Crystal structures of coordination polymers from CaI₂ and proline
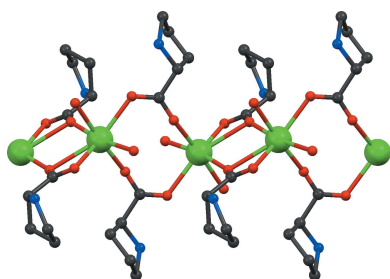
Kevin Lamberts and Ulli Englert*

Institute of Inorganic Chemistry, RWTH Aachen, Landoltweg 1, 52074 Aachen, Germany. *Correspondence e-mail: ullrich.englert@ac.rwth-aachen.de
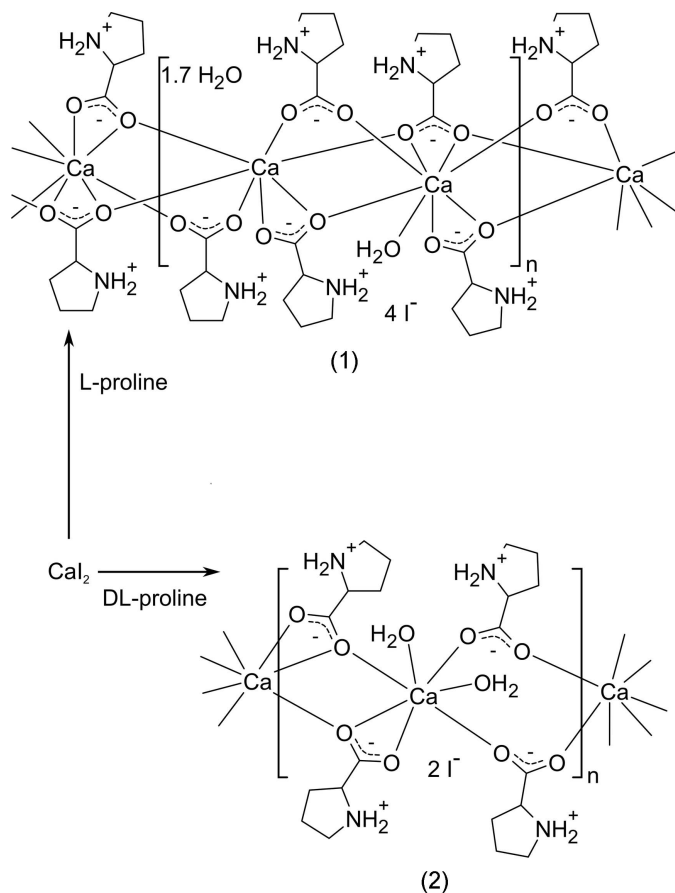
Completing our reports concerning the reaction products from calcium halides and the amino acid proline, two different solids were found for the reaction of L- and DL-proline with CaI₂. The enantiopure amino acid yields the one-dimensional coordination polymer catena-poly[[aqua-μ_3-L-proline-tetra-μ_2-L-proline-dicalcium] tetraiodide 1.7-hydrate], $\{[Ca_2(C_5H_9NO_2)_5(H_2O)]I_4\cdot 1.7H_2O\}_n$, (1), with two independent Ca²⁺ cations in characteristic seven- and eightfold coordination. Five symmetry-independent zwitterionic L-proline molecules bridge the metal sites into a cationic polymer. Racemic proline forms with Ca²⁺ cations heterochiral chains of the one-dimensional polymer catena-poly[[diaquadi-μ_2-DL-proline-calcium] diiodide], $\{[Ca(C_5H_9NO_2)_2(H_2O)_2]I_2\}_n$, (2). The centrosymmetric structure is built by one Ca²⁺ cation that is bridged towards its symmetry equivalents by two zwitterionic proline molecules. In both structures, the iodide ions remain non-coordinating and hydrogen bonds are formed between these counter-anions, the amino groups, coordinating and co-crystallized water molecules. While the overall composition of (1) and (2) is in line with other structures from calcium halides and amino acids, the diversity of the carboxylate coordination geometry is quite surprising.

1. Chemical context

The large field of crystal engineering benefits from the growing amount of structural data obtained by single-crystal diffraction. Amino acids are the building blocks of proteins and important molecules for various applications in chemistry and life sciences. Their metal complexes have, however, been investigated less often than their availability suggests. Many of these studies address the amino acids in their deprotonated form in which it mostly acts as a N,O chelating ligand. (e.g. Ito et al., 1971; Kato et al., 2008; Magill et al., 1993; Marandi & Shahbakhsh, 2007; Mathieson & Welsh, 1952; Mikhalyova et al., 2010; Oki & Yoneda, 1981). In contrast, the zwitterionic overall neutral amino acids show more analogy to carboxylates; for these, a large variety of coordination modes has been established (Batten et al., 2008). While the protonated amino group is no longer nucleophilic, it may act as a hydrogen-bond donor. The pattern formed by these interactions also depends on the chirality of the enantiopure or racemic amino acid. When both carboxylate coordination and intermolecular hydrogen bonds are taken into account, a large number of potentially competitive structures arises and subtle changes in the coordination chemistry may determine which product will be obtained. An overview of the crystal chemistry of amino acids has been published by Fleck & Petrosyan (2014). We here complete our reports concerning the reaction products from calcium halides and the amino acid proline. In this context, we encountered coordination polymers, isoreticular
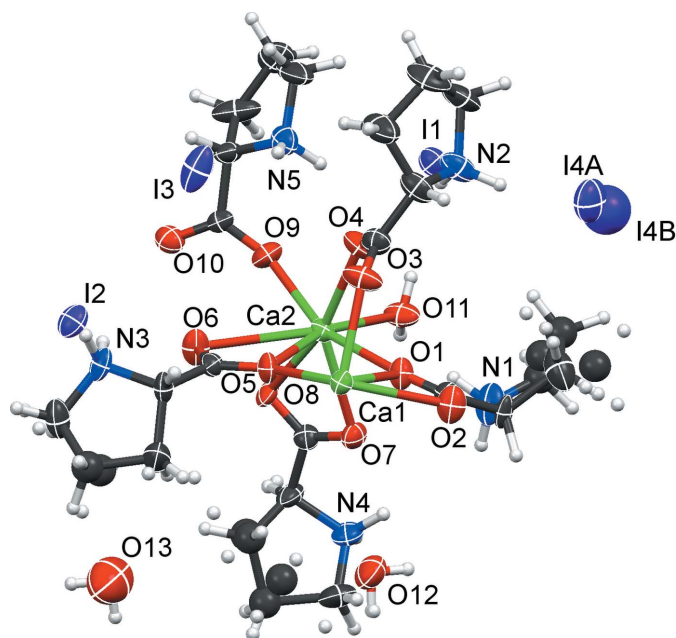
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coordination networks, and polymorphism (Lamberts *et al.*, 2014*b*; Lamberts *et al.*, 2015). The two structures reported here are coordination polymers obtained from calcium iodide and proline: the scheme shows that compounds (1) and (2) form from enantiopure L-proline and racemic proline, respectively.

Figure 1
The asymmetric unit of (1). Displacement ellipsoid are shown at the 80% probability level.

In view of the strongly ionic nature of an interaction between a carboxylate and a calcium dication, the 3.040 (5) Å distance between Ca1 and O9^i [(i) = $-x + 1$, y $- \frac{1}{2}$, $-z + \frac{1}{2}$] represents an additional, energetically favourable contact which, however, is much longer than a classical coordinative bond and does not affect the topology of the compound.

We mentioned in our earlier direct comparison between coordination polymers based on Ca^{2+} and Mn^{2+} (Lamberts *et al.*, 2014*a*) that the absence of crystal field effects is reflected in variable and often less regular coordination spheres about the alkaline earth cation. The two cations in (1) have significantly different coordination environments: Ca1 is seven-coordinated by carboxylato O atoms, while Ca2 offers an additional coordination site towards the water ligand to complete an eightfold coordination environment. The atoms around Ca1

2. Structural commentary

Compound (1) crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with two calcium cations, five proline ligands, one coordinating water ligand, 1.7 non-coordinating water molecules and four iodide anions in the asymmetric unit; all constituents are necessarily located in general positions (Fig. 1).
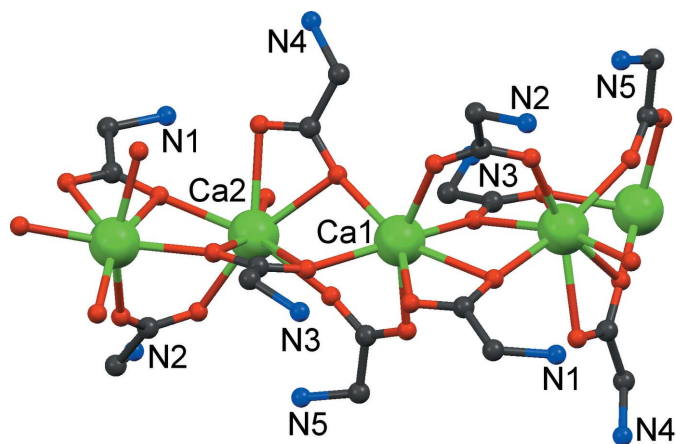
The five independent proline molecules show three different coordination modes; in the following discussion, they are labelled according to their N atom. Proline 1 acts as a chelating ligand towards Ca1 and simultaneously as a bridge to Ca2 in a μ_2-κ^2:κ^1 configuration. An analogous situation is found for proline 4, chelating Ca2 and bridging towards Ca1^{iii} [(iii) = $-x + 1$, y $+ \frac{1}{2}$, $-z + \frac{1}{2}$]. Proline 3 connects three Ca positions in a μ_3-κ^2:κ^2 coordination mode. The remaining proline ligands (2 and 5) do not chelate but only bridge two cations in a *syn–syn* configuration. Herein, proline 2 shows a more symmetric coordination, being located approximately in the middle of Ca1 and Ca2, whereas proline 5 is strongly dislocated towards Ca1.

Figure 2
The polymeric chain of (1). H atoms and C atoms of the proline ring have been omitted for clarity.

Table 1
Selected bond lengths (Å) for (1).

