \times 0.40$ mm

Data collection

Oxford Diffraction Xcalibur Ruby diffractometer
 Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2007)
 $T_{min} = 0.782$, $T_{max} = 1.000$

7257 measured reflections
 3847 independent reflections
 2961 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.121$
 $S = 1.07$
 3847 reflections
 275 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.27$ e Å⁻³
 $\Delta\rho_{min} = -0.26$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------|----------|-------------|-------------|---------------|
| $O1W-H1W1\cdots O5^i$ | 0.76 (3) | 2.05 (3) | 2.779 (2) | 163 (3) |
| $O1-H1O\cdots O6$ | 0.93 (3) | 1.68 (3) | 2.597 (2) | 167 (3) |
| $O1W-H2W1\cdots O6^{ii}$ | 0.89 (3) | 1.90 (3) | 2.754 (2) | 159 (3) |

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2007); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

This work was supported by the Grant of Fundamental Research of Centers of Science and Technology, Republic Uzbekistan F 3–142.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2180).

References

- Cherkezova, V. R., Musaev, F. N. & Karaev, Z. Sh. (1987). *Russ. J. Coord. Chem.* **13**, 903–908.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Oxford Diffraction (2007). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, England.
 Senkovska, I. & Thewalt, U. (2005). *Acta Cryst.* **C61**, m448–m449.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Terakita, A. & Byrn, S. R. (2006). *J. Pharm. Sci.* **95**, 1162–1172.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
 Yano, S., Numata, M., Kato, M., Motoo, S. & Nishimura, T. (2001). *Acta Cryst.* **E57**, m488–m490.
 Zhang, K., Yuan, J., Yuan, L. & Sun, J. (1999). *Wuhan Univ. J. Nat. Sci.* **4**, 89–94.

supporting information

Acta Cryst. (2011). E67, m597 [doi:10.1107/S1600536811013493]

catena-Poly[[aqua(benzoato- κ^2 O,O') (benzoic acid- κ O)calcium]- μ_3 -benzoato- κ^4 O:O,O':O']

Olimjon Azizov, Zuhra Kadirova, Tohir Azizov, Samat Tolipov and Bakhtiyar Ibragimov

S1. Comment

The synthesis and structure determination of inorganic polymers are interesting subject for basic inorganic chemistry and materials science. Depending on the pH and other synthetic conditions, many calcium benzoates with different coordination modes, polymeric arrangements and molecular topologies have been observed, *e.g.*

[Ca(C₆H₅COO)₂] \times 3H₂O (neutral solution; Terakita *et al.*, 2006), Ca(C₆H₅COO)₂(C₆H₅COO)_{0.5} \times 2H₂O (acid solution; Cherkezova *et al.*, 1987), [Ca(C₆H₅COO)(H₂O)₃](C₆H₅COO)]_n (basic solution; Senkovska *et al.*, 2005), [Ca(C₆H₅COO)₂(C₃H₇NO)(H₂O)]_n (dimethylformamide solution; Yano *et al.*, 2001), [Ca(C₆H₅COO)₂] (hydrothermal conditions; Zhang *et al.*, 1999).

In this study we synthesized the Ca^{II} polymeric compound, (I), bridged by a benzoate group, and report the structure of the title compound, (I). The molecular structure is shown on Fig.1 and geometrical parameters are available from archived CIF.

The asymmetric unit of (I) consists of one Ca centre, two benzoate anions, benzoic acid and one water molecule (Fig 1). The calcium ion is surrounded by eight O atoms from two tri- and bidentate benzoates, a monodentate benzoic acid molecule, and a water molecule. The CaO₈ polyhedron deviates extensively from idealized octacoordinated geometries found in other complexes (Senkovska *et al.*, 2005; Yano *et al.*, 2001). There are three different coordination modes of benzoic acid in crystal structure. The tridentate benzoate forms simultaneously the planar four-membered chelate and the buckled four-membered Ca–O–Ca–O rings by bridging adjacent Ca²⁺ ions. The Ca–O bridging bond lengths [2.3204 (14) and 2.3781 (14) Å] are considerably shorter than the Ca–O chelate distances [2.7414 (14) and 2.4567 (14) Å]. The bidentate benzoate has longer Ca–O distances [2.4837 (17) and 2.5628 (15) Å] than observed for monodentate benzoic acid and calcium ion [2.4467 (15) Å].

