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Crystal structure of a calcium(II)–pyrroloquinoline quinone (PQQ) complex outside a protein environment[1]

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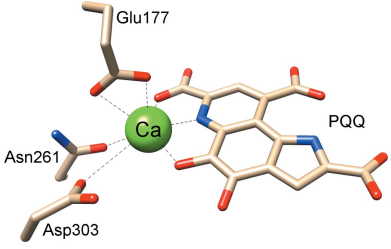
Pyrroloquinoline quinone (PQQ) is an important cofactor of calcium- and lanthanide-dependent alcohol dehydrogenases, and has been known for over 30 years. Crystal structures of Ca–MDH enzymes (MDH is methanol dehydrogenase) have been known for some time; however, crystal structures of PQQ with biorelevant metal ions have been lacking in the literature for decades. We report here the first crystal structure analysis of a Ca–PQQ complex outside the protein environment, namely, poly[[undecaaquabis(μ-4,5-dioxo-4,5-dihydro-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylato)tricalcium(II)] dihydrate], $\{[Ca_3(C_{14}H_3N_2O_8)_2(H_2O)_{11}]\cdot 2H_2O\}_n$. The complex crystallized as $Ca_3PQQ_2\cdot 13H_2O$ with Ca^{2+} in three different positions and PQQ^{3-}, including an extensive hydrogen-bond network. Similarities and differences to the recently reported structure with biorelevant europium (Eu_2PQQ_2) are discussed.

1. Introduction

Pyrroloquinoline quinone (PQQ) is the redox cofactor of glucose dehydrogenase enzymes and alcohol dehydrogenases. In particular, the methanol dehydrogenase (MDH) enzymes, which catalyze the oxidation of methanol for the energy household of many methano- and methylotrophic microorganisms, have attracted attention recently. For proper functionality, a metal ion is needed, which acts as a Lewis acid and which is coordinated by PQQ and several amino acids in the enzymatic active site (Fig. 1). The Ca-dependent MDH, encoded by the mxaF gene, was first discovered by Anthony & Zatman (1964*a*,*b*).

After the structure of MDH was elucidated in 1978–79 (Duine *et al.*, 1978; Westerling *et al.*, 1979; Salisbury *et al.*, 1979), the cofactor attracted much attention in the following years, with articles published concerning its total synthesis (Corey & Tramontano, 1981), redox chemistry (Eckert *et al.*, 1982), metal coordination (Noar *et al.*, 1985) and small-molecule interaction (van Koningsveld *et al.*, 1985). Itoh and coworkers published several articles presenting the interaction of PQQ with Ca and other alkaline earth metals (Itoh *et al.*, 1997, 1998), and the synthesis of model compounds, mimicking the active site of MDH (Itoh *et al.*, 2000). Those publications contributed to a better understanding of the functionality and reactivity of PQQ. However, no crystal structures were presented in those studies, which would reveal in-depth structural information of PQQ–metal interactions. While no Ca–PQQ structure has been published to date, in addition, few other crystal structures exist for PQQ with other metals. Outside of the Ca–MDH network (Blake *et al.*, 1994; Williams *et al.*, 2005), several structures were published with sodium



(Ishida *et al.*, 1989; Ikemoto *et al.*, 2012; Ikemoto *et al.*, 2017), with PQQ structural analogs and iron (Tommasi *et al.*, 1995), with copper and terpyridine (terpy) as co-ligand (Nakamura *et al.*, 1994), with copper and triphenylphosphine (Wanner *et al.*, 1999), with ruthenium and terpy (Mitome *et al.*, 2015), and with ruthenium, silver and terpy (Mitome *et al.*, 2013). In 2014, Pol *et al.* reported a new kind of MDH, found in the extremophile *Methylacidiphilum fumariolicum SolV* (SolV), which is native to volcanic mudpots close to the Solfatara crater in Italy (Pol *et al.*, 2014). This MDH turned out to be strictly dependent on lanthanides (Pol *et al.*, 2014; Lumpe *et al.*, 2018; Bogart *et al.*, 2015). While SolV was originally thought to be a biological curiosity, more and more organisms in all kinds of ecosystems were found to be lanthanide dependent in the following years, not restricted to such extreme environments like SolV (Keltjens *et al.*, 2014; Ramachandran & Walsh, 2015; Taubert *et al.*, 2015). This also pushed lanthanide bioinorganic chemistry as a new and emerging scientific field with several reviews published (Skovran & Martinez-Gomez, 2015; Cheisson & Schelter, 2019; Chistoserdova, 2019; Cotruvo, 2019; Daumann, 2019; Picone & Op den Camp, 2019; Semrau *et al.*, 2018). Recently, also, the first crystal structure of a europium–PQQ complex outside the MDH network was published through a collaborative effort and was reported as an Eu_2PQQ_2 structure (Lumpe *et al.*, 2020) (Fig. 2). In light of those advances and the still scarce structural information available about PQQ–metal interactions, we present here the first crystal structure of a Ca–PQQ complex without the need of structural PQQ analogs or additional co-ligands. The molecular formula of the complex is $Ca_3PQQ_2{\cdot}13H_2O$.

2. Experimental

2.1. Materials

$CaCl_2{\cdot}2H_2O$ (99%) was purchased from VWR. $Na_2PQQ{\cdot}H_2O$ was extracted from Doctor's Best Science-Based Nutrition BioPQQ capsules, as described previously (Lumpe & Daumann, 2019). Milli-Q-grade water (pH 5.5), obtained from a Millipore Synergy UV system from Merck (Darmstadt, Germany), was used for all experiments.