Ca1—O3	2.319 (5)	Ca2—O9	2.337 (5)
Ca1—O5	2.326 (5)	Ca2—O4	2.368 (5)
Ca1—O6^i	2.353 (5)	Ca2—O11	2.378 (5)
Ca1—O8^i	2.358 (5)	Ca2—O1	2.378 (5)
Ca1—O10^i	2.393 (5)	Ca2—O5	2.442 (5)
Ca1—O2	2.477 (5)	Ca2—O8	2.501 (5)
Ca1—O1	2.617 (5)	Ca2—O7	2.572 (5)
Ca1—Ca2	3.8144 (18)	Ca2—O6	2.820 (5)
Ca1—Ca2^i	3.8315 (18)		

Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2
Selected bond lengths (Å) for (2).

Ca1—O1	2.621 (6)	Ca1—O1^{ii}	2.323 (5)
Ca1—O2	2.489 (6)	Ca1—O3	2.252 (5)
Ca1—O4^i	2.396 (5)	Ca1—Ca1^i	4.829 (4)
Ca1—O5	2.376 (5)	Ca1—Ca1^{ii}	4.032 (4)
Ca1—O6	2.365 (6)		

Symmetry codes: (i) $-x + 2, -y, -z$; (ii) $-x + 1, -y, -z$.

are provided by two oxygen atoms of the chelating part of proline 1, and five single oxygen atoms from different bridging proline molecules. Ca2 is coordinated by two chelating carboxylato groups. Only three additional Ca···O contacts are formed from neighbouring, bridging proline ligands, whereas the remaining coordination partner is the coordinating water molecule. Each Ca^{2+} cation is coordinated by the independent *syn–syn* bridging proline ligands 2 and 5; they are arranged on opposite sides around Ca1 and next to each other around Ca2.

Overall, a one dimensional coordination polymer is formed (Fig. 2). The chain extends along *b*; its projection on the *bc* plane is a sinusoidal curve, with alternating Ca1 and Ca2 positions. Each chain segment is triple bridged with two very similar independent Ca···Ca separations of 3.814 (2) and 3.832 (2) Å. The μ_3-κ^2:κ^2 proline 3 coordinates within the sinusoidal plane in the concave parts, while proline 1 and the aqua ligand coordinate on the convex side. Selected distances are compiled in Table 1.

The iodide I4 shows positional disorder over two mutually exclusive sites, and three proline molecules exhibit slight disorder of carbon atoms of the five-membered proline envelopes.

Coordination polymer (2) forms under similar conditions as (1) but from racemic proline. The compound crystallizes in

space group $P\bar{1}$ with one Ca^{II} cation, two proline ligands and two water ligands and two non-coordinating iodide anions in the asymmetric unit, all in general positions (Fig. 3).

One proline molecule chelates the calcium cation with its carboxylato group and additionally bridges towards a second calcium of the polymer chain (μ_2-κ^2:κ^1). The other proline molecule only bridges two adjacent calcium atoms in a *syn–anti* conformation (μ_2-κ^1:κ^1).

Together with the two aqua ligands, this results in a sevenfold coordination of the Ca^{2+} cation. Since the inversion centres lie in between the calcium atoms, two different chain connections are obtained: one is built by two simultaneously bridging and chelating proline ligands [Ca···Ca = 4.032 (4) Å], the other one by two *syn–anti* bridging proline ligands [Ca···Ca = 4.829 (4) Å, parallelogram-shaped motif]. Overall, a zigzag-shaped polymer chain is formed which extends along the shortest unit-cell axis *a* (Fig. 4). Selected distances are given in Table 2.

3. Supramolecular features

Since most hydrogen atoms in (1) have been constrained to calculated positions, their relevance should not be over-estimated. The following points should, however, be mentioned: all hydrogen-bond donors find suitable acceptors. Most hydrogen bonds involve iodide and hence occur between different residues. However, only a few hydrogen bonds actually connect two neighbouring chains, resulting in an overall three-dimensional network (Fig. 5). Interestingly, only

Figure 3
The asymmetric unit of (2). Displacement ellipsoid are shown at the 80% probability level.

Figure 4
The polymeric chain of (2). H atoms have been omitted for clarity.

Table 3
Hydrogen-bond geometry (Å, °) for (1).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$I3^{ii}	0.99	2.60	3.526 (7)	155
N1—H1$B\cdots$O11	0.99	2.10	2.996 (9)	150
N2—H2$A\cdots$I1	0.99	2.75	3.603 (5)	145
N2—H2$B\cdots$I4A	0.99	2.53	3.400 (6)	146
N3—H3$A\cdots$O2^{iii}	0.99	1.94	2.829 (7)	147
N3—H3$B\cdots$I2	0.99	2.61	3.447 (5)	143
N4—H4$A\cdots$O12	0.99	1.80	2.750 (8)	159
N4—H4$B\cdots$I3^{ii}	0.99	2.92	3.674 (6)	133
N5—H5$A\cdots$I1	0.99	2.74	3.627 (6)	149
N5—H5$B\cdots$I3	0.99	2.62	3.478 (6)	146
O11—H11$A\cdots$I1	0.84 (6)	2.56 (6)	3.389 (5)	171 (7)
O11—H11$B\cdots$I2^{iii}	0.83 (7)	2.71 (7)	3.524 (6)	168 (5)
O12—H12$A\cdots$O10^{ii}	0.83 (4)	2.06 (5)	2.732 (7)	137 (4)
O12—H12$B\cdots$O2^{iv}	0.83 (3)	2.54 (4)	3.339 (8)	162 (7)
O13—H13$A\cdots$I4A^{iii}	0.85 (11)	2.90 (11)	3.703 (11)	159 (10)
O13—H13$B\cdots$I4A^{v}	0.85 (8)	2.76 (8)	3.598 (11)	172 (10)

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

Table 4
Hydrogen-bond geometry (Å, °) for (2).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$A\cdots$I2	0.85 (7)	2.67 (7)	3.459 (8)	154 (7)
N1—H1$B\cdots$I1	0.86 (7)	3.33 (7)	3.809 (7)	118 (6)
N1—H1$B\cdots$I2^{iii}	0.86 (7)	3.24 (7)	3.695 (7)	116 (5)
N2—H2$A\cdots$I1^{iv}	0.85 (6)	2.88 (6)	3.700 (8)	161 (7)
N2—H2$B)\cdots$O5^{v}	0.86 (6)	2.13 (7)	2.904 (9)	151 (7)
O5—H1$W\cdots$I1	0.84 (7)	2.68 (7)	3.486 (6)	163 (6)
O5—H2$W\cdots$I1^{vi}	0.83 (3)	2.77 (6)	3.491 (6)	147 (7)
O6—H3$W\cdots$I1^{vii}	0.87 (6)	2.65 (6)	3.509 (7)	167 (5)
O6—H4$W\cdots$I2^{vii}	0.84 (5)	2.77 (4)	3.543 (6)	155 (7)

Symmetry codes: (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z$; (vi) $-x + 1, -y + 1, -z$; (vii) $x + 1, y, z$.

4. Database survey

Database searches (Groom & Allen, 2014) were performed using the Cambridge Crystallographic Database (CSD, Version 5.36, including updates until November 2014). All searches were restricted to error-free entries for which 3D coordinates were available. A search for structures containing calcium and proline or derivatives in any protonation state comes up with eight hits. Six of them correspond to the aforementioned structures published by our group (Lamberts *et al.*, 2014*a*,*b*, 2015). These are coordination polymers and networks based on calcium chloride and bromide with both L-proline and DL-proline. The other two structures are a molecular complex with deprotonated *N,O*-chelating hydroxyproline (Kim *et al.*, 1985), and a coordination network of calcium pyroglutamate (Schmidbaur *et al.*, 1991).

5. Synthesis and crystallization

Single crystals of (1) were obtained by dissolving 92 mg (0.8 mmol) L-proline in 1 ml of aqueous 0.4 molar CaI$_2$ solution. The solvent was evaporated under controlled conditions

one of the five proline molecules contributes to an N—H$\cdots$O hydrogen bond along the chain [N3—H3$A\cdots$O2^{iii}; (iii) = $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$].

Each of the two independent aqua ligands in (2) donates hydrogen bonds towards two iodides. The amino group associated with N2 on the one hand also forms a hydrogen bond towards iodide, on the other hand directly connects two neighbouring chains by finding a coordinating water molecule as acceptor. N1 also interacts with an iodide counter-anion. This second NH donor can, however, not be unambiguously assigned to a hydrogen-bond acceptor: Two iodide anions are situated in its vicinity and may be regarded as acceptors for a bifurcated hydrogen bond with H$\cdots$I distances of 3.24 (5) and 3.33 (8) Å. Overall, a two-dimensional framework is formed in the *ab* plane (Fig. 5). A complete overview of hydrogen-bond geometries is given in Tables 3 and 4.

Figure 5
Hydrogen-bond networks formed in (1) (left) and (2) (right). Hydrogen bonds are drawn as light-blue dashed lines.

Table 5
Experimental details.

	(1)	(2)
Crystal data		
Chemical formula	$[Ca_2(C_5H_9NO_2)_5(H_2O)]I_4 \cdot 1.7H_2O$	$[Ca(C_5H_9NO_2)_2(H_2O)_2]I_2$
M_r	1212.21	560.17
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Triclinic, $P\bar{1}$
Temperature (K)	100	100
a, b, c (Å)	11.5276 (9), 12.7878 (10), 28.285 (2)	7.958 (7), 9.080 (8), 13.591 (11)
α, β, γ (°)	90, 90, 90	105.757 (10), 104.501 (11), 97.911 (12)
V (Å³)	4169.6 (5)	892.5 (13)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm⁻¹)	3.29	3.84
Crystal size (mm)	$0.22 \times 0.20 \times 0.10$	$0.22 \times 0.13 \times 0.05$
Data collection		
Diffractometer	Bruker D8 with APEX CCD area detector and Incoatec microsource	Bruker D8 with APEX CCD area detector and Incoatec microsource
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.563, 0.746	0.447, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	58117, 10475, 9862	8805, 3533, 2603
R_{int}	0.053	0.079
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.669	0.620
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.072, 1.10	0.047, 0.116, 1.02
No. of reflections	10475	3533
No. of parameters	455	214
No. of restraints	10	29
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.93, −0.66	1.05, −2.20
Absolute structure	Flack x determined using 4114 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)	–
Absolute structure parameter	0.023 (8)	–

Computer programs: *SMART* and *SAINT-Plus* (Bruker, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015) and *Mercury* (Macrae *et al.*, 2008).