The bridging interactions and the system of H-bonds form polymeric structure consisted from the infinite ribbons along the *b* axis and separated by the stacked neighbouring phenyl groups. The benzoic acid hydroxyl group and an water molecule act as H-bond donors, and the O5 and O6 atoms of the bidentate COO⁻ group are H-bond acceptors. The combination of these hydrogen bonds, π - π stacking interactions and the Ca–O bonds leads to the formation of a two-dimensional network running parallel to the *ac*-plane (Fig. 2).

S2. Experimental

The Ca(NO₃)₂ \times 4H₂O (1 mmol) and benzoic acid (3 mmol) in 75 ml of ethanol were mixed with the the benzoic acid water solution (2 mmol). The mixture were stirred 6 h at room temperature, and after 3 days the precipitated colourless crystals were filtered off, washed three times with ethanol, dried at room temperature. Crystals of the title compound, suitable to X-ray diffraction analysis, were selected directly from the sample as prepared.

S3. Refinement

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

All the H-atoms were found in the difference Fourier synthesis and refined with restrained O–H 0.82 (2) Å, H···H 1.35 (2) Å, but free isotropic displacement parameters.

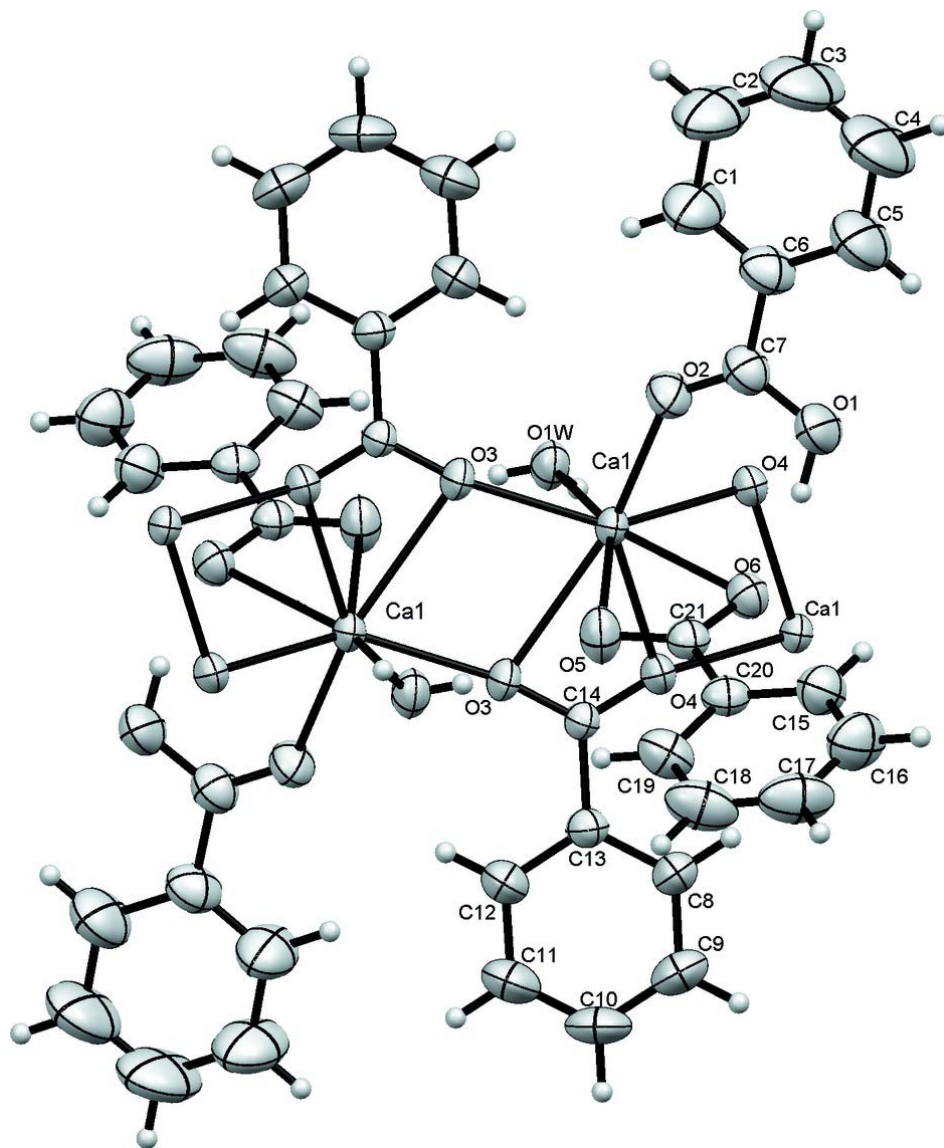
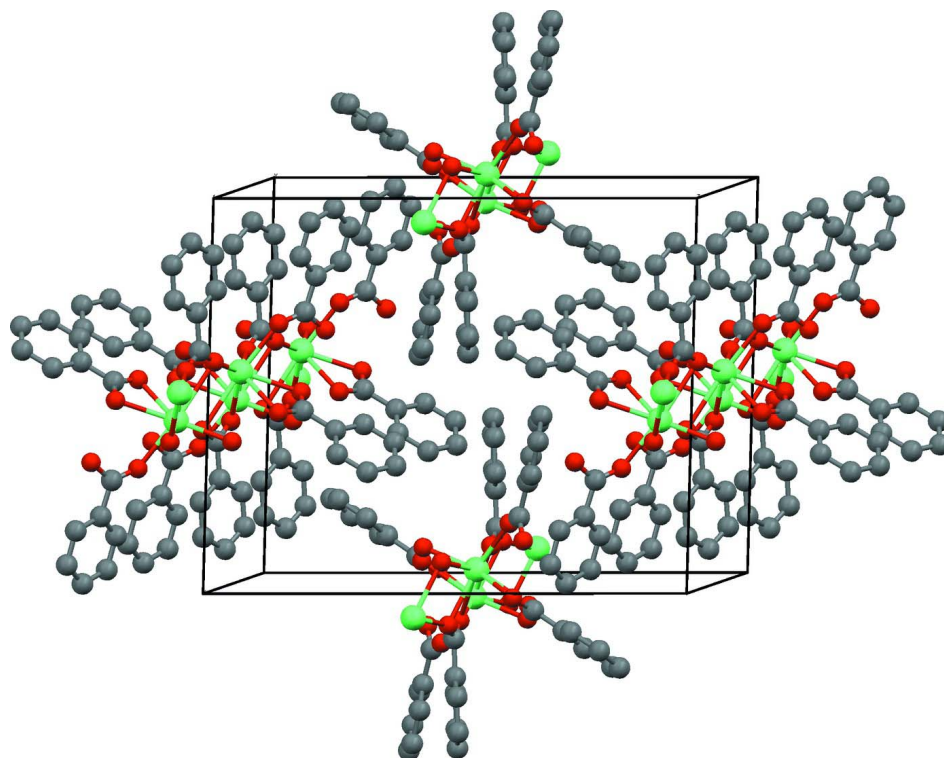


Figure 1

A view of the structure of (I), showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

The crystal structure packing scheme showing the hydrogen bonds system.

catena-Poly[[aqua(benzoato- κ^2 O,O')(benzoic acid- κ O)calcium]- μ_3 -benzoato- κ^4 O:O,O':O']

Crystal data

[Ca(C₇H₅O₂)₂(C₇H₆O₂)(H₂O)]

$M_r = 422.43$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 15.5535$ (3) Å

$b = 6.61183$ (16) Å

$c = 20.1828$ (4) Å

$\beta = 94.3750$ (18)°

$V = 2069.49$ (8) Å³

$Z = 4$

$F(000) = 880$

$D_x = 1.356$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 3133 reflections