2.2. Crystal growth and analysis

$Na_2PQQ{\cdot}H_2O$ (32.8 mg, 0.08 mmol) was dissolved in H_2O (12 ml). $CaCl_2{\cdot}2H_2O$ (2.0 equiv., 23.6 mg, 0.16 mmol) was added as a solid. The metal addition led to precipitation of a pale-grey–brown solid, which was centrifuged, removed and analyzed as a 1:1 PQQ–Ca complex, as described in our previous article (Lumpe & Daumann, 2019). From the supernatant, consisting of a highly diluted aqueous mixture of Na_2PQQ and $CaCl_2$, small dark crystals, suitable for X-ray crystallography, grew over a period of several months. To obtain more crystalline material of better quality, a procedure from our recent publication (Lumpe *et al.*, 2020) was implemented. $Na_2PQQ{\cdot}H_2O$ (24.2 mg, 61.8 µmol) was completely dissolved in H_2O (4 ml) at 80 °C in an ultrasonic bath. $CaCl_2{\cdot}2H_2O$ (27.3 mg, 185.4 µmol, 3 equiv.) was dissolved in a small amount of water (0.2 ml) and was added to the Na_2PQQ solution at 80 °C, which caused precipitation of a grey–brown solid. The mixture was placed directly in a drying oven at 80 °C, which was then switched off and the reaction mixture allowed to cool slowly. After 1 d, small dark crystals had grown between the bulk precipitate. The crystals grew in size over the next few days while consuming the surrounding bulk precipitate. Crystals suitable for X-ray diffraction analysis were then picked out of the reaction mixture. The crystal used for analysis was selected in paraffin oil to prevent dehydration and then placed and measured on a Mitegen Microloop. The crystals obtained from both methods showed the same structure depicted in Fig. 3.

IR (diamond ATR, neat): $\tilde{\nu}$/cm^{-1} 3643–2746 (*w*, broad), 1923–1714 (*w*, broad), 1686 (*w*), 1658 (*w*), 1605 (*s*), 1577 (*m*), 1553 (*m*), 1536 (*m*), 1498 (*m*), 1426 (*w*), 1400 (*m*), 1348 (*s*), 1277 (*m*), 1246 (*m*), 1191 (*m*), 1151 (*m*), 1132 (*w*), 1086 (*w*), 1027 (*w*), 972 (*w*), 951 (*w*), 926 (*w*), 868 (*w*), 824 (*w*), 767 (*w*), 719 (*w*), 700 (*w*), 669 (*w*). Elemental analysis (CHN) calculated (%) for $Ca_3PQQ_2{\cdot}11H_2O$ or $C_{28}H_{28}Ca_3N_4O_{27}$: C 34.57, H 2.90, N 5.76; found: C 34.30, H 3.20, N 6.06. Crystals were picked out of the reaction mixture and then dried for 1 d on filter paper prior to elemental analysis.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Ca_3(C_{14}H_3N_2O_8)_2(H_2O)_{11}]{\cdot}2H_2O$
M_r	1008.81
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	109
a, b, c (Å)	6.9363 (3), 15.9791 (7), 16.9786 (7)
α, β, γ (°)	90.844 (1), 93.106 (1), 98.296 (2)
V (Å^3)	1858.93 (14)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.56
Crystal size (mm)	0.10 × 0.02 × 0.01
Data collection	
Diffractometer	Bruker D8 Venture TXS
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.88, 0.99
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	33048, 8166, 7023
R_{int}	0.043
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.641
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.072, 1.04
No. of reflections	8166
No. of parameters	689
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.39, −0.28

Computer programs: *APEX3* (Bruker, 2016), *SAINT* (Bruker, 2017), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*) and *ORTEP-3* (Farrugia, 2012).

2.3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Four reflections have been

omitted from the refinement. Three of them are hidden by the beam stop and show no intensity. A further omitted reflection of higher order (090) has a significantly higher F_o^2 (63.72) compared to its F_c^2 (1.09). This behaviour is observed quite often for reflections of higher order when multigraded X-ray mirrors are used as monochromators. All C-bound H atoms have been calculated in ideal geometry riding on their parent atoms, while the O- and N-bound H atoms were refined freely. Full details of the refinement strategy can be found in the embedded instruction file in the CIF.

3. Results and discussion

3.1. Investigation of PQQ–Ca complexation

In our previous article, PQQ–metal complexes were reported with the trivalent lanthanides La^{3+}, Eu^{3+} and Lu^{3+}, and with Ca^{2+} (Lumpe & Daumann, 2019). Regardless of the excess of added metal salt, 1:1 complexes were identified by elemental analysis. While no further structural information could be provided in that study, we were recently able to verify the proposed stoichiometry by the crystal structure of an Eu–PQQ complex with the net formula $Eu_2PQQ_2{\cdot}12H_2O$ (Lumpe *et al.*, 2020). The Eu^{3+} ion is coordinated by PQQ in the same fashion as in MDH, with participation of N2, O4 and O5, in addition to the participation of O1 (Fig. 2). The latter residue is not utilized in the enzyme for metal coordination.

