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catena-Poly[[[triaquacalcium(II)]-di-μ-glycine-κ^4O:O'] diiodide]

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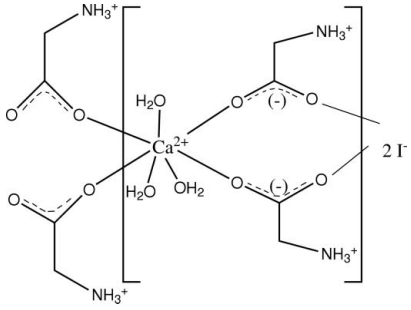
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.020; wR factor = 0.057; data-to-parameter ratio = 8.1.

In the crystal structure of the title compound, $\{[Ca(C_2H_5NO_2)_2(H_2O)_3]I_2\}_n$, there are two formula units per asymmetric unit; both calcium cations are sevenfold coordinated within irregular polyhedra. The polyhedra can be divided into two halves as square pyramidal and triangular prismatic due to the presence of one and two coordinated water molecules above and below the square plane. In all the glycine zwitterions, the amino groups form three two-centred hydrogen bonds, leading to a class I hydrogen-bonding pattern. The backbone conformations of the amino acids are *cis* and *trans*.

Related literature

For related literature on glycine-metal complexes, see: Natarajan, (1976); Natarajan & Mohana Rao (1980); Mohana Rao & Natarajan (1980); Natarajan & Mohana Rao (1981) and Ravikumar *et al.*, (1986) and on values of bond lengths and angles, see: Allen (2002). For information about the importance of calcium in biological systems, see Kretsinger & Nelson, (1976)



Experimental

Crystal data

$[Ca(C_2H_5NO_2)_2(H_2O)_3]I_2$
M_r = 498.07
Orthorhombic, $Pca2_1$
a = 13.065 (8) Å
b = 9.861 (4) Å
c = 22.731 (9) Å
V = 2929 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 4.66 mm^{-1}
T = 293 (2) K
0.24 × 0.19 × 0.15 mm

Data collection

Nonius MACH-3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.337, T_{max} = 0.474
2784 measured reflections
2784 independent reflections
2406 reflections with $I > 2\sigma(I)$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.057
S = 1.11
2784 reflections
342 parameters
19 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.93 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}
Absolute structure: Flack (1983), 137 Friedel pairs
Flack parameter: 0.02 (3)

Table 1
Selected bond lengths (Å).

Ca1—O3	2.352 (4)	Ca2—O7	2.339 (4)
Ca1—O8	2.362 (5)	Ca2—O1	2.340 (4)
Ca1—O2	2.386 (5)	Ca2—O6^{i}	2.391 (4)
Ca1—O1*W*	2.397 (5)	Ca2—O4^{i}	2.398 (4)
Ca1—O5	2.423 (4)	Ca2—O4*W*	2.423 (5)
Ca1—O2*W*	2.427 (5)	Ca2—O5*W*	2.499 (6)
Ca1—O3*W*	2.596 (5)	Ca2—O6*W*	2.533 (5)

Symmetry code: (i) $x, y+1, z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···O4^{i}	0.89	1.95	2.817 (7)	165
N1—H1*B*···I1	0.89	2.70	3.551 (7)	161
N1—H1*C*···I3^{ii}	0.89	3.03	3.743 (5)	139
N2—H2*C*···O2	0.89	1.91	2.790 (7)	169
N2—H2*D*···I2	0.89	2.71	3.566 (6)	161
N2—H2*E*···I4^{ii}	0.89	3.19	3.842 (6)	132
N3—H3*A*···I1^{iii}	0.89	3.11	3.806 (6)	136
N3—H3*B*···I3	0.89	2.70	3.570 (6)	167
N3—H3*C*···O8	0.89	1.93	2.817 (7)	173
N4—H4*C*···I2^{iii}	0.89	3.24	3.882 (5)	131
N4—H4*D*···I4	0.89	2.72	3.592 (6)	168
N4—H4*E*···O6^{i}	0.89	1.97	2.854 (7)	170
O1*W*—H1*W*···I3^{ii}	0.90 (5)	2.68 (6)	3.559 (5)	164 (11)
O1*W*—H2*W*···O3*W*^{iv}	0.86 (4)	2.01 (4)	2.866 (7)	173 (7)
O2*W*—H3*W*···O5*W*^{v}	0.90 (4)	2.13 (5)	3.011 (10)	166 (8)
O2*W*—H4*W*···I2^{vi}	0.89 (4)	2.81 (6)	3.641 (7)	154 (7)
O3*W*—H5*W*···I2^{vi}	0.94 (4)	2.69 (4)	3.629 (5)	174 (6)
O3*W*—H6*W*···O4*W*	0.90 (4)	2.06 (4)	2.951 (7)	172 (7)
O4*W*—H7*W*···O6*W*^{vii}	0.94 (5)	1.92 (5)	2.845 (6)	167 (9)
O4*W*—H8*W*···I1^{vi}	0.90 (4)	2.67 (5)	3.538 (5)	161 (6)
O5*W*—H9*W*···I3^{ii}	0.92 (5)	2.96 (9)	3.641 (6)	132 (8)
O6*W*—H11*W*···I4^{viii}	0.86 (4)	2.75 (5)	3.573 (5)	161 (6)
O6*W*—H12*W*···O5^{i}	0.94 (4)	1.89 (5)	2.742 (6)	150 (6)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXTL/PC* (Bruker, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2061).