$\theta = 3.5$ – 70.6 °

$\mu = 2.96$ mm⁻¹

$T = 293$ K

Monoclinic, colourless

$0.55 \times 0.45 \times 0.40$ mm

Data collection

Oxford Diffraction Xcalibur Ruby
diffractometer

Radiation source: Enhance (Cu) X-ray Source

Graphite monochromator

Detector resolution: 10.2576 pixels mm⁻¹

$q/2\theta$ scans

Absorption correction: multi-scan

(*CrysAlis PRO*; Oxford Diffraction, 2007)

$T_{\min} = 0.782$, $T_{\max} = 1.000$

7257 measured reflections

3847 independent reflections

2961 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 71.1$ °, $\theta_{\min} = 3.5$ °

$h = -17$ → 18

$k = -7$ → 7

$l = -22$ → 24

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.041$ $wR(F^2) = 0.121$ $S = 1.07$

3847 reflections

275 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
mapHydrogen site location: inferred from
neighbouring sitesH atoms treated by a mixture of independent
and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0754P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.27 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.26 \text{ e } \text{\AA}^{-3}$ Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0050 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|---------------|----------------------------------|
| Ca1 | 0.45197 (2) | 0.25532 (5) | 0.033347 (19) | 0.03194 (16) |
| O1W | 0.39727 (11) | 0.2332 (3) | -0.08057 (9) | 0.0443 (4) |
| O1 | 0.36276 (12) | 0.5693 (3) | 0.16770 (10) | 0.0675 (6) |
| O2 | 0.33262 (10) | 0.2999 (3) | 0.10426 (9) | 0.0508 (4) |
| O3 | 0.59059 (9) | 0.0795 (2) | -0.02003 (7) | 0.0394 (3) |
| O4 | 0.58487 (8) | 0.4064 (2) | -0.00286 (7) | 0.0368 (3) |
| O5 | 0.54914 (11) | 0.1360 (2) | 0.12874 (8) | 0.0528 (4) |
| O6 | 0.51357 (9) | 0.4557 (2) | 0.13481 (7) | 0.0430 (4) |
| C1 | 0.1629 (2) | 0.2997 (6) | 0.14566 (18) | 0.0862 (11) |
| H1A | 0.1815 | 0.1822 | 0.1258 | 0.103* |
| C2 | 0.0778 (2) | 0.3155 (8) | 0.1610 (2) | 0.1124 (15) |
| H2A | 0.0396 | 0.2089 | 0.1522 | 0.135* |
| C3 | 0.0512 (3) | 0.4885 (8) | 0.1889 (2) | 0.1325 (19) |
| H3A | -0.0059 | 0.5006 | 0.1990 | 0.159* |
| C4 | 0.1074 (3) | 0.6473 (9) | 0.2026 (3) | 0.1310 (18) |
| H4A | 0.0881 | 0.7654 | 0.2216 | 0.157* |
| C5 | 0.1927 (2) | 0.6303 (6) | 0.18807 (18) | 0.0944 (12) |
| H5A | 0.2312 | 0.7358 | 0.1975 | 0.113* |
| C6 | 0.21971 (16) | 0.4540 (4) | 0.15927 (12) | 0.0590 (7) |
| C7 | 0.31009 (15) | 0.4324 (4) | 0.14106 (12) | 0.0499 (6) |
| C8 | 0.76481 (14) | 0.4308 (4) | 0.02152 (12) | 0.0492 (6) |