From a similar experimental approach using Ca^{2+} instead of Eu^{3+}, single crystals suitable for X-ray analysis were grown over a period of several days. Fig. 3 illustrates the composition of the asymmetric unit: the charges of two triply deprotonated PQQ units are balanced by three Ca^{2+} ions supplemented by 13 water molecules. The structural motif depicted in Fig. 2 – the formation of binuclear units by means of two PQQ ligands acting as linkers between the metal centres – is realized in $Ca_3PQQ_2{\cdot}13H_2O$ in a comparable fashion for two of the three Ca ions (Ca1 and Ca3). Ca1 is coordinated by PQQ in a similar fashion to Eu; however, the coordination sphere is completed by a carboxylate group of a nearby pyridine moiety of PQQ (instead of a carboxylate of a pyrrole ring). Ca3, on the other hand, uses the same pocket and residues as Eu; however, this interaction is assisted by a hydrogen bond of a Ca3-bound water molecule to the carboxylate group of the pyrrole ring (Fig. 3*b*, green arrows). In the structure, these two types of alternating Ca1 and Ca3 units are connected *via* Ca1 into strands along [$\bar{1}$11]. The charge of the Ca_2PQQ_2 unit is balanced by Ca2, which is coordinated solely by water molecules and carboxylate groups, however, never in the biologically relevant ONO pocket of PQQ. All N—H and O—H donor groups are involved in classical hydrogen bonds with either carboxylate groups, keto groups or water molecules,

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O8	0.86 (2)	2.01 (2)	2.7232 (19)	139.6 (19)
N3—H4···O16	0.86 (2)	1.83 (2)	2.6163 (19)	151 (2)
O17—H171···O10^{iii}	0.85 (3)	1.91 (3)	2.7543 (18)	170 (3)
O17—H172···O1	0.86 (3)	2.08 (3)	2.9287 (19)	170 (2)
O18—H181···O28	0.88 (3)	1.82 (3)	2.681 (2)	166 (2)
O18—H182···O1^{iv}	0.84 (3)	1.97 (3)	2.8107 (19)	176 (3)
O19—H191···O20^{ii}	0.81 (3)	2.10 (3)	2.8789 (19)	161 (3)
O19—H192···O5^{i}	0.85 (3)	1.89 (3)	2.7350 (18)	174 (3)
O20—H201···O11^{v}	0.82 (3)	2.00 (3)	2.8221 (18)	173 (3)
O20—H202···O2^{vi}	0.84 (3)	1.94 (3)	2.7620 (18)	169 (3)
O21—H211···O29^{iii}	0.80 (3)	2.05 (3)	2.845 (2)	173 (3)
O21—H212···O16	0.85 (3)	1.90 (3)	2.7320 (18)	163 (3)
O22—H221···O19^{vi}	0.76 (3)	2.26 (3)	2.958 (2)	152 (3)
O22—H222···O6^{vii}	0.87 (3)	1.83 (3)	2.6985 (19)	175 (3)
O23—H231···O3^{viii}	0.76 (3)	2.10 (3)	2.8398 (19)	164 (3)
O23—H232···O9^{iii}	0.83 (3)	1.90 (3)	2.7217 (19)	169 (3)
O24—H241···O7^{ix}	0.81 (3)	2.03 (3)	2.8040 (19)	163 (3)
O24—H242···O29	0.82 (3)	1.93 (3)	2.750 (2)	172 (3)
O25—H251···O13^{ix}	0.85 (3)	2.02 (3)	2.8578 (18)	168 (3)
O25—H252···O3^{viii}	0.81 (3)	2.41 (3)	3.0258 (19)	133 (2)
O25—H252···O4^{viii}	0.81 (3)	2.28 (3)	3.0405 (18)	155 (3)
O26—H261···O27^{x}	0.86 (3)	2.11 (3)	2.9018 (19)	154 (3)
O26—H262···O13^{ix}	0.80 (3)	2.06 (3)	2.8506 (19)	170 (3)
O27—H271···O25^{iv}	0.85 (3)	2.08 (3)	2.9022 (19)	164 (3)
O27—H272···O9^{v}	0.83 (3)	1.99 (3)	2.8125 (18)	171 (2)
O28—H281···O10^{v}	0.89 (4)	1.88 (4)	2.721 (2)	159 (3)
O28—H282···O26^{x}	0.83 (4)	2.59 (3)	3.098 (2)	121 (3)
O29—H291···O6^{ix}	0.84 (3)	1.85 (3)	2.6582 (19)	160 (3)
O29—H292···O11	0.79 (3)	2.27 (3)	3.021 (2)	159 (3)
O29—H292···O12	0.79 (3)	2.40 (3)	2.7789 (19)	110 (2)

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

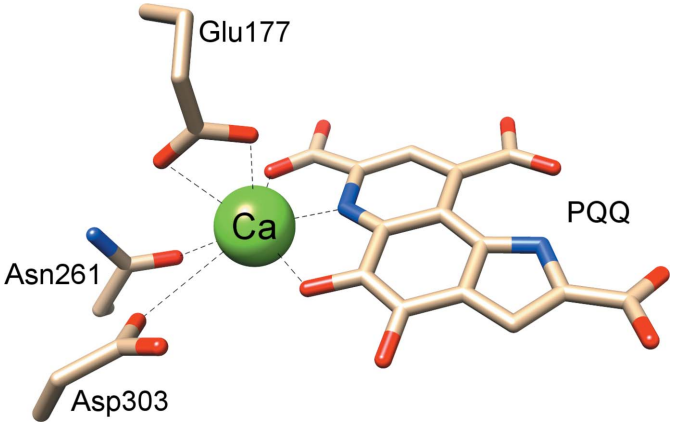


Figure 1
The structure of the active site from Ca-dependent MDH (PDB code 1w6s).