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supplementary materials

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catena-Poly[[[triaquacalcium(II)]-di-μ-glycine-$\kappa^4O:O'$] diiodide]

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Comment

Glycine, the simplest amino acid, readily forms coordination complexes with many inorganic acids. Calcium has unique biological functions such as contraction of the muscle, mitochondrial functions, activation of enzymes, passage through cell membrances and other biological processes (Kretsinger & Nelson, 1976).

A systematic study on glycine-calcium coordination complexes were carried out from our laboratory (Natarajan, 1976) and the structures of bis(glycine) calcium(II) dichloride tetrahydrate (Natarajan & Mohana Rao, 1980), tris(glycine) calcium(II) dibromide (Mohana Rao & Natarajan, 1980), tris(glycine) calcium(II) diiodide monohydrate (Natarajan & Mohana Rao, 1981) and tris(glycine) calcium (II) dichloride (Ravikumar *et al.*, 1986) were already reported. Here, the crystal structure of another complex of glycine is presented.

The asymmetric unit of the title compound, (I), contains two calcium(II) cations, four glycine zwitterions, six water molecules and four iodine anions (Fig. 1). The zwitterionic nature of glycine is evident from the C—O and C—N bond distances. The back bone conformation angles are observed to be *cis* and *trans* forms in all the glycine zwitterions. Each calcium(II) is linked to four glycine oxygen atoms and three water oxygen atoms, leading to a sevenfold coordination. The calcium(II) ion surrounded by four glycine O atoms, within a square planar geometry. Water O atoms are oriented above and below this square-plane. One halve of the polyhedra is a square pyrimidal in which the square plane is capped by one water molecule and the other halve is a square prism with two water molecules above the square plane. The Ca(II) cations are connected by the glycine molecules into chains which elongate in the direction of the *a* axis (Fig. 2)..

Eventhough the metal coordination dominates, the crystal structure is further stabilized by three dimensional hydrogen bonding (Table 2). The iodine anions are acting as acceptors for N—H···I and O—H···I hydrogen bonds The amino groups of the glycine molecules are involved in three two-centered hydrogen bonds leading to class I hydrogen bonding pattern.

Experimental

The title compound, (I), was crystallized from an aqueous solution containing glycine and calcium(II) diiodide, in the stochiometric ratio of 2:1, at room temperature, by the technique of slow evaporation.

Refinement

Not all of the N—H H atoms were located in difference map but the zwitterionic nature of the glycine molecule is evident from the C—O and C—N bond distances. Thus, all the H atoms except water H atoms were positioned with idealized geometry and refined using a riding model, with C—H = 0.97 Å and N—H = 0.89 Å and U_{iso}(H) = 1.2–1.5 U_{eq} (parent atom). The H atoms of the water molecules were located in the difference fourier map and refined with varying coordinates isotropically. The absolute structure was determined and 135 Friedel pairs have been measured.

Figures

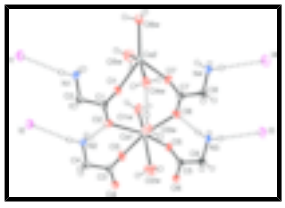

Fig. 1. The molecular structure of (I) with the atom numbering scheme and 50% probability displacement ellipsoids. H bonds are shown as dashed lines.