| | | | | |
|------|--------------|------------|---------------|-------------|
| H8A | 0.7323 | 0.5391 | 0.0351 | 0.059* |
| C9 | 0.85412 (16) | 0.4419 (5) | 0.02713 (15) | 0.0660 (8) |
| H9A | 0.8813 | 0.5579 | 0.0444 | 0.079* |
| C10 | 0.90217 (16) | 0.2842 (5) | 0.00760 (17) | 0.0744 (9) |
| H10A | 0.962 | 0.2931 | 0.0110 | 0.089* |
| C11 | 0.86257 (17) | 0.1122 (5) | -0.01702 (18) | 0.0801 (10) |
| H11A | 0.8957 | 0.0043 | -0.0301 | 0.096* |
| C12 | 0.77321 (15) | 0.0979 (4) | -0.02254 (14) | 0.0590 (7) |
| H12A | 0.7466 | -0.0201 | -0.0386 | 0.071* |
| C13 | 0.72419 (13) | 0.2590 (3) | -0.00417 (11) | 0.0378 (5) |
| C14 | 0.62723 (12) | 0.2463 (3) | -0.01012 (9) | 0.0306 (4) |
| C15 | 0.59799 (16) | 0.4938 (4) | 0.26173 (12) | 0.0542 (6) |
| H15A | 0.5636 | 0.6006 | 0.2455 | 0.065* |
| C16 | 0.64396 (19) | 0.5095 (5) | 0.32353 (14) | 0.0721 (8) |
| H16A | 0.6395 | 0.626 | 0.3489 | 0.087* |
| C17 | 0.69539 (17) | 0.3548 (6) | 0.34678 (14) | 0.0765 (9) |
| H17A | 0.7262 | 0.3663 | 0.3879 | 0.092* |
| C18 | 0.70210 (18) | 0.1819 (6) | 0.31004 (15) | 0.0743 (9) |
| H18A | 0.7377 | 0.0771 | 0.3261 | 0.089* |
| C19 | 0.65589 (15) | 0.1632 (5) | 0.24906 (12) | 0.0553 (6) |
| H19A | 0.6600 | 0.0453 | 0.2244 | 0.066* |
| C20 | 0.60356 (13) | 0.3198 (4) | 0.22475 (10) | 0.0401 (5) |
| C21 | 0.55280 (13) | 0.3005 (3) | 0.15892 (10) | 0.0379 (5) |
| H1W1 | 0.4060 (18) | 0.139 (5) | -0.1002 (14) | 0.062 (10)* |
| H2W1 | 0.4184 (19) | 0.325 (5) | -0.1072 (15) | 0.074 (10)* |
| H1O | 0.420 (2) | 0.543 (5) | 0.1603 (16) | 0.090 (10)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Ca1 | 0.0308 (2) | 0.0223 (2) | 0.0429 (2) | -0.00138 (15) | 0.00329 (15) | -0.00246 (16) |
| O1W | 0.0509 (9) | 0.0296 (9) | 0.0512 (9) | 0.0004 (7) | -0.0051 (7) | -0.0028 (8) |
| O1 | 0.0524 (11) | 0.0671 (13) | 0.0837 (13) | 0.0043 (9) | 0.0102 (9) | -0.0329 (11) |
| O2 | 0.0478 (9) | 0.0470 (10) | 0.0600 (10) | -0.0015 (7) | 0.0187 (7) | -0.0103 (8) |
| O3 | 0.0376 (7) | 0.0237 (8) | 0.0574 (9) | -0.0041 (6) | 0.0064 (6) | -0.0038 (6) |
| O4 | 0.0330 (7) | 0.0254 (7) | 0.0518 (8) | 0.0025 (6) | 0.0030 (6) | -0.0031 (6) |