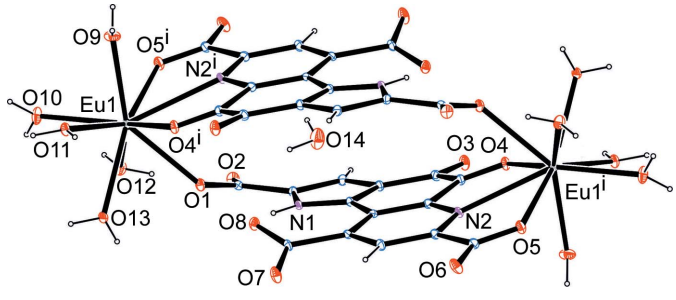


Figure 2
The crystal structure of the inversion-symmetric Eu_2PQQ_2 complex. The CIF is taken from Lumpe *et al.* (2020). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x+1, -y+1, -z+1$.]

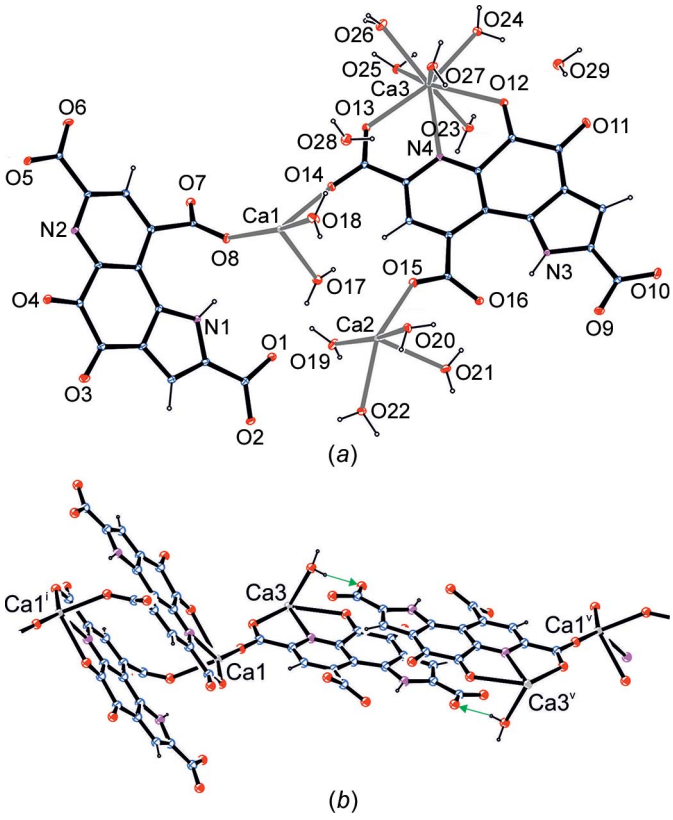


Figure 3
(*a*) The asymmetric unit of $Ca_3PQQ_2{\cdot}13H_2O$. (*b*) A strand along [$\bar{1}$11] consisting of inversion-symmetric $Ca_2PQQ_2^{2-}$ pairs. Here, for clarity, all water molecules, except for that involved in intra-pair hydrogen bonds (green arrows), have been omitted. For symmetry codes, see Table 2.

acting as acceptors establishing a three-dimensional network (see Table 2 for hydrogen-bond details).

Table 3
Selected bond lengths (Å) of the $Ca_3PQQ_2{\cdot}13H_2O$ complex in comparison with the previously reported $Eu_2PQQ_2{\cdot}12H_2O$ structure.

For symmetry data for $Eu_2PQQ_2{\cdot}12H_2O$, see Lumpe *et al.* (2020).

$Ca_3PQQ_2{\cdot}13H_2O$		$Eu_2PQQ_2{\cdot}12H_2O$	
Ca1^{i}—O4	2.5928 (12)	Eu1—O4	2.584 (2)
Ca1^{i}—N2	2.5069 (14)	Eu1—N2	2.648 (2)
Ca1^{i}—O5	2.3784 (12)	Eu1—O5	2.440 (2)
Ca1—O14	2.2514 (12)	Eu1—O1	2.409 (2)
Ca1—O8	2.3137 (12)	Eu1—O_{water} (5 bonds)	2.389 (2)–2.464 (2)
Ca1—O17	2.3694 (13)		
Ca1—O18	2.3145 (14)	Ca3—O12	2.5703 (12)
Ca2^{ii}—O1	2.4812 (12)	Ca3—N4	2.5460 (14)
Ca2^{ii}—O2	2.5279 (12)	Ca3—O13	2.3963 (12)
Ca2—O15	2.3522 (12)	Ca3—O23	2.4362 (14)
Ca2—O19	2.3894 (14)	Ca3—O24	2.3607 (13)
Ca2—O20	2.4382 (13)	Ca3—O25	2.5787 (14)
Ca2—O21	2.3824 (14)	Ca3—O26	2.3962 (14)
Ca2—O22	2.3383 (14)	Ca3—O27	2.4924 (14)

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

Interestingly, while the elemental analysis of the initially precipitated (amorphous) solid showed a 1:1 Ca–PQQ stoichiometry (Lumpe & Daumann, 2019), the present structure from slowly crystallized material reveals a network of three different Ca^{2+} ions and two differently-coordinated PQQ anionic ligands, resulting in a 3:2 stoichiometry. Also, in the Ca–PQQ structure, both PQQ molecules coordinate in the same fashion as in the MDH enzyme (Fig. 1), in addition to the participation of several carboxylate groups. One of the PQQ ligands coordinates to calcium with the participation of all three carboxylate groups: Ca1 *via* O8, N2, O5 and O4, and Ca2 *via* O1 and O2 in a bidentate manner. The second PQQ molecule coordinates with only two of the three carboxylate groups and coordinates Ca1 with O14, Ca2 with O15 and Ca3 with N4, O12 and O13. In total, 13 water molecules are present