(Lamberts *et al.*, 2014b) at 313 K. Suitable crystals were obtained after 5 d as yellow blocks. Crystals of (2) were obtained by using DL-proline under the same conditions and grew after 5 d as yellow plates.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. Non-hydrogen atoms were refined with anisotropic displacement parameters where possible. H atoms connected to carbon were placed in idealized positions and treated as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$.

In (1), significant residual density maxima indicated disorder. An alternative position for I4 was assigned and refined with an isotropic displacement parameter to a refined occupancy of 0.134 (7) (total occupancy of I4 over both positions constrained to 1). Atoms C4 and C5, C18 and C19, and C14 were also refined as split over two positions. They were given a common isotropic displacement parameter and their occupancy was refined. The occupancy of the alternative positions refined to 0.519 (12) for C4 and C5, 0.218 (12) for C18 and C19, and 0.270 (12) for C14; the occupancy sum of the alternative sites for each atom was constrained to unity. Carbon atoms connected to disordered neighbours were given

two alternative geometries of calculated hydrogen positions. The occupancy of the non-coordinating water molecule associated with O13 refined to 0.707 (17); tentative refinement with full occupancy resulted in an unusually large displacement parameter. Given the limited data quality, H atoms connected to nitrogen atoms were not refined but treated as riding in idealized positions, with N—H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. The hydrogen atoms of the three water molecules were modelled as oriented towards the closest acceptor and restrained to O—H distances of 0.84 Å. Further distance restraints were applied to ensure stable refinement of a reasonable hydrogen-bond geometry.

In (2), no disorder was encountered. Hydrogen atoms attached to non-carbon atoms were located in a difference Fourier map and treated as riding, with $U_{iso}(H) = 1.2U_{eq}$(non-H). N—H distances were refined with similarity restraints whereas O—H distances were restrained to 0.84 Å. H3W was assigned a distance restraint towards a neighbouring I1 anion to ensure suitable hydrogen-bond geometry. Reflection $0\bar{1}1$ was omitted from the final refinement because it was obstructed by the beamstop.

research communications

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supporting information

Crystal structures of coordination polymers from CaI₂ and proline

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Computing details

For both compounds, data collection: *SMART* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2013* (Sheldrick, 2015).

(1) *catena*-poly[[aqua-μ_3-L-proline-tetra-μ_2-L-proline-dicalcium] tetraiodide 1.7-hydrate]

Crystal data

$[Ca_2(C_5H_9NO_2)_5(H_2O)]I_4 \cdot 1.7H_2O$	$D_x = 1.931$ Mg m^{-3}
$M_r = 1212.21$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 9906 reflections
$a = 11.5276$ (9) Å	$\theta = 2.4$–$26.3°$
$b = 12.7878$ (10) Å	$\mu = 3.29$ mm^{-1}
$c = 28.285$ (2) Å	$T = 100$ K
$V = 4169.6$ (5) Å^3	Block, yellow
$Z = 4$	$0.22 \times 0.20 \times 0.10$ mm
$F(000) = 2356$	

Data collection

Bruker D8 with APEX CCD area detector and Incoatec microsource diffractometer	10475 independent reflections
	9862 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.053$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$\theta_{max} = 28.4°$, $\theta_{min} = 1.9°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.563$, $T_{max} = 0.746$	$k = -17 \rightarrow 17$
58117 measured reflections	$l = -37 \rightarrow 37$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.005P)^2 + 7.P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} < 0.001$
10475 reflections	$\Delta\rho_{max} = 0.93$ e Å^{-3}
455 parameters	$\Delta\rho_{min} = -0.66$ e Å^{-3}
10 restraints	Absolute structure: Flack x determined using 4114 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons & Flack, 2004)
Hydrogen site location: mixed	
	Absolute structure parameter: 0.023 (8)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
I1	0.50063 (4)	0.78534 (4)	0.46773 (2)	0.02285 (11)	
I2	0.09876 (4)	0.41042 (4)	0.14734 (2)	0.02416 (11)	
I3	0.11459 (5)	0.59585 (4)	0.30876 (2)	0.03516 (14)	
I4A	0.56556 (15)	0.30647 (9)	0.51264 (3)	0.0380 (4)	0.866 (7)
I4B	0.6104 (12)	0.3290 (8)	0.5192 (3)	0.063 (3)*	0.134 (7)
Ca1	0.53455 (11)	0.37203 (10)	0.27820 (5)	0.0131 (3)	
Ca2	0.55317 (12)	0.66087 (10)	0.31101 (5)	0.0138 (3)	
O1	0.6580 (4)	0.5048 (4)	0.32742 (16)	0.0182 (10)	
O2	0.7001 (5)	0.3367 (4)	0.33170 (18)	0.0239 (12)	
O3	0.4226 (4)	0.4116 (4)	0.34390 (16)	0.0247 (11)	
O4	0.4391 (4)	0.5772 (4)	0.36946 (16)	0.0236 (11)	
O5	0.4838 (4)	0.5378 (4)	0.25134 (16)	0.0183 (10)	
O6	0.4223 (5)	0.6927 (4)	0.22803 (16)	0.0223 (11)	
O7	0.7622 (4)	0.6802 (4)	0.28044 (16)	0.0183 (10)	
O8	0.6321 (4)	0.7962 (4)	0.25585 (16)	0.0204 (10)	
O9	0.4242 (4)	0.7994 (4)	0.32275 (16)	0.0213 (11)	
O10	0.3145 (4)	0.9020 (4)	0.27825 (16)	0.0216 (10)	
O11	0.6681 (5)	0.7372 (4)	0.37170 (18)	0.0226 (11)	
H11B	0.716 (6)	0.783 (5)	0.364 (3)	0.027*	
H11A	0.632 (6)	0.755 (6)	0.3963 (18)	0.027*	
O12	1.0987 (5)	0.9338 (4)	0.24099 (19)	0.0306 (13)	
H12A	1.141 (4)	0.928 (7)	0.2647 (10)	0.037*	
H12B	1.154 (3)	0.924 (6)	0.2225 (8)	0.037*	
O13	0.6478 (10)	0.6644 (9)	0.0612 (4)	0.059 (4)	0.707 (17)
H13B	0.712 (6)	0.670 (13)	0.047 (4)	0.070*	0.707 (17)
H13A	0.612 (10)	0.691 (12)	0.038 (3)	0.070*	0.707 (17)
N1	0.8513 (6)	0.5710 (5)	0.3712 (2)	0.0291 (15)	
H1A	0.9093	0.5919	0.3472	0.035*	
H1B	0.7779	0.6077	0.3639	0.035*	
N2	0.4256 (6)	0.5121 (4)	0.4621 (2)	0.0242 (14)	
H2A	0.4539	0.5790	0.4488	0.029*	
H2B	0.4922	0.4751	0.4765	0.029*	
N3	0.2892 (5)	0.6171 (4)	0.1571 (2)	0.0192 (13)	
H3A	0.2875	0.6855	0.1735	0.023*	
H3B	0.2114	0.5849	0.1598	0.023*	
N4	0.9412 (5)	0.7729 (5)	0.2348 (2)	0.0218 (13)	
H4A	0.9849	0.8373	0.2425	0.026*	
H4B	0.9402	0.7276	0.2632	0.026*	
N5	0.2588 (5)	0.7619 (5)	0.3864 (2)	0.0222 (14)	

H5A	0.3409	0.7607	0.3967	0.027*	
H5B	0.2396	0.6934	0.3721	0.027*	
C1	0.7208 (6)	0.4304 (5)	0.3402 (2)	0.0171 (14)	
C2	0.8318 (6)	0.4551 (5)	0.3680 (2)	0.0174 (14)	
H2	0.8996	0.4219	0.3519	0.021*	
C3A	0.8275 (8)	0.4183 (7)	0.4196 (3)	0.035 (2)	0.481 (12)
H3A1	0.8986	0.3795	0.4285	0.042*	0.481 (12)
H3A2	0.7586	0.3742	0.4258	0.042*	0.481 (12)
C4A	0.8195 (15)	0.5273 (13)	0.4458 (6)	0.0263 (10)*	0.481 (12)
H4A1	0.7378	0.5509	0.4479	0.032*	0.481 (12)
H4A2	0.8516	0.5221	0.4782	0.032*	0.481 (12)
C5A	0.8904 (16)	0.6024 (14)	0.4161 (6)	0.0263 (10)*	0.481 (12)
H5A1	0.8710	0.6763	0.4229	0.032*	0.481 (12)
H5A2	0.9748	0.5912	0.4201	0.032*	0.481 (12)
C3B	0.8275 (8)	0.4183 (7)	0.4196 (3)	0.035 (2)	0.519 (12)
H3B1	0.7466	0.4191	0.4313	0.042*	0.519 (12)
H3B2	0.8577	0.3460	0.4221	0.042*	0.519 (12)
C4B	0.8989 (14)	0.4893 (11)	0.4475 (5)	0.0263 (10)*	0.519 (12)
H4B1	0.9827	0.4784	0.4418	0.032*	0.519 (12)
H4B2	0.8823	0.4838	0.4817	0.032*	0.519 (12)
C5B	0.8564 (15)	0.5922 (14)	0.4269 (5)	0.0263 (10)*	0.519 (12)
H5B1	0.9110	0.6497	0.4343	0.032*	0.519 (12)
H5B2	0.7788	0.6103	0.4394	0.032*	0.519 (12)
C6	0.4157 (6)	0.4818 (5)	0.3747 (2)	0.0199 (15)	
C7	0.3731 (7)	0.4458 (6)	0.4233 (2)	0.0235 (16)	
H7	0.3953	0.3710	0.4283	0.028*	
C8	0.2421 (7)	0.4584 (7)	0.4310 (3)	0.0323 (19)	
H8A	0.1990	0.3970	0.4188	0.039*	
H8B	0.2126	0.5224	0.4154	0.039*	
C9	0.2318 (8)	0.4665 (7)	0.4850 (3)	0.035 (2)	
H9A	0.1578	0.5001	0.4942	0.042*	
H9B	0.2362	0.3965	0.4999	0.042*	
C10	0.3337 (8)	0.5329 (6)	0.4991 (3)	0.0308 (19)	
H10A	0.3620	0.5130	0.5309	0.037*	
H10B	0.3121	0.6078	0.4995	0.037*	
C11	0.4304 (6)	0.5976 (5)	0.2230 (2)	0.0145 (13)	
C12	0.3783 (6)	0.5474 (5)	0.1796 (2)	0.0174 (14)	
H12	0.3422	0.4790	0.1883	0.021*	
C13A	0.4678 (7)	0.5310 (7)	0.1402 (3)	0.0322 (19)	0.730 (12)
H13C	0.5022	0.4601	0.1418	0.039*	0.730 (12)
H13D	0.5305	0.5837	0.1419	0.039*	0.730 (12)
C14A	0.3950 (10)	0.5447 (8)	0.0946 (4)	0.0263 (10)*	0.730 (12)
H14A	0.4451	0.5608	0.0672	0.032*	0.730 (12)
H14B	0.3492	0.4810	0.0877	0.032*	0.730 (12)
C15A	0.3196 (8)	0.6325 (6)	0.1059 (3)	0.0274 (18)	0.730 (12)
H15A	0.2491	0.6316	0.0859	0.033*	0.730 (12)
H15B	0.3605	0.6998	0.1011	0.033*	0.730 (12)
C13B	0.4678 (7)	0.5310 (7)	0.1402 (3)	0.0322 (19)	0.270 (12)