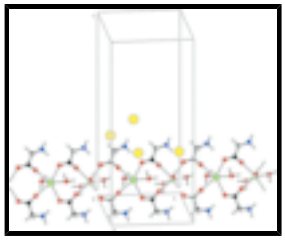

Fig. 2. Crystal structure of I, viewed down the *b*-axis. Hydrogen bonding is not shown for clarity.

catena-Poly[[[triaquacalcium(II)]-di-μ-glycine-κ^4*O*:*O*'] diiodide]

Crystal data

$[Ca(C_2H_5NO_2)_2(H_2O)_3]I_2$	F_{000} = 1888
	D_x = 2.259 Mg m^{-3}
M_r = 498.07	D_m = 2.24 (2) Mg m^{-3} D_m measured by flotation in a mixture of carbon tetrachloride and bromoform
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: P 2c -2ac	Cell parameters from 25 reflections
a = 13.065 (8) Å	θ = 10.4–12.9º
b = 9.861 (4) Å	μ = 4.66 mm^{-1}
c = 22.731 (9) Å	T = 293 (2) K
V = 2929 (2) Å^3	Block, colourless
Z = 8	0.24 × 0.19 × 0.15 mm

Data collection

Nonius MACH-3 sealed-tube diffractometer	2406 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.0000
Monochromator: graphite	θ_{max} = 25.0º
T = 293(2) K	θ_{min} = 2.1º
ω–2θ scans	h = 0→11
Absorption correction: ψ scan (North *et al.*, 1968)	k = 0→15
T_{min} = 0.337, T_{max} = 0.474	l = −1→27
2784 measured reflections	3 standard reflections
2784 independent reflections	every 60 min

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.020$	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 1.5679P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.057$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.11$	$\Delta\rho_{max} = 0.93$ e Å^{-3}
2784 reflections	$\Delta\rho_{min} = -0.42$ e Å^{-3}
342 parameters	Extinction correction: SHELXTL/PC (Bruker, 2000), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
19 restraints	Extinction coefficient: 0.00170 (7)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 135 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.02 (3)

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.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.35756 (8)	0.41229 (10)	−0.39714 (7)	0.0216 (2)
Ca2	0.41323 (8)	0.90112 (10)	−0.40719 (6)	0.0202 (2)
C1	0.3206 (4)	0.6346 (6)	−0.4993 (3)	0.0217 (12)
C2	0.2920 (5)	0.6822 (5)	−0.5600 (3)	0.0288 (16)
H2A	0.3125	0.6145	−0.5886	0.035*
H2B	0.2183	0.6927	−0.5624	0.035*
C3	0.3316 (4)	0.1391 (6)	−0.4988 (3)	0.0227 (13)
C4	0.3037 (5)	0.1800 (5)	−0.5612 (3)	0.0288 (16)
H4A	0.3312	0.1144	−0.5887	0.035*
H4B	0.2298	0.1813	−0.5655	0.035*
C5	0.4259 (4)	0.1518 (6)	−0.3058 (3)	0.0202 (12)
C6	0.4047 (5)	0.1935 (5)	−0.2419 (3)	0.0255 (13)
H6A	0.3316	0.2048	−0.2359	0.031*
H6B	0.4288	0.1235	−0.2153	0.031*