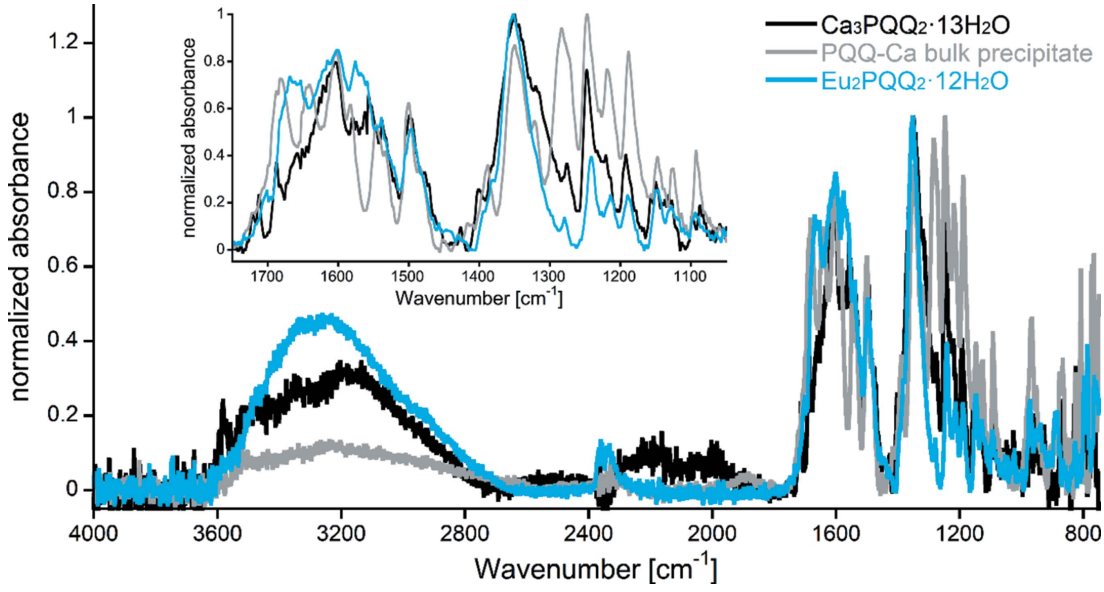


Figure 4
Normalized IR absorption spectra of the Ca_3PQQ_2 complex in black, the 1:1 Ca–PQQ precipitate in grey and the Eu_2PQQ_2 complex in blue. Inset: close-up of the PQQ-related IR absorption peaks.

in the crystal structure, of which 11 directly coordinate to atoms Ca1–Ca3 and two water molecules (O28 and O29) have no direct coordination partners. Interestingly, elemental analysis of the dried crystalline material fits best to only 11 water molecules, most likely due to the disappearance of the two noncoordinating water molecules during the drying process. Ca1 and Ca2 show pentagonal–bipyramidal geometries, with coordination numbers (CNs) of 7 and Ca3 shows a distorted geometry with a CN of 8. All metal-to-ligand bond lengths and angles of Ca_3PQQ_2 are given in Table 3, in addition to the values for Eu_2PQQ_2. The known PQQ–water adduct (diol in C5 position), which is formed to some extent in aqueous solution (Dekker *et al.*, 1982), is not present in the complex, and this is in line with all known crystal structures of PQQ, to the best of our knowledge.

In the Eu_2PQQ_2 complex, the Eu ions are coordinated in a similar fashion by PQQ. The bonds to Eu are up to 0.141 Å longer than to Ca1 and Ca3. The CN of Eu in the complex is 9, which corresponds to an ionic radius of 1.12 Å according to Shannon (1976), while the ionic radius of Ca is 1.06 Å for a CN of 7 and 1.12 Å for a CN of 8. Therefore, the larger bond lengths to Eu can hardly be explained by different ionic radii, which are overall similar, but by differences in the CNs and different participation in coordination of a second PQQ molecule.

The IR spectra of the precipitated Ca–PQQ amorphous solid, Eu_2PQQ_2 and Ca_3PQQ_2 crystals were recorded and compared (Fig. 4). The spectra can be roughly divided into two areas. While PQQ C=O stretching vibrations of the carboxylate and quinone groups absorb in the range 1750–1600 cm^{-1} (Zhejiang Hisun Pharmaceutical Co. Ltd, 2020), the peaks with smaller wavenumbers are largely related to PQQ lattice vibrations. While the heights of the large absorption bands in the range 3600–2600 cm^{-1} are a direct result of the different amounts and coordination modes of cocrystallized water, the differences in the area 1750–1550 cm^{-1} further indicate the different coordination modes already depicted in the crystal structures.

4. Conclusion

We present here the first crystal structure of PQQ with the biologically relevant metal ion calcium. The complex consists of PQQ and the metal ion alone, unlike previously reported structures with other metal ions. Those complexes often needed additional co-ligands, which limited the use of the structures for comparison with the biologically active site. However, in particular, the use of methylated $PQQMe_3$ (with all three carboxyl groups esterified) prevented participation of (nonbiogenic) carboxyl groups in complexation. This is not the case in the presented structure, where calcium is coordinated by PQQ in the same pocket as in MDH, in addition to further carboxyl-group participation, spanning a three-dimensional coordination network. However, considering the few crystal structures of PQQ complexes reported over the years, we are confident that the presented structure will help to better explain the coordination behaviour of PQQ outside the MDH enzyme and help guide the design of mononuclear model complexes for these fascinating enzymes.