H13E	0.4528	0.4647	0.1231	0.039*	0.270 (12)
H13F	0.5474	0.5290	0.1533	0.039*	0.270 (12)
C14B	0.452 (3)	0.627 (2)	0.1061 (10)	0.0263 (10)*	0.270 (12)
H14C	0.4877	0.6916	0.1193	0.032*	0.270 (12)
H14D	0.4844	0.6134	0.0743	0.032*	0.270 (12)
C15B	0.3196 (8)	0.6325 (6)	0.1059 (3)	0.0274 (18)	0.270 (12)
H15C	0.2921	0.7012	0.0943	0.033*	0.270 (12)
H15D	0.2860	0.5765	0.0860	0.033*	0.270 (12)
C16	0.7340 (6)	0.7567 (5)	0.2558 (2)	0.0162 (14)	
C17A	0.8181 (6)	0.8005 (6)	0.2205 (2)	0.0214 (15)	0.782 (12)
H17A	0.8082	0.8777	0.2167	0.026*	0.782 (12)
C18A	0.8031 (10)	0.7417 (9)	0.1718 (4)	0.0263 (10)*	0.782 (12)
H18A	0.7791	0.6682	0.1766	0.032*	0.782 (12)
H18B	0.7451	0.7772	0.1515	0.032*	0.782 (12)
C19A	0.9234 (8)	0.7480 (8)	0.1502 (3)	0.0263 (10)*	0.782 (12)
H19A	0.9417	0.8193	0.1389	0.032*	0.782 (12)
H19B	0.9335	0.6974	0.1241	0.032*	0.782 (12)
C20A	0.9976 (7)	0.7173 (7)	0.1949 (3)	0.0341 (18)	0.782 (12)
H20A	0.9963	0.6407	0.2000	0.041*	0.782 (12)
H20B	1.0791	0.7403	0.1911	0.041*	0.782 (12)
C17B	0.8181 (6)	0.8005 (6)	0.2205 (2)	0.0214 (15)	0.218 (12)
H17B	0.8127	0.8781	0.2242	0.026*	0.218 (12)
C18B	0.812 (3)	0.784 (3)	0.1740 (13)	0.0263 (10)*	0.218 (12)
H18C	0.8451	0.8431	0.1561	0.032*	0.218 (12)
H18D	0.7305	0.7729	0.1639	0.032*	0.218 (12)
C19B	0.884 (3)	0.684 (3)	0.1670 (12)	0.0263 (10)*	0.218 (12)
H19C	0.9006	0.6698	0.1332	0.032*	0.218 (12)
H19D	0.8468	0.6217	0.1814	0.032*	0.218 (12)
C20B	0.9976 (7)	0.7173 (7)	0.1949 (3)	0.0341 (18)	0.218 (12)
H20C	1.0432	0.6561	0.2057	0.041*	0.218 (12)
H20D	1.0477	0.7643	0.1760	0.041*	0.218 (12)
C21	0.3319 (6)	0.8491 (5)	0.3143 (2)	0.0142 (13)	
C22	0.2389 (6)	0.8479 (5)	0.3520 (2)	0.0178 (14)	
H22	0.1625	0.8356	0.3362	0.021*	
C23	0.2274 (7)	0.9435 (6)	0.3836 (3)	0.033 (2)	
H23A	0.1725	0.9946	0.3698	0.040*	
H23B	0.3036	0.9780	0.3880	0.040*	
C24	0.1817 (8)	0.9015 (9)	0.4305 (3)	0.046 (3)	
H24A	0.2325	0.9242	0.4568	0.055*	
H24B	0.1024	0.9282	0.4365	0.055*	
C25	0.1804 (7)	0.7848 (8)	0.4272 (3)	0.039 (2)	
H25A	0.2100	0.7526	0.4566	0.047*	
H25B	0.1010	0.7586	0.4211	0.047*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
I1	0.0253 (2)	0.0261 (2)	0.01717 (19)	0.0004 (2)	−0.0012 (2)	−0.00403 (18)

I2	0.0162 (2)	0.0236 (2)	0.0327 (2)	−0.0018 (2)	−0.0035 (2)	0.0007 (2)
I3	0.0306 (3)	0.0202 (2)	0.0547 (3)	0.0013 (2)	−0.0197 (3)	−0.0077 (2)
I4A	0.0449 (7)	0.0271 (5)	0.0421 (4)	0.0087 (4)	−0.0073 (4)	0.0069 (3)
Ca1	0.0131 (7)	0.0115 (6)	0.0148 (6)	−0.0007 (5)	−0.0016 (5)	−0.0011 (5)
Ca2	0.0152 (7)	0.0120 (6)	0.0143 (6)	−0.0013 (5)	0.0007 (5)	0.0003 (5)
O1	0.020 (3)	0.014 (2)	0.021 (2)	−0.003 (2)	−0.006 (2)	0.0020 (19)
O2	0.028 (3)	0.013 (2)	0.030 (3)	−0.003 (2)	−0.009 (2)	−0.002 (2)
O3	0.031 (3)	0.024 (3)	0.020 (2)	−0.010 (2)	0.010 (2)	−0.008 (2)
O4	0.032 (3)	0.023 (3)	0.016 (2)	−0.005 (2)	0.005 (2)	0.001 (2)
O5	0.019 (3)	0.019 (2)	0.016 (2)	0.000 (2)	−0.007 (2)	0.0007 (18)
O6	0.031 (3)	0.011 (2)	0.025 (3)	0.001 (2)	−0.009 (2)	−0.0040 (19)
O7	0.017 (3)	0.017 (2)	0.022 (2)	0.003 (2)	0.001 (2)	0.0052 (19)
O8	0.009 (2)	0.028 (3)	0.024 (2)	0.002 (2)	−0.0005 (19)	0.010 (2)
O9	0.014 (3)	0.022 (3)	0.028 (3)	0.003 (2)	0.002 (2)	−0.001 (2)
O10	0.021 (3)	0.023 (3)	0.020 (2)	−0.004 (2)	0.002 (2)	0.001 (2)
O11	0.018 (3)	0.026 (3)	0.024 (3)	−0.009 (2)	0.007 (2)	−0.005 (2)
O12	0.020 (3)	0.035 (3)	0.036 (3)	0.002 (3)	−0.002 (2)	0.005 (3)
O13	0.054 (7)	0.055 (7)	0.067 (8)	0.001 (6)	0.007 (6)	0.022 (6)
N1	0.029 (4)	0.022 (4)	0.036 (4)	−0.007 (3)	−0.013 (3)	0.000 (3)
N2	0.040 (4)	0.015 (3)	0.018 (3)	0.000 (3)	0.007 (3)	−0.002 (2)
N3	0.015 (3)	0.016 (3)	0.026 (3)	0.000 (2)	−0.010 (2)	−0.001 (2)
N4	0.014 (3)	0.027 (3)	0.025 (3)	−0.002 (3)	0.005 (2)	0.001 (3)
N5	0.019 (3)	0.029 (4)	0.019 (3)	−0.004 (3)	−0.002 (2)	0.001 (3)
C1	0.017 (3)	0.017 (4)	0.017 (3)	−0.003 (3)	−0.001 (3)	−0.002 (3)
C2	0.019 (4)	0.010 (3)	0.023 (3)	0.005 (3)	−0.010 (3)	0.000 (3)
C3A	0.042 (5)	0.039 (5)	0.026 (4)	−0.009 (4)	−0.009 (4)	0.007 (4)
C3B	0.042 (5)	0.039 (5)	0.026 (4)	−0.009 (4)	−0.009 (4)	0.007 (4)
C6	0.021 (4)	0.020 (3)	0.018 (3)	−0.001 (3)	0.001 (3)	−0.003 (3)
C7	0.034 (5)	0.021 (4)	0.016 (3)	−0.008 (3)	0.002 (3)	−0.004 (3)
C8	0.028 (5)	0.047 (5)	0.023 (4)	−0.009 (4)	0.006 (3)	0.001 (4)
C9	0.041 (5)	0.039 (5)	0.026 (4)	−0.014 (4)	0.017 (4)	0.003 (4)
C10	0.045 (5)	0.031 (4)	0.016 (4)	0.001 (4)	0.011 (3)	−0.003 (3)
C11	0.015 (3)	0.014 (3)	0.014 (3)	0.000 (3)	0.001 (2)	0.003 (3)
C12	0.022 (4)	0.013 (3)	0.017 (3)	0.003 (3)	−0.008 (3)	0.001 (2)
C13A	0.029 (5)	0.046 (5)	0.021 (4)	0.015 (4)	−0.002 (3)	−0.002 (3)
C15A	0.039 (5)	0.020 (4)	0.023 (4)	0.004 (3)	−0.011 (3)	0.001 (3)
C13B	0.029 (5)	0.046 (5)	0.021 (4)	0.015 (4)	−0.002 (3)	−0.002 (3)
C15B	0.039 (5)	0.020 (4)	0.023 (4)	0.004 (3)	−0.011 (3)	0.001 (3)
C16	0.015 (4)	0.016 (3)	0.018 (3)	−0.003 (3)	0.000 (3)	0.001 (3)
C17A	0.012 (3)	0.025 (4)	0.027 (4)	0.003 (3)	0.005 (3)	0.010 (3)
C20A	0.022 (4)	0.046 (5)	0.034 (4)	0.010 (4)	0.010 (4)	−0.004 (4)
C17B	0.012 (3)	0.025 (4)	0.027 (4)	0.003 (3)	0.005 (3)	0.010 (3)
C20B	0.022 (4)	0.046 (5)	0.034 (4)	0.010 (4)	0.010 (4)	−0.004 (4)
C21	0.012 (3)	0.013 (3)	0.018 (3)	−0.002 (3)	0.000 (3)	−0.006 (3)
C22	0.016 (3)	0.018 (3)	0.020 (3)	0.004 (3)	0.006 (3)	0.001 (3)
C23	0.024 (4)	0.028 (4)	0.047 (5)	−0.006 (3)	0.018 (4)	−0.015 (4)
C24	0.036 (5)	0.077 (7)	0.024 (4)	0.021 (5)	−0.004 (4)	−0.024 (5)
C25	0.022 (4)	0.076 (7)	0.019 (4)	−0.005 (5)	0.008 (3)	−0.001 (4)