| O5 | 0.0690 (10) | 0.0360 (9) | 0.0523 (9) | 0.0049 (8) | -0.0028 (8) | -0.0066 (8) |
| O6 | 0.0437 (8) | 0.0357 (9) | 0.0490 (8) | 0.0028 (6) | -0.0005 (6) | 0.0012 (7) |
| C1 | 0.0648 (19) | 0.103 (2) | 0.096 (2) | -0.0124 (18) | 0.0364 (17) | -0.032 (2) |
| C2 | 0.065 (2) | 0.153 (4) | 0.124 (3) | -0.024 (2) | 0.044 (2) | -0.046 (3) |
| C3 | 0.062 (2) | 0.193 (5) | 0.148 (4) | 0.011 (3) | 0.043 (2) | -0.056 (4) |
| C4 | 0.079 (3) | 0.162 (4) | 0.157 (4) | 0.029 (3) | 0.039 (3) | -0.064 (4) |
| C5 | 0.074 (2) | 0.105 (3) | 0.107 (3) | 0.015 (2) | 0.0255 (18) | -0.039 (2) |
| C6 | 0.0508 (14) | 0.0750 (19) | 0.0526 (13) | 0.0080 (13) | 0.0136 (11) | -0.0091 (13) |
| C7 | 0.0498 (13) | 0.0520 (15) | 0.0491 (13) | 0.0048 (11) | 0.0109 (10) | -0.0039 (12) |
| C8 | 0.0369 (11) | 0.0421 (14) | 0.0681 (15) | -0.0041 (10) | 0.0007 (10) | -0.0077 (12) |
| C9 | 0.0414 (13) | 0.0679 (19) | 0.0874 (19) | -0.0160 (13) | -0.0035 (12) | -0.0104 (16) |
| C10 | 0.0273 (11) | 0.094 (2) | 0.102 (2) | -0.0010 (14) | 0.0051 (13) | -0.0049 (19) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C11 | 0.0390 (13) | 0.083 (2) | 0.119 (3) | 0.0131 (15) | 0.0089 (14) | -0.023 (2) |
| C12 | 0.0383 (12) | 0.0518 (15) | 0.0873 (19) | 0.0051 (11) | 0.0074 (11) | -0.0166 (14) |
| C13 | 0.0307 (10) | 0.0364 (12) | 0.0462 (11) | -0.0009 (8) | 0.0028 (8) | 0.0014 (9) |
| C14 | 0.0296 (9) | 0.0256 (10) | 0.0368 (10) | -0.0008 (8) | 0.0045 (7) | 0.0006 (8) |
| C15 | 0.0518 (13) | 0.0597 (16) | 0.0507 (13) | 0.0025 (12) | 0.0003 (10) | -0.0096 (12) |
| C16 | 0.0679 (17) | 0.089 (2) | 0.0579 (15) | -0.0055 (16) | -0.0038 (13) | -0.0217 (16) |
| C17 | 0.0522 (15) | 0.126 (3) | 0.0501 (15) | 0.0002 (18) | -0.0076 (12) | 0.0002 (18) |
| C18 | 0.0553 (16) | 0.106 (2) | 0.0605 (16) | 0.0200 (17) | -0.0007 (13) | 0.0175 (18) |
| C19 | 0.0498 (13) | 0.0640 (17) | 0.0524 (13) | 0.0115 (12) | 0.0053 (11) | 0.0037 (13) |
| C20 | 0.0339 (10) | 0.0482 (13) | 0.0388 (11) | -0.0014 (9) | 0.0059 (8) | 0.0021 (10) |
| C21 | 0.0338 (10) | 0.0386 (12) | 0.0415 (11) | -0.0004 (9) | 0.0053 (8) | 0.0002 (9) |