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supporting information

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Crystal structure of a calcium(II)–pyrroloquinoline quinone (PQQ) complex outside a protein environment

Henning Lumpe, Peter Mayer and Lena J. Daumann

Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2017); data reduction: *SAINT* (Bruker, 2017); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *ORTEP-3* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015b).

Poly[[undecaaquabis(μ-4,5-dioxo-4,5-dihydro-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylato)tricalcium(II)] dihydrate]

Crystal data

$[Ca_3(C_{14}H_3N_2O_8)_2(H_2O)_{11}]\cdot 2H_2O$
$M_r = 1008.81$
Triclinic, $P\overline{1}$
$a = 6.9363$ (3) Å
$b = 15.9791$ (7) Å
$c = 16.9786$ (7) Å
$\alpha = 90.844$ (1)°
$\beta = 93.106$ (1)°
$\gamma = 98.296$ (2)°
$V = 1858.93$ (14) Å^3
$Z = 2$
$F(000) = 1040$
$D_x = 1.802$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9854 reflections
$\theta = 2.7$–$27.1°$
$\mu = 0.56$ mm^{-1}
$T = 109$ K
Rod, brown
0.10 × 0.02 × 0.01 mm

Data collection

Bruker D8 Venture TXS diffractometer
Radiation source: rotating anode (TXS), Bruker TXS
Focusing mirrors monochromator
Detector resolution: 7.3910 pixels mm^{-1}
mix of phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min} = 0.88$, $T_{max} = 0.99$
33048 measured reflections
8166 independent reflections
7023 reflections with $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 27.1°$, $\theta_{min} = 2.9°$
$h = -8\rightarrow 8$
$k = -20\rightarrow 20$
$l = -21\rightarrow 21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.072$
$S = 1.04$
8166 reflections
689 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 1.5469P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Special details

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

Refinement. H(C) constr, H(O,N) refall

The X-ray intensity data of $Ca_3PQQ_2.13H_2O$ were measured on a Bruker D8 Venture TXS system equipped with a multilayer mirror monochromator and an Mo *Kα* rotating anode X-ray tube (λ = 0.71073 Å). The frames were integrated with the Bruker *SAINT* software package (Bruker, 2012). Data were corrected for absorption effects using the multi-scan method (*SADABS*; Sheldrick, 1996). The structure was solved and refined using the Bruker *SHELXTL* software package (Sheldrick, 2015).

The figures have been drawn at the 50% ellipsoid probability level (Farrugia, 2012). CCDC reference number 2019890 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0551 (2)	0.15843 (11)	0.45568 (10)	0.0109 (3)
C2	0.0302 (2)	0.23438 (11)	0.50409 (10)	0.0109 (3)
C3	0.0676 (3)	0.24585 (11)	0.58398 (10)	0.0118 (3)
H3	0.044989	0.204050	0.622953	0.014*
C4	0.1464 (2)	0.33192 (10)	0.59713 (10)	0.0106 (3)
C5	0.2090 (3)	0.37785 (11)	0.67020 (10)	0.0112 (3)
C6	0.2975 (2)	0.47079 (11)	0.66033 (10)	0.0101 (3)
C7	0.2934 (2)	0.50827 (10)	0.57991 (10)	0.0093 (3)
C8	0.3650 (2)	0.63184 (10)	0.51260 (10)	0.0092 (3)
C9	0.2907 (2)	0.59109 (10)	0.44200 (10)	0.0097 (3)
H9A	0.286091	0.622433	0.394992	0.012*
C10	0.2233 (2)	0.50464 (11)	0.43996 (10)	0.0095 (3)
C11	0.2231 (2)	0.46006 (10)	0.51131 (10)	0.0085 (3)
C12	0.1552 (2)	0.37072 (11)	0.52343 (10)	0.0095 (3)
C13	0.4498 (2)	0.72499 (10)	0.51886 (10)	0.0096 (3)
C14	0.1589 (2)	0.46574 (10)	0.35822 (10)	0.0092 (3)
C15	0.8745 (2)	−0.19201 (10)	−0.04981 (10)	0.0101 (3)
C16	0.8334 (2)	−0.10395 (10)	−0.06229 (10)	0.0091 (3)
C17	0.8475 (2)	−0.05705 (10)	−0.12909 (10)	0.0097 (3)
H17	0.881560	−0.075253	−0.179338	0.012*
C18	0.8015 (2)	0.02382 (11)	−0.10895 (10)	0.0096 (3)
C19	0.7972 (2)	0.09630 (11)	−0.15653 (10)	0.0107 (3)
C20	0.7502 (2)	0.17425 (11)	−0.11221 (9)	0.0095 (3)
C21	0.6921 (2)	0.16752 (10)	−0.02863 (9)	0.0083 (3)
C22	0.5978 (2)	0.24379 (10)	0.07438 (9)	0.0089 (3)
C23	0.6126 (2)	0.17681 (10)	0.12466 (10)	0.0099 (3)
H23	0.584351	0.182354	0.178455	0.012*
C24	0.6684 (2)	0.10142 (10)	0.09720 (10)	0.0088 (3)