Geometric parameters (Å, º)

Ca1—O3	2.319 (5)	C3A—H3A1	0.9900
Ca1—O5	2.326 (5)	C3A—H3A2	0.9900
Ca1—O6ⁱ	2.353 (5)	C4A—C5A	1.51 (2)
Ca1—O8ⁱ	2.358 (5)	C4A—H4A1	0.9900
Ca1—O10ⁱ	2.393 (5)	C4A—H4A2	0.9900
Ca1—O2	2.477 (5)	C5A—H5A1	0.9900
Ca1—O1	2.617 (5)	C5A—H5A2	0.9900
Ca1—Ca2	3.8144 (18)	C4B—C5B	1.52 (2)
Ca1—Ca2ⁱ	3.8315 (18)	C4B—H4B1	0.9900
Ca2—O9	2.337 (5)	C4B—H4B2	0.9900
Ca2—O4	2.368 (5)	C5B—H5B1	0.9900
Ca2—O11	2.378 (5)	C5B—H5B2	0.9900
Ca2—O1	2.378 (5)	C6—C7	1.531 (9)
Ca2—O5	2.442 (5)	C7—C8	1.534 (11)
Ca2—O8	2.501 (5)	C7—H7	1.0000
Ca2—O7	2.572 (5)	C8—C9	1.536 (11)
Ca2—O6	2.820 (5)	C8—H8A	0.9900
Ca1—C1	2.871 (7)	C8—H8B	0.9900
Ca1—C21ⁱ	3.049 (7)	C9—C10	1.504 (12)
Ca2—C11	2.976 (6)	C9—H9A	0.9900
O1—C1	1.249 (8)	C9—H9B	0.9900
O2—C1	1.245 (8)	C10—H10A	0.9900
O3—C6	1.254 (8)	C10—H10B	0.9900
O4—C6	1.258 (8)	C11—C12	1.510 (9)
O5—C11	1.267 (8)	C12—C13A	1.534 (10)
O6—C11	1.229 (8)	C12—H12	1.0000
O6—Ca1ⁱⁱ	2.353 (5)	C13A—C14A	1.547 (13)
O7—C16	1.245 (8)	C13A—H13C	0.9900
O8—C16	1.278 (8)	C13A—H13D	0.9900
O8—Ca1ⁱⁱ	2.358 (5)	C14A—C15A	1.455 (12)
O9—C21	1.262 (8)	C14A—H14A	0.9900
O9—Ca1ⁱⁱ	3.040 (5)	C14A—H14B	0.9900
O10—C21	1.240 (8)	C15A—H15A	0.9900
O10—Ca1ⁱⁱ	2.393 (5)	C15A—H15B	0.9900
O11—H11B	0.83 (3)	C14B—H14C	0.9900
O11—H11A	0.84 (3)	C14B—H14D	0.9900
O12—H12A	0.84 (3)	C16—C17A	1.501 (9)
O12—H12B	0.84 (2)	C17A—C18A	1.579 (13)
O13—H13B	0.84 (3)	C17A—H17A	1.0000
O13—H13A	0.84 (3)	C18A—C19A	1.517 (15)
N1—C5A	1.406 (18)	C18A—H18A	0.9900
N1—C2	1.502 (9)	C18A—H18B	0.9900
N1—C5B	1.599 (17)	C19A—C20A	1.575 (12)
N1—H1A	0.9900	C19A—H19A	0.9900
N1—H1B	0.9900	C19A—H19B	0.9900
N2—C7	1.511 (9)	C20A—H20A	0.9900

N2—C10	1.514 (9)	C20A—H20B	0.9900
N2—H2A	0.9900	C18B—C19B	1.54 (5)
N2—H2B	0.9900	C18B—H18C	0.9900
N3—C12	1.501 (8)	C18B—H18D	0.9900
N3—C15A	1.505 (9)	C19B—H19C	0.9900
N3—H3A	0.9900	C19B—H19D	0.9900
N3—H3B	0.9900	C21—C22	1.512 (9)
N4—C20A	1.485 (9)	C21—Ca1ii	3.049 (7)
N4—C17A	1.517 (9)	C22—C23	1.522 (10)
N4—H4A	0.9900	C22—H22	1.0000
N4—H4B	0.9900	C23—C24	1.526 (12)
N5—C22	1.487 (9)	C23—H23A	0.9900
N5—C25	1.495 (9)	C23—H23B	0.9900
N5—H5A	0.9900	C24—C25	1.496 (14)
N5—H5B	0.9900	C24—H24A	0.9900
C1—C2	1.535 (9)	C24—H24B	0.9900
C2—C3A	1.533 (10)	C25—H25A	0.9900
C2—H2	1.0000	C25—H25B	0.9900
C3A—C4A	1.582 (18)		
O3—Ca1—O5	85.58 (18)	C20A—N4—C17A	108.5 (6)
O3—Ca1—O6i	112.99 (18)	C20A—N4—H4A	110.0
O5—Ca1—O6i	156.43 (17)	C17A—N4—H4A	110.0
O3—Ca1—O8i	87.92 (17)	C20A—N4—H4B	110.0
O5—Ca1—O8i	92.09 (18)	C17A—N4—H4B	110.0
O6i—Ca1—O8i	74.98 (18)	H4A—N4—H4B	108.4
O3—Ca1—O10i	154.78 (18)	C22—N5—C25	105.5 (6)
O5—Ca1—O10i	79.57 (18)	C22—N5—H5A	110.6
O6i—Ca1—O10i	87.28 (18)	C25—N5—H5A	110.6
O8i—Ca1—O10i	112.72 (17)	C22—N5—H5B	110.6
O3—Ca1—O2	88.79 (18)	C25—N5—H5B	110.6
O5—Ca1—O2	124.01 (17)	H5A—N5—H5B	108.8
O6i—Ca1—O2	72.86 (17)	O2—C1—O1	124.5 (6)
O8i—Ca1—O2	143.35 (18)	O2—C1—C2	117.2 (6)
O10i—Ca1—O2	82.90 (18)	O1—C1—C2	118.3 (6)
O3—Ca1—O1	74.61 (17)	O2—C1—Ca1	59.2 (4)
O5—Ca1—O1	73.69 (16)	O1—C1—Ca1	65.7 (4)
O6i—Ca1—O1	123.88 (17)	C2—C1—Ca1	171.9 (5)
O8i—Ca1—O1	158.03 (17)	N1—C2—C3A	104.6 (6)
O10i—Ca1—O1	81.68 (17)	N1—C2—C1	111.0 (5)
O2—Ca1—O1	51.27 (15)	C3A—C2—C1	113.4 (6)
O3—Ca1—C1	82.51 (19)	N1—C2—H2	109.2
O5—Ca1—C1	98.66 (18)	C3A—C2—H2	109.2
O6i—Ca1—C1	98.12 (19)	C1—C2—H2	109.2
O8i—Ca1—C1	164.98 (19)	C2—C3A—C4A	100.2 (8)
O10i—Ca1—C1	79.75 (18)	C2—C3A—H3A1	111.7
O2—Ca1—C1	25.59 (17)	C4A—C3A—H3A1	111.7
O1—Ca1—C1	25.78 (16)	C2—C3A—H3A2	111.7