Geometric parameters (Å, °)

| | | | |
|----------------------|-------------|----------|-------------|
| O4—Ca1 | 2.4566 (13) | C4—C5 | 1.385 (5) |
| Ca1—O3 ⁱ | 2.3204 (14) | C4—H4A | 0.9300 |
| Ca1—O4 ⁱⁱ | 2.3781 (14) | C5—C6 | 1.382 (4) |
| Ca1—O1W | 2.3943 (17) | C5—H5A | 0.9300 |
| Ca1—O2 | 2.4467 (15) | C6—C7 | 1.487 (3) |
| Ca1—O5 | 2.4837 (17) | C8—C13 | 1.382 (3) |
| Ca1—O6 | 2.5628 (15) | C8—C9 | 1.387 (3) |
| Ca1—O3 | 2.7414 (14) | C8—H8A | 0.9300 |
| Ca1—C21 | 2.892 (2) | C9—C10 | 1.359 (4) |
| Ca1—C14 | 2.9272 (18) | C9—H9A | 0.9300 |
| O1W—Ca1 | 2.3944 (17) | C10—C11 | 1.369 (4) |
| O1W—H1W1 | 0.75 (3) | C10—H10A | 0.9300 |
| O1W—H2W1 | 0.89 (3) | C11—C12 | 1.389 (4) |
| O1—C7 | 1.309 (3) | C11—H11A | 0.9300 |
| O1—H1O | 0.92 (4) | C12—C13 | 1.377 (3) |
| O2—C7 | 1.217 (3) | C12—H12A | 0.9300 |
| O3—C14 | 1.250 (2) | C13—C14 | 1.506 (3) |
| O3—Ca1 | 2.7414 (14) | C14—Ca1 | 2.9273 (18) |
| O4—C14 | 1.261 (2) | C15—C20 | 1.378 (3) |
| O4—Ca1 | 2.4567 (13) | C15—C16 | 1.394 (3) |
| O5—C21 | 1.245 (3) | C15—H15A | 0.9300 |
| O5—Ca1 | 2.4838 (17) | C16—C17 | 1.360 (4) |
| O6—C21 | 1.272 (2) | C16—H16A | 0.9300 |
| O6—Ca1 | 2.5628 (15) | C17—C18 | 1.371 (5) |
| C1—C6 | 1.364 (4) | C17—H17A | 0.9300 |
| C1—C2 | 1.386 (4) | C18—C19 | 1.383 (4) |
| C1—H1A | 0.9300 | C18—H18A | 0.9300 |
| C2—C3 | 1.354 (6) | C19—C20 | 1.384 (3) |
| C2—H2A | 0.9300 | C19—H19A | 0.9300 |
| C3—C4 | 1.381 (6) | C20—C21 | 1.498 (3) |
| C3—H3A | 0.9300 | C21—Ca1 | 2.892 (2) |
| O1W—Ca1—O2 | 109.84 (6) | C5—C6—C7 | 120.6 (2) |
| O1W—Ca1—O3 | 80.16 (5) | C1—C6—C7 | 119.3 (3) |