C25	0.7027 (2)	0.09418 (10)	0.01609 (9)	0.0077 (3)
C26	0.7593 (2)	0.02301 (10)	−0.02847 (9)	0.0085 (3)
C27	0.5362 (2)	0.32716 (10)	0.09921 (9)	0.0093 (3)
C28	0.6930 (2)	0.03531 (11)	0.15995 (10)	0.0098 (3)
N1	0.0833 (2)	0.31067 (9)	0.46858 (9)	0.0101 (3)
N2	0.3651 (2)	0.59035 (9)	0.58038 (8)	0.0090 (3)
H2	0.084 (3)	0.3176 (13)	0.4186 (13)	0.015 (5)*
N3	0.7800 (2)	−0.05460 (9)	−0.00212 (8)	0.0086 (3)
N4	0.6427 (2)	0.23938 (9)	−0.00095 (8)	0.0086 (3)
H4	0.748 (4)	−0.0682 (15)	0.0449 (15)	0.030 (6)*
O1	−0.06633 (18)	0.16506 (7)	0.38093 (7)	0.0128 (3)
O2	−0.11654 (18)	0.09119 (7)	0.48944 (7)	0.0136 (3)
O3	0.2007 (2)	0.34951 (8)	0.73630 (7)	0.0169 (3)
O4	0.37574 (18)	0.51241 (7)	0.71690 (7)	0.0127 (3)
O5	0.52358 (18)	0.75182 (7)	0.58571 (7)	0.0120 (2)
O6	0.4405 (2)	0.76768 (8)	0.45848 (7)	0.0164 (3)
O7	0.06140 (18)	0.50722 (8)	0.31437 (7)	0.0130 (3)
O8	0.21731 (18)	0.39705 (7)	0.34077 (7)	0.0125 (3)
O9	0.87842 (18)	−0.21856 (8)	0.01978 (7)	0.0136 (3)
O10	0.90747 (19)	−0.23220 (8)	−0.11050 (7)	0.0151 (3)
O11	0.8269 (2)	0.10239 (8)	−0.22705 (7)	0.0171 (3)
O12	0.76438 (18)	0.24116 (7)	−0.14539 (7)	0.0125 (3)
O13	0.53948 (18)	0.38361 (7)	0.04724 (7)	0.0123 (3)
O14	0.48287 (18)	0.33522 (7)	0.16717 (7)	0.0122 (2)
O15	0.74044 (19)	0.06498 (8)	0.22821 (7)	0.0151 (3)
O16	0.66342 (19)	−0.04197 (7)	0.14100 (7)	0.0134 (3)
O17	0.2228 (2)	0.21676 (8)	0.26500 (8)	0.0155 (3)
H171	0.173 (4)	0.2165 (17)	0.2180 (17)	0.042 (8)*
H172	0.130 (4)	0.1974 (16)	0.2943 (15)	0.032 (7)*
O18	0.7774 (2)	0.29042 (9)	0.29412 (8)	0.0191 (3)
H181	0.851 (4)	0.3119 (16)	0.2567 (16)	0.035 (7)*
H182	0.823 (4)	0.2513 (19)	0.3180 (17)	0.048 (8)*
O19	0.4610 (2)	0.08055 (9)	0.37538 (8)	0.0166 (3)
H191	0.352 (4)	0.0580 (17)	0.3624 (15)	0.038 (8)*
H192	0.460 (4)	0.1327 (18)	0.3851 (15)	0.037 (7)*
O20	1.07981 (19)	−0.01918 (8)	0.36462 (8)	0.0138 (3)
H201	1.099 (4)	−0.0466 (18)	0.3251 (18)	0.049 (9)*
H202	1.095 (4)	−0.0465 (17)	0.4056 (17)	0.041 (8)*
O21	0.6842 (2)	−0.11057 (9)	0.28711 (8)	0.0191 (3)
H211	0.601 (4)	−0.1501 (18)	0.2910 (15)	0.037 (8)*
H212	0.679 (4)	−0.0997 (17)	0.2380 (17)	0.042 (8)*
O22	0.6175 (2)	−0.07062 (9)	0.45523 (8)	0.0218 (3)
H221	0.616 (4)	−0.0567 (18)	0.4984 (18)	0.048 (9)*
H222	0.563 (4)	−0.1236 (19)	0.4537 (16)	0.047 (8)*
O23	0.3675 (2)	0.26664 (9)	−0.13577 (9)	0.0155 (3)
H231	0.307 (4)	0.2808 (16)	−0.1708 (16)	0.033 (7)*
H232	0.291 (4)	0.2457 (17)	−0.1028 (16)	0.039 (8)*
O24	0.6812 (2)	0.39272 (9)	−0.22016 (8)	0.0182 (3)