C7	0.4335 (4)	0.6509 (6)	−0.3023 (3)	0.0221 (13)
C8	0.4128 (5)	0.6959 (5)	−0.2390 (3)	0.0251 (13)
H8A	0.3397	0.7017	−0.2323	0.030*
H8B	0.4412	0.6303	−0.2117	0.030*
N1	0.3420 (4)	0.8134 (4)	−0.5744 (3)	0.0296 (12)
H1A	0.3252	0.8749	−0.5474	0.044*
H1B	0.3212	0.8414	−0.6096	0.044*
H1C	0.4096	0.8025	−0.5747	0.044*
N2	0.3458 (4)	0.3167 (4)	−0.5744 (3)	0.0292 (12)
H2C	0.3247	0.3753	−0.5472	0.044*
H2D	0.3241	0.3435	−0.6097	0.044*
H2E	0.4139	0.3131	−0.5742	0.044*
N3	0.4583 (4)	0.3227 (4)	−0.2296 (3)	0.0288 (12)
H3A	0.5256	0.3097	−0.2318	0.043*
H3B	0.4420	0.3513	−0.1937	0.043*
H3C	0.4396	0.3846	−0.2560	0.043*
N4	0.4604 (5)	0.8292 (4)	−0.2294 (3)	0.0293 (12)
H4C	0.5281	0.8213	−0.2319	0.044*
H4D	0.4435	0.8598	−0.1939	0.044*
H4E	0.4383	0.8870	−0.2567	0.044*
O1	0.3517 (4)	0.7195 (4)	−0.4632 (2)	0.0355 (10)
O2	0.3073 (3)	0.5119 (4)	−0.4883 (2)	0.0301 (10)
O3	0.3535 (4)	0.2306 (4)	−0.4641 (2)	0.0361 (10)
O4	0.3284 (3)	0.0146 (4)	−0.4867 (2)	0.0290 (10)
O5	0.4493 (3)	0.2426 (4)	−0.34088 (18)	0.0283 (9)
O6	0.4156 (3)	0.0272 (4)	−0.31733 (19)	0.0291 (10)
O7	0.4621 (4)	0.7375 (4)	−0.33814 (19)	0.0357 (10)
O8	0.4172 (3)	0.5275 (4)	−0.3127 (2)	0.0321 (10)
I1	0.32577 (3)	0.93569 (4)	−0.721030 (18)	0.03548 (13)
I2	0.32429 (3)	0.44141 (4)	−0.721120 (18)	0.03469 (12)
I3	0.43649 (3)	0.42713 (4)	−0.079737 (17)	0.03247 (12)
I4	0.43004 (3)	0.93532 (4)	−0.079283 (19)	0.03562 (12)
O1W	0.5271 (4)	0.4429 (6)	−0.4352 (2)	0.0472 (13)
O2W	0.2138 (4)	0.2778 (6)	−0.3631 (3)	0.0565 (15)
O3W	0.2119 (3)	0.5782 (5)	−0.3679 (2)	0.0352 (10)
O4W	0.2409 (3)	0.8749 (5)	−0.3696 (2)	0.0381 (10)
O5W	0.5691 (4)	0.8135 (5)	−0.4583 (3)	0.0502 (14)
O6W	0.5463 (3)	1.0843 (4)	−0.4229 (2)	0.0307 (10)
H1W	0.531 (8)	0.492 (11)	−0.469 (3)	0.15 (5)*
H2W	0.579 (4)	0.437 (7)	−0.412 (3)	0.06 (2)*
H3W	0.175 (5)	0.263 (9)	−0.395 (3)	0.07 (3)*
H4W	0.184 (6)	0.324 (8)	−0.334 (3)	0.09 (4)*
H5W	0.198 (6)	0.548 (7)	−0.329 (2)	0.06 (2)*
H6W	0.219 (6)	0.669 (4)	−0.365 (3)	0.05 (2)*
H7W	0.182 (5)	0.894 (10)	−0.392 (4)	0.12 (4)*
H8W	0.220 (5)	0.911 (7)	−0.335 (2)	0.05 (2)*
H9W	0.563 (10)	0.808 (10)	−0.498 (2)	0.16 (6)*
H10W	0.565 (5)	0.721 (4)	−0.455 (4)	0.05 (2)*
H11W	0.546 (5)	1.100 (7)	−0.460 (2)	0.05 (2)*

H12W	0.518 (5)	1.162 (5)	−0.405 (3)	0.05 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0268 (5)	0.0221 (5)	0.0158 (5)	−0.0007 (4)	−0.0028 (5)	−0.0002 (5)
Ca2	0.0252 (5)	0.0184 (5)	0.0172 (5)	−0.0015 (4)	−0.0024 (5)	0.0002 (5)
C1	0.025 (3)	0.019 (3)	0.022 (3)	0.002 (2)	−0.002 (2)	−0.001 (3)
C2	0.033 (3)	0.025 (3)	0.029 (4)	−0.005 (2)	−0.008 (3)	0.001 (2)
C3	0.026 (3)	0.023 (3)	0.019 (3)	0.006 (2)	0.000 (2)	0.000 (3)
C4	0.031 (3)	0.028 (3)	0.028 (4)	−0.005 (2)	−0.005 (3)	−0.001 (2)
C5	0.020 (3)	0.018 (3)	0.023 (3)	0.005 (2)	−0.008 (2)	0.000 (2)
C6	0.036 (3)	0.022 (3)	0.019 (3)	0.002 (2)	0.004 (3)	−0.004 (2)
C7	0.025 (3)	0.017 (3)	0.024 (4)	0.007 (2)	−0.010 (3)	0.000 (3)
C8	0.029 (3)	0.022 (3)	0.024 (4)	0.002 (2)	0.000 (3)	−0.006 (2)
N1	0.043 (3)	0.020 (2)	0.026 (3)	−0.0022 (18)	−0.004 (3)	0.004 (2)
N2	0.046 (3)	0.023 (3)	0.019 (3)	−0.0089 (19)	−0.002 (3)	0.002 (2)
N3	0.048 (3)	0.024 (3)	0.014 (3)	−0.006 (2)	−0.003 (3)	−0.001 (2)
N4	0.049 (3)	0.021 (2)	0.017 (3)	−0.003 (2)	−0.003 (3)	−0.001 (2)
O1	0.057 (3)	0.028 (2)	0.022 (2)	−0.004 (2)	−0.009 (2)	−0.004 (2)
O2	0.045 (2)	0.018 (2)	0.028 (2)	−0.0014 (18)	−0.0062 (19)	0.0009 (19)
O3	0.061 (3)	0.026 (2)	0.021 (2)	0.006 (2)	−0.006 (2)	−0.006 (2)
O4	0.038 (2)	0.021 (2)	0.028 (3)	0.0011 (16)	−0.0073 (19)	0.0024 (19)
O5	0.048 (2)	0.021 (2)	0.016 (2)	0.0006 (18)	−0.0002 (19)	−0.0008 (17)
O6	0.043 (2)	0.022 (2)	0.023 (2)	−0.0017 (18)	−0.0002 (19)	−0.0042 (18)
O7	0.064 (3)	0.022 (2)	0.021 (2)	−0.001 (2)	−0.002 (2)	0.0025 (18)
O8	0.043 (2)	0.024 (2)	0.029 (3)	−0.0011 (18)	−0.006 (2)	−0.005 (2)
I1	0.0308 (2)	0.0491 (3)	0.0266 (2)	−0.00419 (16)	−0.00330 (18)	0.0049 (2)
I2	0.0313 (2)	0.0459 (2)	0.0269 (2)	−0.00344 (15)	−0.00259 (17)	0.0064 (2)
I3	0.0314 (2)	0.0413 (2)	0.0248 (2)	0.00207 (15)	−0.00133 (19)	−0.0039 (2)
I4	0.0296 (2)	0.0507 (3)	0.0265 (2)	0.00068 (16)	−0.0012 (2)	−0.0064 (2)
O1W	0.032 (3)	0.085 (4)	0.024 (2)	−0.002 (2)	−0.005 (2)	0.012 (3)
O2W	0.046 (3)	0.058 (3)	0.065 (4)	−0.018 (3)	0.015 (3)	−0.009 (3)
O3W	0.037 (2)	0.038 (2)	0.030 (3)	0.0003 (19)	0.002 (2)	0.006 (2)
O4W	0.031 (2)	0.055 (3)	0.028 (3)	0.000 (2)	0.001 (2)	−0.007 (2)
O5W	0.049 (3)	0.049 (3)	0.053 (4)	0.008 (2)	0.004 (3)	−0.016 (3)
O6W	0.033 (2)	0.033 (2)	0.026 (3)	0.0022 (17)	0.0013 (18)	−0.003 (2)