O3—Ca1—O9ⁱ	155.05 (17)	C4A—C3A—H3A2	111.7
O5—Ca1—O9ⁱ	90.62 (15)	H3A1—C3A—H3A2	109.5
O6ⁱ—Ca1—O9ⁱ	66.36 (15)	C5A—C4A—C3A	105.5 (12)
O8ⁱ—Ca1—O9ⁱ	67.56 (14)	C5A—C4A—H4A1	110.6
O10ⁱ—Ca1—O9ⁱ	46.25 (15)	C3A—C4A—H4A1	110.6
O2—Ca1—O9ⁱ	113.43 (16)	C5A—C4A—H4A2	110.6
O1—Ca1—O9ⁱ	127.79 (15)	C3A—C4A—H4A2	110.6
C1—Ca1—O9ⁱ	122.43 (17)	H4A1—C4A—H4A2	108.8
O3—Ca1—C21ⁱ	171.73 (18)	N1—C5A—C4A	98.5 (13)
O5—Ca1—C21ⁱ	86.23 (17)	N1—C5A—H5A1	112.1
O6ⁱ—Ca1—C21ⁱ	74.66 (17)	C4A—C5A—H5A1	112.1
O8ⁱ—Ca1—C21ⁱ	91.22 (17)	N1—C5A—H5A2	112.1
O10ⁱ—Ca1—C21ⁱ	22.46 (17)	C4A—C5A—H5A2	112.1
O2—Ca1—C21ⁱ	96.76 (18)	H5A1—C5A—H5A2	109.7
O1—Ca1—C21ⁱ	104.14 (17)	C5B—C4B—H4B1	112.0
C1—Ca1—C21ⁱ	99.89 (19)	C5B—C4B—H4B2	112.0
O9ⁱ—Ca1—C21ⁱ	23.91 (15)	H4B1—C4B—H4B2	109.7
O3—Ca1—Ca2	67.96 (13)	C4B—C5B—N1	104.0 (12)
O5—Ca1—Ca2	37.94 (11)	C4B—C5B—H5B1	110.9
O6ⁱ—Ca1—Ca2	161.81 (13)	N1—C5B—H5B1	110.9
O8ⁱ—Ca1—Ca2	122.92 (13)	C4B—C5B—H5B2	110.9
O10ⁱ—Ca1—Ca2	88.06 (13)	N1—C5B—H5B2	110.9
O2—Ca1—Ca2	89.12 (12)	H5B1—C5B—H5B2	109.0
O1—Ca1—Ca2	37.96 (11)	O3—C6—O4	126.7 (6)
C1—Ca1—Ca2	63.74 (14)	O3—C6—C7	115.4 (6)
O9ⁱ—Ca1—Ca2	121.02 (10)	O4—C6—C7	117.9 (6)
C21ⁱ—Ca1—Ca2	105.87 (13)	N2—C7—C6	110.7 (6)
O3—Ca1—Ca2ⁱ	122.34 (13)	N2—C7—C8	103.5 (6)
O5—Ca1—Ca2ⁱ	111.14 (12)	C6—C7—C8	114.3 (6)
O6ⁱ—Ca1—Ca2ⁱ	47.13 (12)	N2—C7—H7	109.4
O8ⁱ—Ca1—Ca2ⁱ	39.30 (12)	C6—C7—H7	109.4
O10ⁱ—Ca1—Ca2ⁱ	82.27 (13)	C8—C7—H7	109.4
O2—Ca1—Ca2ⁱ	118.50 (12)	C7—C8—C9	102.9 (7)
O1—Ca1—Ca2ⁱ	162.03 (12)	C7—C8—H8A	111.2
C1—Ca1—Ca2ⁱ	141.53 (14)	C9—C8—H8A	111.2
O9ⁱ—Ca1—Ca2ⁱ	37.58 (9)	C7—C8—H8B	111.2
C21ⁱ—Ca1—Ca2ⁱ	60.03 (13)	C9—C8—H8B	111.2
Ca2—Ca1—Ca2ⁱ	149.04 (4)	H8A—C8—H8B	109.1
O9—Ca2—O4	83.70 (18)	C10—C9—C8	104.0 (6)
O9—Ca2—O11	86.60 (18)	C10—C9—H9A	111.0
O4—Ca2—O11	89.47 (17)	C8—C9—H9A	111.0
O9—Ca2—O1	158.70 (18)	C10—C9—H9B	111.0
O4—Ca2—O1	76.51 (17)	C8—C9—H9B	111.0
O11—Ca2—O1	85.43 (18)	H9A—C9—H9B	109.0
O9—Ca2—O5	112.25 (17)	C9—C10—N2	105.3 (6)
O4—Ca2—O5	90.55 (16)	C9—C10—H10A	110.7
O11—Ca2—O5	161.04 (19)	N2—C10—H10A	110.7
O1—Ca2—O5	76.15 (16)	C9—C10—H10B	110.7

O9—Ca2—O8	78.20 (17)	N2—C10—H10B	110.7
O4—Ca2—O8	161.84 (18)	H10A—C10—H10B	108.8
O11—Ca2—O8	87.91 (17)	O6—C11—O5	124.1 (6)
O1—Ca2—O8	121.14 (17)	O6—C11—C12	119.0 (6)
O5—Ca2—O8	97.70 (16)	O5—C11—C12	116.8 (6)
O9—Ca2—O7	124.82 (17)	O6—C11—Ca2	70.7 (4)
O4—Ca2—O7	142.96 (17)	O5—C11—Ca2	53.4 (3)
O11—Ca2—O7	71.41 (17)	C12—C11—Ca2	170.1 (5)
O1—Ca2—O7	70.74 (16)	N3—C12—C11	111.4 (5)
O5—Ca2—O7	97.83 (17)	N3—C12—C13A	103.5 (5)
O8—Ca2—O7	51.90 (15)	C11—C12—C13A	112.5 (6)
O9—Ca2—O6	70.63 (15)	N3—C12—H12	109.8
O4—Ca2—O6	110.47 (17)	C11—C12—H12	109.8
O11—Ca2—O6	147.10 (17)	C13A—C12—H12	109.8
O1—Ca2—O6	123.75 (15)	C12—C13A—C14A	103.0 (7)
O5—Ca2—O6	48.91 (14)	C12—C13A—H13C	111.2
O8—Ca2—O6	64.88 (15)	C14A—C13A—H13C	111.2
O7—Ca2—O6	101.97 (16)	C12—C13A—H13D	111.2
O9—Ca2—C16	102.41 (19)	C14A—C13A—H13D	111.2
O4—Ca2—C16	166.73 (19)	H13C—C13A—H13D	109.1
O11—Ca2—C16	79.26 (19)	C15A—C14A—C13A	103.3 (7)
O1—Ca2—C16	95.45 (19)	C15A—C14A—H14A	111.1
O5—Ca2—C16	97.83 (18)	C13A—C14A—H14A	111.1
O8—Ca2—C16	26.30 (17)	C15A—C14A—H14B	111.1
O7—Ca2—C16	25.62 (16)	C13A—C14A—H14B	111.1
O6—Ca2—C16	82.76 (17)	H14A—C14A—H14B	109.1
O9—Ca2—C11	91.29 (18)	C14A—C15A—N3	104.4 (6)
O4—Ca2—C11	101.37 (18)	C14A—C15A—H15A	110.9
O11—Ca2—C11	168.68 (18)	N3—C15A—H15A	110.9
O1—Ca2—C11	100.18 (18)	C14A—C15A—H15B	110.9
O5—Ca2—C11	24.62 (17)	N3—C15A—H15B	110.9
O8—Ca2—C11	80.77 (17)	H15A—C15A—H15B	108.9
O7—Ca2—C11	100.99 (16)	H14C—C14B—H14D	109.7
O6—Ca2—C11	24.29 (15)	O7—C16—O8	123.4 (6)
C16—Ca2—C11	90.36 (18)	O7—C16—C17A	119.8 (6)
O9—Ca2—Ca1	137.14 (13)	O8—C16—C17A	116.6 (6)
O4—Ca2—Ca1	72.60 (12)	O7—C16—Ca2	63.3 (4)
O11—Ca2—Ca1	127.19 (14)	O8—C16—Ca2	60.2 (3)
O1—Ca2—Ca1	42.59 (11)	C17A—C16—Ca2	171.1 (5)
O5—Ca2—Ca1	35.85 (11)	C16—C17A—N4	109.8 (6)
O8—Ca2—Ca1	122.59 (13)	C16—C17A—C18A	109.4 (7)
O7—Ca2—Ca1	93.67 (11)	N4—C17A—C18A	103.0 (6)
O6—Ca2—Ca1	84.68 (10)	C16—C17A—H17A	111.4
C16—Ca2—Ca1	108.72 (14)	N4—C17A—H17A	111.4
C11—Ca2—Ca1	60.42 (13)	C18A—C17A—H17A	111.4
O9—Ca2—Ca1ii	52.50 (12)	C19A—C18A—C17A	103.0 (8)
O4—Ca2—Ca1ii	129.19 (14)	C19A—C18A—H18A	111.2
O11—Ca2—Ca1ii	109.46 (14)	C17A—C18A—H18A	111.2

O1—Ca2—Ca1ii	148.63 (13)	C19A—C18A—H18B	111.2
O5—Ca2—Ca1ii	84.99 (11)	C17A—C18A—H18B	111.2
O8—Ca2—Ca1ii	36.66 (11)	H18A—C18A—H18B	109.1
O7—Ca2—Ca1ii	87.60 (11)	C18A—C19A—C20A	99.3 (8)
O6—Ca2—Ca1ii	37.70 (10)	C18A—C19A—H19A	111.9
C16—Ca2—Ca1ii	62.21 (14)	C20A—C19A—H19A	111.9
C11—Ca2—Ca1ii	61.01 (13)	C18A—C19A—H19B	111.9
Ca1—Ca2—Ca1ii	120.49 (4)	C20A—C19A—H19B	111.9
C1—O1—Ca2	171.9 (4)	H19A—C19A—H19B	109.6
C1—O1—Ca1	88.5 (4)	N4—C20A—C19A	104.6 (6)
Ca2—O1—Ca1	99.45 (17)	N4—C20A—H20A	110.8
C1—O2—Ca1	95.2 (4)	C19A—C20A—H20A	110.8
C6—O3—Ca1	138.5 (5)	N4—C20A—H20B	110.8
C6—O4—Ca2	129.8 (4)	C19A—C20A—H20B	110.8
C11—O5—Ca1	151.4 (4)	H20A—C20A—H20B	108.9
C11—O5—Ca2	102.0 (4)	C19B—C18B—H18C	111.1
Ca1—O5—Ca2	106.21 (18)	C19B—C18B—H18D	111.1
C11—O6—Ca1ii	160.2 (5)	H18C—C18B—H18D	109.1
C11—O6—Ca2	85.0 (4)	C18B—C19B—H19C	112.0
Ca1ii—O6—Ca2	95.17 (16)	C18B—C19B—H19D	112.0
C16—O7—Ca2	91.1 (4)	H19C—C19B—H19D	109.6
C16—O8—Ca1ii	155.6 (4)	O10—C21—O9	124.6 (6)
C16—O8—Ca2	93.5 (4)	O10—C21—C22	118.0 (6)
Ca1ii—O8—Ca2	104.04 (17)	O9—C21—C22	117.3 (6)
C21—O9—Ca2	153.0 (4)	O10—C21—Ca1ii	47.5 (3)
C21—O9—Ca1ii	78.5 (4)	O9—C21—Ca1ii	77.6 (4)
Ca2—O9—Ca1ii	89.92 (15)	C22—C21—Ca1ii	164.5 (5)
C21—O10—Ca1ii	110.1 (4)	N5—C22—C21	111.1 (5)
Ca2—O11—H11B	117 (5)	N5—C22—C23	102.9 (6)
Ca2—O11—H11A	115 (6)	C21—C22—C23	117.9 (6)
H11B—O11—H11A	111 (8)	N5—C22—H22	108.2
H12A—O12—H12B	92 (3)	C21—C22—H22	108.2
H13B—O13—H13A	91 (4)	C23—C22—H22	108.2
C5A—N1—C2	112.5 (9)	C22—C23—C24	105.0 (7)
C2—N1—C5B	103.4 (8)	C22—C23—H23A	110.7
C5A—N1—H1A	109.1	C24—C23—H23A	110.7
C2—N1—H1A	109.1	C22—C23—H23B	110.7
C5A—N1—H1B	109.1	C24—C23—H23B	110.7
C2—N1—H1B	109.1	H23A—C23—H23B	108.8
H1A—N1—H1B	107.8	C25—C24—C23	107.4 (6)
C7—N2—C10	108.6 (6)	C25—C24—H24A	110.2
C7—N2—H2A	110.0	C23—C24—H24A	110.2
C10—N2—H2A	110.0	C25—C24—H24B	110.2
C7—N2—H2B	110.0	C23—C24—H24B	110.2
C10—N2—H2B	110.0	H24A—C24—H24B	108.5
H2A—N2—H2B	108.3	N5—C25—C24	103.8 (7)
C12—N3—C15A	109.0 (5)	N5—C25—H25A	111.0
C12—N3—H3A	109.9	C24—C25—H25A	111.0