| | | | |
|---------------|-------------|---------------------------------------|-------------|
| O1W—Ca1—O4 | 89.11 (5) | C1—C6—C5 | 120.2 (3) |
| O1W—Ca1—O5 | 151.11 (6) | O1—C7—C6 | 114.0 (2) |
| O1W—Ca1—O6 | 151.97 (6) | O2—C7—C6 | 122.8 (2) |
| O2—Ca1—O3 | 159.31 (6) | O1—C7—O2 | 123.3 (2) |
| O2—Ca1—O4 | 144.90 (6) | C9—C8—C13 | 120.0 (2) |
| O2—Ca1—O5 | 91.65 (6) | C8—C9—C10 | 120.4 (3) |
| O2—Ca1—O6 | 74.00 (5) | C9—C10—C11 | 120.1 (2) |
| O3—Ca1—O4 | 49.51 (4) | C10—C11—C12 | 120.4 (3) |
| O3—Ca1—O5 | 73.72 (5) | C3—C4—H4A | 120.00 |
| O3—Ca1—O6 | 106.02 (4) | C5—C4—H4A | 120.00 |
| O4—Ca1—O5 | 83.32 (5) | C4—C5—H5A | 121.00 |
| O4—Ca1—O6 | 75.86 (5) | C6—C5—H5A | 120.00 |
| O5—Ca1—O6 | 51.43 (4) | C9—C8—H8A | 120.00 |
| C11—C12—C13 | 119.8 (2) | C13—C8—H8A | 120.00 |
| C8—C13—C12 | 119.4 (2) | C8—C9—H9A | 120.00 |
| C8—C13—C14 | 120.15 (18) | C10—C9—H9A | 120.00 |
| C12—C13—C14 | 120.46 (19) | C9—C10—H10A | 120.00 |
| O4—C14—C13 | 118.21 (17) | C11—C10—H10A | 120.00 |
| O3—C14—O4 | 121.54 (17) | C10—C11—H11A | 120.00 |
| O3—C14—C13 | 120.22 (17) | C12—C11—H11A | 120.00 |
| C16—C15—C20 | 119.9 (2) | C11—C12—H12A | 120.00 |
| C15—C16—C17 | 120.1 (3) | C13—C12—H12A | 120.00 |
| C16—C17—C18 | 120.5 (3) | C16—C15—H15A | 120.00 |
| C17—C18—C19 | 120.0 (3) | C20—C15—H15A | 120.00 |
| C18—C19—C20 | 120.0 (3) | C15—C16—H16A | 120.00 |
| C15—C20—C19 | 119.5 (2) | C17—C16—H16A | 120.00 |
| C15—C20—C21 | 120.1 (2) | C16—C17—H17A | 120.00 |
| C19—C20—C21 | 120.4 (2) | C18—C17—H17A | 120.00 |
| O5—C21—C20 | 120.62 (19) | C17—C18—H18A | 120.00 |
| O6—C21—C20 | 118.40 (18) | C19—C18—H18A | 120.00 |
| O5—C21—O6 | 120.98 (19) | C18—C19—H19A | 120.00 |
| C2—C1—H1A | 120.00 | C20—C19—H19A | 120.00 |
| C6—C1—H1A | 120.00 | Ca1—O4—C14 | 98.75 (11) |
| C1—C2—H2A | 120.00 | O1W—Ca1—O3 ⁱ | 75.71 (6) |
| C3—C2—H2A | 121.00 | O1W—Ca1—O4 ⁱⁱ | 75.41 (6) |
| C2—C3—H3A | 119.00 | O2—Ca1—O3 ⁱ | 87.72 (6) |
| C4—C3—H3A | 119.00 | O2—Ca1—O4 ⁱⁱ | 81.92 (6) |
| Ca1—O2—C7 | 135.25 (16) | O3—Ca1—O3 ⁱ | 77.05 (5) |
| Ca1—O3—C14 | 85.74 (11) | O3—Ca1—O4 ⁱⁱ | 118.58 (4) |
| Ca1—O5—C21 | 95.98 (12) | O3 ⁱ —Ca1—O4 | 126.34 (5) |
| Ca1—O6—C21 | 91.59 (11) | O4—Ca1—O4 ⁱⁱ | 74.47 (4) |
| C7—O1—H1O | 112 (2) | O3 ⁱ —Ca1—O5 | 86.45 (5) |
| Ca1—O1W—H1W1 | 119 (2) | O4 ⁱⁱ —Ca1—O5 | 128.29 (5) |
| Ca1—O1W—H2W1 | 115 (2) | O3 ⁱ —Ca1—O6 | 132.20 (5) |
| H1W1—O1W—H2W1 | 99 (3) | O4 ⁱⁱ —Ca1—O6 | 77.79 (5) |
| C2—C1—C6 | 120.9 (4) | O3 ⁱ —Ca1—O4 ⁱⁱ | 143.74 (5) |
| C1—C2—C3 | 119.0 (4) | Ca1—O3—Ca1 ⁱ | 102.95 (5) |
| C2—C3—C4 | 121.1 (4) | Ca1 ⁱ —O3—C14 | 169.26 (13) |

| | | | |
|----------|-----------|---------------------------|-------------|
| C3—C4—C5 | 119.9 (5) | Ca1—O4—Ca1 ⁱⁱ | 105.53 (5) |
| C4—C5—C6 | 119.0 (4) | Ca1 ⁱⁱ —O4—C14 | 151.28 (12) |

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

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|---|------------|--------------|--------------|----------------|
| O1 <i>W</i> —H1 <i>W</i> 1...O5 ⁱ | 0.76 (3) | 2.05 (3) | 2.779 (2) | 163 (3) |
| O1—H1 <i>O</i> ...O6 | 0.93 (3) | 1.68 (3) | 2.597 (2) | 167 (3) |
| O1 <i>W</i> —H2 <i>W</i> 1...O6 ⁱⁱ | 0.89 (3) | 1.90 (3) | 2.754 (2) | 159 (3) |

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