Geometric parameters (Å, °)

Ca1—O3	2.352 (4)	C7—O7	1.239 (8)
Ca1—O8	2.362 (5)	C7—O8	1.258 (7)
Ca1—O2	2.386 (5)	C7—C8	1.529 (9)
Ca1—O1W	2.397 (5)	C8—N4	1.469 (7)
Ca1—O5	2.423 (4)	C8—H8A	0.9700
Ca1—O2W	2.427 (5)	C8—H8B	0.9700
Ca1—O3W	2.596 (5)	N1—H1A	0.8900
Ca2—O7	2.339 (4)	N1—H1B	0.8900
Ca2—O1	2.340 (4)	N1—H1C	0.8900

Ca2—O6^{i}	2.391 (4)	N2—H2C	0.8900
Ca2—O4^{i}	2.398 (4)	N2—H2D	0.8900
Ca2—O4W	2.423 (5)	N2—H2E	0.8900
Ca2—O5W	2.499 (6)	N3—H3A	0.8900
Ca2—O6W	2.533 (5)	N3—H3B	0.8900
C1—O1	1.240 (7)	N3—H3C	0.8900
C1—O2	1.248 (7)	N4—H4C	0.8900
C1—C2	1.505 (9)	N4—H4D	0.8900
C2—N1	1.485 (7)	N4—H4E	0.8900
C2—H2A	0.9700	O4—Ca2^{ii}	2.398 (4)
C2—H2B	0.9700	O6—Ca2^{ii}	2.391 (4)
C3—O3	1.231 (7)	O1W—H1W	0.90 (5)
C3—O4	1.259 (7)	O1W—H2W	0.86 (4)
C3—C4	1.519 (9)	O2W—H3W	0.90 (4)
C4—N2	1.486 (7)	O2W—H4W	0.89 (4)
C4—H4A	0.9700	O3W—H5W	0.94 (4)
C4—H4B	0.9700	O3W—H6W	0.90 (4)
C5—O5	1.237 (7)	O4W—H7W	0.94 (5)
C5—O6	1.264 (7)	O4W—H8W	0.90 (4)
C5—C6	1.535 (8)	O5W—H9W	0.92 (5)
C6—N3	1.481 (7)	O5W—H10W	0.92 (4)
C6—H6A	0.9700	O6W—H11W	0.86 (4)
C6—H6B	0.9700	O6W—H12W	0.94 (4)
O3—Ca1—O8	154.10 (16)	N3—C6—H6A	109.9
O3—Ca1—O2	75.24 (15)	C5—C6—H6A	109.9
O8—Ca1—O2	126.78 (14)	N3—C6—H6B	109.9
O3—Ca1—O1W	83.28 (18)	C5—C6—H6B	109.9
O8—Ca1—O1W	85.87 (17)	H6A—C6—H6B	108.3
O2—Ca1—O1W	83.63 (17)	O7—C7—O8	126.5 (6)
O3—Ca1—O5	80.00 (15)	O7—C7—C8	118.1 (5)
O8—Ca1—O5	74.94 (14)	O8—C7—C8	115.4 (5)
O2—Ca1—O5	151.50 (15)	N4—C8—C7	109.0 (5)
O1W—Ca1—O5	79.64 (17)	N4—C8—H8A	109.9
O3—Ca1—O2W	76.9 (2)	C7—C8—H8A	109.9
O8—Ca1—O2W	105.0 (2)	N4—C8—H8B	109.9
O2—Ca1—O2W	106.8 (2)	C7—C8—H8B	109.9
O1W—Ca1—O2W	154.1 (2)	H8A—C8—H8B	108.3
O5—Ca1—O2W	80.62 (19)	C2—N1—H1A	109.5
O3—Ca1—O3W	129.02 (16)	C2—N1—H1B	109.5
O8—Ca1—O3W	74.37 (16)	H1A—N1—H1B	109.5
O2—Ca1—O3W	76.21 (15)	C2—N1—H1C	109.5
O1W—Ca1—O3W	133.69 (17)	H1A—N1—H1C	109.5
O5—Ca1—O3W	131.48 (15)	H1B—N1—H1C	109.5
O2W—Ca1—O3W	72.24 (18)	C4—N2—H2C	109.5
O7—Ca2—O1	86.05 (16)	C4—N2—H2D	109.5
O7—Ca2—O6^{i}	77.39 (15)	H2C—N2—H2D	109.5
O1—Ca2—O6^{i}	150.14 (16)	C4—N2—H2E	109.5