C15A—N3—H3A	109.9	N5—C25—H25B	111.0
C12—N3—H3B	109.9	C24—C25—H25B	111.0
C15A—N3—H3B	109.9	H25A—C25—H25B	109.0
H3A—N3—H3B	108.3		

Symmetry codes: (i) $-x+1$, $y-1/2$, $-z+1/2$; (ii) $-x+1$, $y+1/2$, $-z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···I3^{iii}	0.99	2.60	3.526 (7)	155
N1—H1B···O11	0.99	2.10	2.996 (9)	150
N2—H2A···I1	0.99	2.75	3.603 (5)	145
N2—H2B···I4A	0.99	2.53	3.400 (6)	146
N3—H3A···O2^{ii}	0.99	1.94	2.829 (7)	147
N3—H3B···I2	0.99	2.61	3.447 (5)	143
N4—H4A···O12	0.99	1.80	2.750 (8)	159
N4—H4B···I3^{iii}	0.99	2.92	3.674 (6)	133
N5—H5A···I1	0.99	2.74	3.627 (6)	149
N5—H5B···I3	0.99	2.62	3.478 (6)	146
O11—H11A···I1	0.84 (6)	2.56 (6)	3.389 (5)	171 (7)
O11—H11B···I2^{ii}	0.83 (7)	2.71 (7)	3.524 (6)	168 (5)
O12—H12A···O10^{iii}	0.83 (4)	2.06 (5)	2.732 (7)	137 (4)
O12—H12B···O2^{iv}	0.83 (3)	2.54 (4)	3.339 (8)	162 (7)
O13—H13A···I4A^{ii}	0.85 (11)	2.90 (11)	3.703 (11)	159 (10)
O13—H13B···I4A^{v}	0.85 (8)	2.76 (8)	3.598 (11)	172 (10)

Symmetry codes: (ii) $-x+1$, $y+1/2$, $-z+1/2$; (iii) $x+1$, y, z; (iv) $-x+2$, $y+1/2$, $-z+1/2$; (v) $-x+3/2$, $-y+1$, $z-1/2$.

(2) *catena*-Poly[[diaquadi-m$_2$-*DL*-proline-calcium] diiodide]

Crystal data

[Ca(C$_5$H$_9$NO$_2$)$_2$(H$_2$O)$_2$]I$_2$	$Z = 2$
$M_r = 560.17$	$F(000) = 540$
Triclinic, $P\bar{1}$	$D_x = 2.084$ Mg m^{-3}
$a = 7.958$ (7) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.080$ (8) Å	Cell parameters from 1555 reflections
$c = 13.591$ (11) Å	$\theta = 2.4$–23.8°
$\alpha = 105.757$ (10)°	$\mu = 3.84$ mm^{-1}
$\beta = 104.501$ (11)°	$T = 100$ K
$\gamma = 97.911$ (12)°	Plate, yellow
$V = 892.5$ (13) Å^3	0.22 × 0.13 × 0.05 mm

Data collection

Bruker D8 with APEX CCD area detector and Incoatec microsource diffractometer	3533 independent reflections
	2603 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.079$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$\theta_{max} = 26.1°$, $\theta_{min} = 2.4°$
	$h = -9 \rightarrow 9$
$T_{min} = 0.447$, $T_{max} = 0.745$	$k = -11 \rightarrow 11$
8805 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.047$	and constrained refinement
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.020P)^2]$
$S = 1.02$	where $P = (F_o^2 + 2F_c^2)/3$
3533 reflections	$(\Delta/\sigma)_{max} = 0.001$
214 parameters	$\Delta\rho_{max} = 1.05$ e Å⁻³
29 restraints	$\Delta\rho_{min} = -2.20$ e Å⁻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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
Ca1	0.7566 (2)	0.11114 (16)	0.03989 (10)	0.0214 (3)
O1	0.4901 (7)	0.0237 (6)	0.1072 (4)	0.0294 (12)
O2	0.7073 (7)	0.2219 (6)	0.2165 (4)	0.0302 (12)
O5	0.6524 (7)	0.3423 (6)	0.0331 (4)	0.0248 (12)
H1W	0.576 (8)	0.367 (9)	0.063 (6)	0.030*
H2W	0.625 (10)	0.331 (9)	−0.032 (2)	0.030*
O6	1.0260 (8)	0.2610 (7)	0.1713 (4)	0.0360 (14)
H3W	1.125 (6)	0.313 (7)	0.169 (6)	0.043*
H4W	1.028 (12)	0.256 (10)	0.232 (3)	0.043*
O3	0.8632 (7)	−0.1067 (6)	0.0374 (4)	0.0303 (13)
O4	1.0911 (7)	−0.2226 (6)	0.0632 (4)	0.0305 (13)
N2	0.9542 (9)	−0.4002 (8)	0.1626 (5)	0.0257 (15)
H2A	1.053 (7)	−0.415 (9)	0.153 (6)	0.031*
H2B	0.896 (10)	−0.491 (6)	0.120 (5)	0.031*
N1	0.5637 (9)	0.2912 (7)	0.3744 (5)	0.0250 (14)
H1A	0.480 (8)	0.329 (9)	0.393 (6)	0.030*
H1B	0.625 (9)	0.362 (7)	0.358 (6)	0.030*
C10	0.8593 (11)	−0.1694 (9)	0.2437 (6)	0.0308 (18)
H8	0.8894	−0.0586	0.2463	0.037*
H9	0.7423	−0.1900	0.2563	0.037*
C9	1.0000 (12)	−0.2034 (10)	0.3254 (6)	0.038 (2)
H10	0.9776	−0.1760	0.3959	0.045*
H11	1.1193	−0.1437	0.3336	0.045*
C8	0.9858 (11)	−0.3790 (9)	0.2807 (5)	0.0312 (19)
H12	1.0970	−0.4091	0.3119	0.037*
H13	0.8848	−0.4402	0.2933	0.037*
C7	0.8560 (10)	−0.2808 (8)	0.1353 (5)	0.0246 (16)
H14	0.7302	−0.3332	0.0914	0.030*
C6	0.9462 (10)	−0.1969 (8)	0.0726 (5)	0.0240 (16)
C5	0.4773 (11)	0.0135 (9)	0.3293 (6)	0.0292 (18)

H1	0.3804	−0.0009	0.3617	0.035*
H2	0.4713	−0.0866	0.2749	0.035*
C4	0.6589 (12)	0.0713 (9)	0.4148 (6)	0.034 (2)
H3	0.6670	0.0152	0.4683	0.041*
H4	0.7560	0.0567	0.3821	0.041*
C3	0.6678 (11)	0.2433 (9)	0.4655 (5)	0.0287 (18)
H5	0.7926	0.3041	0.4943	0.034*
H6	0.6129	0.2594	0.5243	0.034*
C2	0.4668 (11)	0.1463 (8)	0.2801 (5)	0.0251 (15)
H7	0.3402	0.1509	0.2497	0.030*
C1	0.5620 (10)	0.1303 (8)	0.1964 (5)	0.0211 (12)
I1	0.40641 (6)	0.52553 (5)	0.18903 (3)	0.02488 (16)
I2	0.18089 (7)	0.31320 (6)	0.44926 (3)	0.02940 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0248 (8)	0.0207 (7)	0.0185 (6)	0.0044 (6)	0.0025 (6)	0.0100 (5)
O1	0.034 (3)	0.032 (2)	0.0183 (17)	0.007 (2)	0.0011 (17)	0.0083 (16)
O2	0.029 (2)	0.034 (3)	0.025 (2)	0.0015 (19)	0.0045 (18)	0.0125 (19)
O5	0.033 (3)	0.025 (3)	0.019 (2)	0.010 (2)	0.008 (2)	0.011 (2)
O6	0.034 (4)	0.046 (4)	0.023 (2)	−0.003 (3)	0.006 (2)	0.011 (2)
O3	0.037 (3)	0.026 (3)	0.034 (3)	0.014 (3)	0.009 (2)	0.018 (2)
O4	0.032 (3)	0.040 (3)	0.032 (3)	0.013 (3)	0.013 (2)	0.023 (2)
N2	0.032 (4)	0.026 (3)	0.020 (3)	0.012 (3)	0.005 (3)	0.009 (2)
N1	0.032 (4)	0.022 (3)	0.023 (3)	0.007 (3)	0.008 (3)	0.010 (2)
C10	0.041 (5)	0.026 (4)	0.032 (4)	0.010 (4)	0.017 (4)	0.012 (3)
C9	0.039 (5)	0.048 (5)	0.018 (3)	0.001 (4)	0.002 (3)	0.010 (3)
C8	0.038 (5)	0.034 (4)	0.025 (3)	0.011 (4)	0.008 (3)	0.016 (3)
C7	0.027 (4)	0.024 (4)	0.026 (3)	0.007 (3)	0.006 (3)	0.014 (3)
C6	0.026 (4)	0.020 (4)	0.021 (3)	0.004 (3)	0.005 (3)	0.002 (3)
C5	0.031 (5)	0.027 (4)	0.028 (4)	−0.002 (4)	0.010 (3)	0.009 (3)
C4	0.042 (5)	0.035 (5)	0.028 (4)	0.009 (4)	0.006 (3)	0.017 (3)
C3	0.030 (5)	0.038 (5)	0.019 (3)	0.012 (4)	0.005 (3)	0.011 (3)
C2	0.033 (4)	0.018 (4)	0.024 (2)	0.002 (3)	0.008 (3)	0.008 (2)
C1	0.025 (2)	0.023 (3)	0.0176 (18)	0.0091 (18)	0.0015 (16)	0.0138 (16)
I1	0.0270 (3)	0.0256 (3)	0.0244 (2)	0.0070 (2)	0.00549 (19)	0.01326 (19)
I2	0.0328 (3)	0.0318 (3)	0.0246 (2)	0.0078 (2)	0.0083 (2)	0.0107 (2)

Geometric parameters (Å, º)

Ca1—O1	2.621 (6)	N1—C3	1.512 (8)
Ca1—O2	2.489 (6)	N1—H1A	0.86 (4)
Ca1—O4^i	2.396 (5)	N1—H1B	0.86 (4)
Ca1—O5	2.376 (5)	C10—C9	1.496 (10)
Ca1—O6	2.365 (6)	C10—C7	1.536 (10)
Ca1—O1^{ii}	2.323 (5)	C10—H8	0.9900
Ca1—O3	2.252 (5)	C10—H9	0.9900

Ca1—Ca1ⁱ	4.829 (4)	C9—C8	1.521 (11)
Ca1—Ca1ⁱⁱ	4.032 (4)	C9—H10	0.9900
Ca1—C1	2.911 (8)	C9—H11	0.9900
Ca1—C6ⁱ	3.238 (8)	C8—H12	0.9900
O1—C1	1.263 (8)	C8—H13	0.9900
O1—Ca1ⁱⁱ	2.323 (5)	C7—C6	1.527 (10)
O2—C1	1.248 (9)	C7—H14	1.0000
O5—H1W	0.83 (2)	C6—Ca1ⁱ	3.238 (8)
O5—H2W	0.83 (2)	C5—C4	1.527 (10)
O6—H3W	0.876 (17)	C5—C2	1.531 (10)
O6—H4W	0.84 (2)	C5—H1	0.9900
O3—C6	1.241 (8)	C5—H2	0.9900
O4—C6	1.237 (9)	C4—C3	1.510 (11)
O4—Ca1ⁱ	2.396 (5)	C4—H3	0.9900
N2—C7	1.493 (9)	C4—H4	0.9900
N2—C8	1.515 (9)	C3—H5	0.9900
N2—H2A	0.85 (4)	C3—H6	0.9900
N2—H2B	0.85 (4)	C2—C1	1.505 (10)
N1—C2	1.509 (9)	C2—H7	1.0000
O3—Ca1—O1ⁱⁱ	92.68 (19)	H3W—O6—H4W	114 (8)
O3—Ca1—O6	88.9 (2)	C6—O3—Ca1	158.2 (5)
O1ⁱⁱ—Ca1—O6	171.4 (2)	C6—O4—Ca1ⁱ	122.8 (4)
O3—Ca1—O5	176.2 (2)	C7—N2—C8	108.4 (6)
O1ⁱⁱ—Ca1—O5	86.69 (18)	C7—N2—H2A	127 (6)
O6—Ca1—O5	91.2 (2)	C8—N2—H2A	103 (5)
O3—Ca1—O4ⁱ	102.3 (2)	C7—N2—H2B	109 (5)
O1ⁱⁱ—Ca1—O4ⁱ	93.50 (19)	C8—N2—H2B	115 (5)
O6—Ca1—O4ⁱ	77.94 (19)	H2A—N2—H2B	94 (7)
O5—Ca1—O4ⁱ	73.95 (19)	C2—N1—C3	109.3 (5)
O3—Ca1—O2	109.18 (18)	C2—N1—H1A	104 (5)
O1ⁱⁱ—Ca1—O2	118.14 (19)	C3—N1—H1A	108 (5)
O6—Ca1—O2	69.1 (2)	C2—N1—H1B	114 (5)
O5—Ca1—O2	74.40 (17)	C3—N1—H1B	114 (5)
O4ⁱ—Ca1—O2	133.12 (19)	H1A—N1—H1B	107 (7)
O3—Ca1—O1	94.58 (19)	C9—C10—C7	105.1 (6)
O1ⁱⁱ—Ca1—O1	70.85 (19)	C9—C10—H8	110.7
O6—Ca1—O1	117.43 (18)	C7—C10—H8	110.7
O5—Ca1—O1	88.80 (18)	C9—C10—H9	110.7
O4ⁱ—Ca1—O1	157.57 (16)	C7—C10—H9	110.7
O2—Ca1—O1	50.92 (16)	H8—C10—H9	108.8
O3—Ca1—C1	103.14 (19)	C10—C9—C8	104.3 (6)
O1ⁱⁱ—Ca1—C1	94.8 (2)	C10—C9—H10	110.9
O6—Ca1—C1	93.0 (2)	C8—C9—H10	110.9
O5—Ca1—C1	80.70 (18)	C10—C9—H11	110.9
O4ⁱ—Ca1—C1	152.77 (19)	C8—C9—H11	110.9
O2—Ca1—C1	25.20 (17)	H10—C9—H11	108.9
O1—Ca1—C1	25.71 (17)	N2—C8—C9	101.0 (6)

O3—Ca1—C6ⁱ	85.3 (2)	N2—C8—H12	111.6
O1ⁱⁱ—Ca1—C6ⁱ	102.18 (19)	C9—C8—H12	111.6
O6—Ca1—C6ⁱ	69.55 (19)	N2—C8—H13	111.6
O5—Ca1—C6ⁱ	91.14 (19)	C9—C8—H13	111.6
O4ⁱ—Ca1—C6ⁱ	18.73 (16)	H12—C8—H13	109.4
O2—Ca1—C6ⁱ	135.61 (18)	N2—C7—C6	110.1 (6)
O1—Ca1—C6ⁱ	173.02 (16)	N2—C7—C10	105.0 (5)
C1—Ca1—C6ⁱ	160.72 (19)	C6—C7—C10	112.6 (6)
O3—Ca1—Ca1ⁱⁱ	94.52 (16)	N2—C7—H14	109.7
O1ⁱⁱ—Ca1—Ca1ⁱⁱ	37.88 (14)	C6—C7—H14	109.7
O6—Ca1—Ca1ⁱⁱ	150.35 (15)	C10—C7—H14	109.7
O5—Ca1—Ca1ⁱⁱ	87.31 (15)	O4—C6—O3	127.2 (7)
O4ⁱ—Ca1—Ca1ⁱⁱ	129.49 (14)	O4—C6—C7	118.5 (6)
O2—Ca1—Ca1ⁱⁱ	82.06 (14)	O3—C6—C7	114.2 (7)
O1—Ca1—Ca1ⁱⁱ	32.97 (10)	O4—C6—Ca1ⁱ	38.4 (3)
C1—Ca1—Ca1ⁱⁱ	57.49 (15)	O3—C6—Ca1ⁱ	88.8 (5)
C6ⁱ—Ca1—Ca1ⁱⁱ	140.06 (13)	C7—C6—Ca1ⁱ	156.9 (5)
O3—Ca1—H2W	159.2 (9)	C4—C5—C2	102.8 (6)
O1ⁱⁱ—Ca1—H2W	74.4 (14)	C4—C5—H1	111.2
O6—Ca1—H2W	101.6 (15)	C2—C5—H1	111.2
O5—Ca1—H2W	17.6 (9)	C4—C5—H2	111.2
O4ⁱ—Ca1—H2W	63.2 (15)	C2—C5—H2	111.2
O2—Ca1—H2W	91.5 (10)	H1—C5—H2	109.1
O1—Ca1—H2W	96.4 (16)	C3—C4—C5	103.7 (6)
C1—Ca1—H2W	94.3 (13)	C3—C4—H3	111.0
C6ⁱ—Ca1—H2W	81.7 (15)	C5—C4—H3	111.0
Ca1ⁱⁱ—Ca1—H2W	85.2 (17)	C3—C4—H4	111.0
O3—Ca1—H4W	85.8 (18)	C5—C4—H4	111.0
O1ⁱⁱ—Ca1—H4W	172.4 (12)	H3—C4—H4	109.0
O6—Ca1—H4W	16.2 (12)	C4—C3—N1	103.9 (5)
O5—Ca1—H4W	95.3 (18)	C4—C3—H5	111.0
O4ⁱ—Ca1—H4W	94.1 (12)	N1—C3—H5	111.0
O2—Ca1—H4W	55.7 (15)	C4—C3—H6	111.0
O1—Ca1—H4W	101.8 (12)	N1—C3—H6	111.0
C1—Ca1—H4W	78.3 (13)	H5—C3—H6	109.0
C6ⁱ—Ca1—H4W	85.2 (12)	C1—C2—N1	109.3 (6)
Ca1ⁱⁱ—Ca1—H4W	134.7 (12)	C1—C2—C5	111.5 (6)
H2W—Ca1—H4W	109 (2)	N1—C2—C5	103.2 (5)
C1—O1—Ca1ⁱⁱ	150.9 (5)	C1—C2—H7	110.9
C1—O1—Ca1	90.1 (5)	N1—C2—H7	110.9
Ca1ⁱⁱ—O1—Ca1	109.15 (19)	C5—C2—H7	110.9
C1—O2—Ca1	96.7 (4)	O2—C1—O1	122.3 (7)
Ca1—O5—H1W	120 (6)	O2—C1—C2	119.6 (6)
Ca1—O5—H2W	102 (5)	O1—C1—C2	118.1 (7)
H1W—O5—H2W	115 (8)	O2—C1—Ca1	58.1 (4)

| Ca1—O6—H3W | 134 (5) | O1—C1—Ca1 | 64.2 (4) |
| Ca1—O6—H4W | 112 (6) | C2—C1—Ca1 | 177.7 (5) |

Symmetry codes: (i) −*x*+2, −*y*, −*z*; (ii) −*x*+1, −*y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···I2	0.85 (7)	2.67 (7)	3.459 (8)	154 (7)
N1—H1*B*···I1	0.86 (7)	3.33 (7)	3.809 (7)	118 (6)
N1—H1*B*···I2[iii]	0.86 (7)	3.24 (7)	3.695 (7)	116 (5)
N2—H2*A*···I1[iv]	0.85 (6)	2.88 (6)	3.700 (8)	161 (7)
N2—H2*B*)···O5[v]	0.86 (6)	2.13 (7)	2.904 (9)	151 (7)
O5—H1*W*···I1	0.84 (7)	2.68 (7)	3.486 (6)	163 (6)
O5—H2*W*···I1[vi]	0.83 (3)	2.77 (6)	3.491 (6)	147 (7)
O6—H3*W*···I1[vii]	0.87 (6)	2.65 (6)	3.509 (7)	167 (5)
O6—H4*W*···I2[vii]	0.84 (5)	2.77 (4)	3.543 (6)	155 (7)

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