O7—Ca2—O4^{i}	162.50 (15)	H2C—N2—H2E	109.5
O1—Ca2—O4^{i}	77.75 (15)	H2D—N2—H2E	109.5
O6^{i}—Ca2—O4^{i}	114.06 (15)	C6—N3—H3A	109.5
O7—Ca2—O4W	86.73 (17)	C6—N3—H3B	109.5
O1—Ca2—O4W	77.96 (16)	H3A—N3—H3B	109.5
O6^{i}—Ca2—O4W	76.46 (16)	C6—N3—H3C	109.5
O4^{i}—Ca2—O4W	83.48 (16)	H3A—N3—H3C	109.5
O7—Ca2—O5W	81.4 (2)	H3B—N3—H3C	109.5
O1—Ca2—O5W	76.25 (17)	C8—N4—H4C	109.5
O6^{i}—Ca2—O5W	124.48 (18)	C8—N4—H4D	109.5
O4^{i}—Ca2—O5W	100.82 (19)	H4C—N4—H4D	109.5
O4W—Ca2—O5W	152.23 (17)	C8—N4—H4E	109.5
O7—Ca2—O6W	113.54 (15)	H4C—N4—H4E	109.5
O1—Ca2—O6W	134.82 (16)	H4D—N4—H4E	109.5
O6^{i}—Ca2—O6W	74.98 (15)	C1—O1—Ca2	171.5 (4)
O4^{i}—Ca2—O6W	83.00 (14)	C1—O2—Ca1	122.3 (4)
O4W—Ca2—O6W	139.82 (16)	C3—O3—Ca1	167.8 (4)
O5W—Ca2—O6W	67.76 (16)	C3—O4—Ca2^{ii}	127.1 (4)
O1—C1—O2	124.6 (6)	C5—O5—Ca1	135.8 (4)
O1—C1—C2	118.5 (5)	C5—O6—Ca2^{ii}	133.1 (4)
O2—C1—C2	116.8 (5)	C7—O7—Ca2	146.6 (4)
N1—C2—C1	111.4 (5)	C7—O8—Ca1	132.4 (4)
N1—C2—H2A	109.4	Ca1—O1W—H1W	115 (7)
C1—C2—H2A	109.4	Ca1—O1W—H2W	121 (5)
N1—C2—H2B	109.4	H1W—O1W—H2W	120 (7)
C1—C2—H2B	109.4	Ca1—O2W—H3W	106 (5)
H2A—C2—H2B	108.0	Ca1—O2W—H4W	107 (6)
O3—C3—O4	125.6 (6)	H3W—O2W—H4W	116 (7)
O3—C3—C4	117.3 (5)	Ca1—O3W—H5W	100 (4)
O4—C3—C4	117.0 (5)	Ca1—O3W—H6W	125 (5)
N2—C4—C3	109.9 (5)	H5W—O3W—H6W	105 (6)
N2—C4—H4A	109.7	Ca2—O4W—H7W	123 (6)
C3—C4—H4A	109.7	Ca2—O4W—H8W	123 (5)
N2—C4—H4B	109.7	H7W—O4W—H8W	99 (6)
C3—C4—H4B	109.7	Ca2—O5W—H9W	114 (8)
H4A—C4—H4B	108.2	Ca2—O5W—H10W	106 (5)
O5—C5—O6	126.6 (6)	H9W—O5W—H10W	90 (6)
O5—C5—C6	117.4 (5)	Ca2—O6W—H11W	105 (5)
O6—C5—C6	115.9 (5)	Ca2—O6W—H12W	105 (4)
N3—C6—C5	108.9 (5)	H11W—O6W—H12W	106 (6)
O1—C1—C2—N1	21.7 (8)	O2W—Ca1—O3—C3	42 (2)
O2—C1—C2—N1	−160.9 (5)	O3W—Ca1—O3—C3	−12 (2)
O3—C3—C4—N2	21.5 (8)	O3—C3—O4—Ca2^{ii}	−22.0 (8)
O4—C3—C4—N2	−159.8 (5)	C4—C3—O4—Ca2^{ii}	159.4 (4)
O5—C5—C6—N3	−24.0 (7)	O6—C5—O5—Ca1	98.4 (7)
O6—C5—C6—N3	157.3 (5)	C6—C5—O5—Ca1	−80.2 (7)

O7—C7—C8—N4	−16.5 (7)	O3—Ca1—O5—C5	−88.7 (6)
O8—C7—C8—N4	164.9 (5)	O8—Ca1—O5—C5	97.9 (6)
O2—C1—O1—Ca2	169 (2)	O2—Ca1—O5—C5	−118.6 (6)
C2—C1—O1—Ca2	−14 (3)	O1W—Ca1—O5—C5	−173.6 (6)
O7—Ca2—O1—C1	−157 (3)	O2W—Ca1—O5—C5	−10.5 (6)
O6^{i}—Ca2—O1—C1	147 (3)	O3W—Ca1—O5—C5	45.5 (6)
O4^{i}—Ca2—O1—C1	30 (3)	O5—C5—O6—Ca2^{ii}	−8.6 (9)
O4W—Ca2—O1—C1	116 (3)	C6—C5—O6—Ca2^{ii}	170.0 (4)
O5W—Ca2—O1—C1	−75 (3)	O8—C7—O7—Ca2	89.7 (9)
O6W—Ca2—O1—C1	−37 (3)	C8—C7—O7—Ca2	−88.7 (8)
O1—C1—O2—Ca1	−6.9 (8)	O1—Ca2—O7—C7	−66.8 (8)
C2—C1—O2—Ca1	175.9 (4)	O6^{i}—Ca2—O7—C7	88.1 (8)
O3—Ca1—O2—C1	−156.4 (4)	O4^{i}—Ca2—O7—C7	−44.7 (11)
O8—Ca1—O2—C1	8.3 (5)	O4W—Ca2—O7—C7	11.3 (8)
O1W—Ca1—O2—C1	−71.7 (4)	O5W—Ca2—O7—C7	−143.5 (8)
O5—Ca1—O2—C1	−125.9 (4)	O6W—Ca2—O7—C7	155.4 (7)
O2W—Ca1—O2—C1	132.5 (4)	O7—C7—O8—Ca1	−31.9 (9)
O3W—Ca1—O2—C1	66.3 (4)	C8—C7—O8—Ca1	146.5 (4)
O4—C3—O3—Ca1	−101 (2)	O3—Ca1—O8—C7	142.7 (5)
C4—C3—O3—Ca1	77 (2)	O2—Ca1—O8—C7	−1.6 (6)
O8—Ca1—O3—C3	139 (2)	O1W—Ca1—O8—C7	77.3 (5)
O2—Ca1—O3—C3	−70 (2)	O5—Ca1—O8—C7	157.7 (5)
O1W—Ca1—O3—C3	−155 (2)	O2W—Ca1—O8—C7	−126.6 (5)
O5—Ca1—O3—C3	124 (2)	O3W—Ca1—O8—C7	−60.3 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O4^{i}	0.89	1.95	2.817 (7)	165
N1—H1B···I1	0.89	2.70	3.551 (7)	161
N1—H1C···I3^{iii}	0.89	3.03	3.743 (5)	139
N2—H2C···O2	0.89	1.91	2.790 (7)	169
N2—H2D···I2	0.89	2.71	3.566 (6)	161
N2—H2E···I4^{iii}	0.89	3.19	3.842 (6)	132
N3—H3A···I1^{iv}	0.89	3.11	3.806 (6)	136
N3—H3B···I3	0.89	2.70	3.570 (6)	167
N3—H3C···O8	0.89	1.93	2.817 (7)	173
N4—H4C···I2^{iv}	0.89	3.24	3.882 (5)	131
N4—H4D···I4	0.89	2.72	3.592 (6)	168
N4—H4E···O6^{i}	0.89	1.97	2.854 (7)	170
O1W—H1W···I3^{iii}	0.90 (5)	2.68 (6)	3.559 (5)	164 (11)
O1W—H2W···O3W^{v}	0.86 (4)	2.01 (4)	2.866 (7)	173 (7)
O2W—H3W···O5W^{vi}	0.90 (4)	2.13 (5)	3.011 (10)	166 (8)
O2W—H4W···I2^{vii}	0.89 (4)	2.81 (6)	3.641 (7)	154 (7)
O3W—H5W···I2^{vii}	0.94 (4)	2.69 (4)	3.629 (5)	174 (6)

O3W—H6W···O4W	0.90 (4)	2.06 (4)	2.951 (7)	172 (7)
O4W—H7W···O6W^{viii}	0.94 (5)	1.92 (5)	2.845 (6)	167 (9)
O4W—H8W···I1^{vii}	0.90 (4)	2.67 (5)	3.538 (5)	161 (6)
O5W—H9W···I3^{iii}	0.92 (5)	2.96 (9)	3.641 (6)	132 (8)
O6W—H11W···I4^{ix}	0.86 (4)	2.75 (5)	3.573 (5)	161 (6)
O6W—H12W···O5^{i}	0.94 (4)	1.89 (5)	2.742 (6)	150 (6)

Symmetry codes: (i) *x*, *y*+1, *z*; (iii) −*x*+1, −*y*+1, *z*−1/2; (iv) −*x*+1, −*y*+1, *z*+1/2; (v) *x*+1/2, −*y*+1, *z*; (vi) *x*−1/2, −*y*+1, *z*; (vii) −*x*+1/2, *y*, *z*+1/2; (viii) *x*−1/2, −*y*+2, *z*; (ix) −*x*+1, −*y*+2, *z*−1/2.

Fig. 1

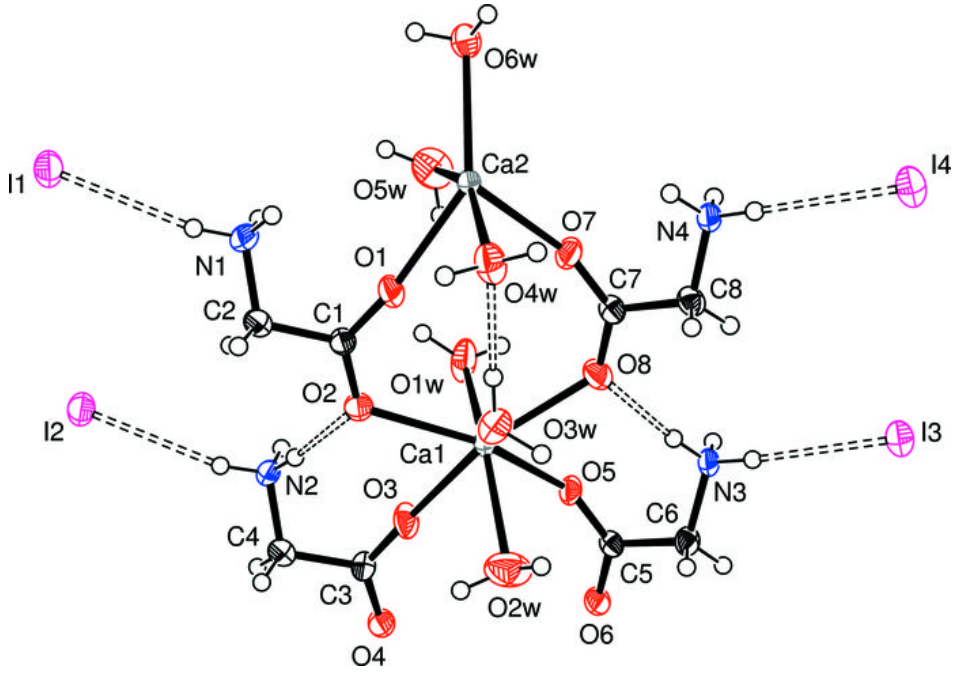
O6w
Ca2
I1
O5w
I4
O7
N4
N1
O1
O4w
C7
C8
C2
C1
O8
O1w
O2
I2
O3w
I3
Ca1
O5
N2
O3
N3
C6
C4
C5
C3
O2w
O6
O4

Fig. 2