H241	0.768 (4)	0.4241 (17)	−0.2383 (15)	0.036 (8)*
H242	0.678 (4)	0.3485 (19)	−0.2459 (16)	0.043 (8)*
O25	0.34868 (19)	0.45056 (8)	−0.11501 (8)	0.0143 (3)
H251	0.367 (4)	0.5014 (18)	−0.0984 (16)	0.040 (8)*
H252	0.336 (4)	0.4522 (17)	−0.1628 (18)	0.043 (8)*
O26	0.7643 (2)	0.51788 (8)	−0.07189 (8)	0.0177 (3)
H261	0.865 (5)	0.5441 (19)	−0.0459 (18)	0.054 (9)*
H262	0.684 (4)	0.5490 (17)	−0.0700 (15)	0.035 (7)*
O27	0.9930 (2)	0.37549 (9)	−0.04551 (8)	0.0152 (3)
H271	1.082 (4)	0.3989 (18)	−0.0735 (16)	0.043 (8)*
H272	1.021 (4)	0.3284 (17)	−0.0340 (14)	0.031 (7)*
O28	0.9475 (2)	0.36727 (10)	0.17111 (9)	0.0212 (3)
H281	1.013 (5)	0.333 (2)	0.1450 (19)	0.067 (10)*
H282	1.030 (5)	0.409 (2)	0.182 (2)	0.069 (11)*
O29	0.6350 (2)	0.24139 (9)	−0.30317 (9)	0.0210 (3)
H291	0.640 (4)	0.2383 (16)	−0.3524 (16)	0.034 (7)*
H292	0.711 (4)	0.2134 (17)	−0.2848 (16)	0.039 (8)*
Ca1	0.47149 (5)	0.33132 (2)	0.29935 (2)	0.00881 (8)
Ca2	0.75264 (5)	0.02017 (2)	0.35950 (2)	0.00913 (8)
Ca3	0.63978 (5)	0.37014 (2)	−0.08465 (2)	0.00934 (8)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0099 (8)	0.0095 (8)	0.0132 (8)	0.0014 (7)	0.0000 (6)	−0.0006 (6)
C2	0.0104 (8)	0.0087 (8)	0.0134 (8)	−0.0004 (7)	0.0022 (6)	0.0016 (6)
C3	0.0136 (8)	0.0088 (8)	0.0126 (8)	−0.0004 (7)	0.0013 (7)	0.0009 (6)
C4	0.0111 (8)	0.0075 (8)	0.0126 (8)	−0.0004 (6)	−0.0009 (7)	0.0013 (6)
C5	0.0119 (8)	0.0090 (8)	0.0126 (8)	0.0011 (7)	−0.0006 (7)	0.0010 (6)
C6	0.0095 (8)	0.0113 (8)	0.0096 (8)	0.0026 (7)	0.0007 (6)	−0.0005 (6)
C7	0.0081 (8)	0.0078 (8)	0.0119 (8)	0.0010 (6)	0.0006 (6)	0.0012 (6)
C8	0.0093 (8)	0.0074 (8)	0.0109 (8)	0.0009 (6)	0.0011 (6)	0.0008 (6)
C9	0.0099 (8)	0.0101 (8)	0.0090 (8)	0.0013 (7)	0.0001 (6)	0.0016 (6)
C10	0.0071 (8)	0.0105 (8)	0.0108 (8)	0.0013 (6)	0.0004 (6)	−0.0003 (6)
C11	0.0068 (8)	0.0077 (8)	0.0108 (8)	0.0003 (6)	0.0004 (6)	−0.0002 (6)
C12	0.0071 (8)	0.0093 (8)	0.0117 (8)	0.0005 (6)	0.0005 (6)	−0.0013 (6)
C13	0.0094 (8)	0.0081 (8)	0.0110 (8)	0.0002 (6)	0.0019 (6)	−0.0007 (6)
C14	0.0083 (8)	0.0085 (8)	0.0096 (8)	−0.0034 (6)	0.0022 (6)	−0.0003 (6)
C15	0.0061 (8)	0.0084 (8)	0.0152 (8)	−0.0010 (6)	−0.0001 (6)	0.0000 (6)
C16	0.0072 (8)	0.0095 (8)	0.0103 (8)	0.0008 (6)	−0.0006 (6)	−0.0024 (6)
C17	0.0080 (8)	0.0093 (8)	0.0115 (8)	0.0009 (6)	0.0000 (6)	−0.0024 (6)
C18	0.0090 (8)	0.0105 (8)	0.0091 (8)	0.0012 (6)	−0.0012 (6)	−0.0011 (6)
C19	0.0117 (8)	0.0113 (8)	0.0091 (8)	0.0023 (7)	−0.0001 (6)	−0.0011 (6)
C20	0.0094 (8)	0.0107 (8)	0.0082 (8)	0.0014 (6)	−0.0012 (6)	0.0001 (6)
C21	0.0070 (8)	0.0081 (8)	0.0091 (8)	−0.0007 (6)	−0.0009 (6)	−0.0010 (6)
C22	0.0086 (8)	0.0083 (8)	0.0093 (8)	0.0001 (6)	−0.0005 (6)	−0.0001 (6)
C23	0.0112 (8)	0.0102 (8)	0.0079 (8)	0.0003 (7)	0.0003 (6)	−0.0005 (6)
C24	0.0071 (8)	0.0095 (8)	0.0093 (8)	−0.0002 (6)	−0.0011 (6)	0.0004 (6)

C25	0.0054 (7)	0.0079 (8)	0.0093 (8)	0.0002 (6)	−0.0011 (6)	0.0009 (6)
C26	0.0064 (8)	0.0090 (8)	0.0098 (8)	0.0004 (6)	−0.0008 (6)	0.0003 (6)
C27	0.0090 (8)	0.0087 (8)	0.0093 (8)	−0.0008 (6)	−0.0012 (6)	−0.0009 (6)
C28	0.0100 (8)	0.0106 (8)	0.0089 (8)	0.0006 (7)	0.0024 (6)	0.0017 (6)
N1	0.0122 (7)	0.0086 (7)	0.0087 (7)	−0.0003 (6)	0.0002 (6)	−0.0008 (6)
N2	0.0079 (7)	0.0079 (7)	0.0112 (7)	0.0008 (5)	0.0001 (5)	0.0004 (5)
N3	0.0103 (7)	0.0074 (7)	0.0080 (7)	0.0004 (6)	0.0005 (5)	0.0004 (5)
N4	0.0086 (7)	0.0084 (7)	0.0088 (7)	0.0015 (5)	−0.0003 (5)	0.0003 (5)
O1	0.0168 (6)	0.0104 (6)	0.0104 (6)	−0.0005 (5)	0.0003 (5)	0.0006 (5)
O2	0.0190 (7)	0.0086 (6)	0.0117 (6)	−0.0022 (5)	0.0001 (5)	0.0010 (5)
O3	0.0247 (7)	0.0132 (6)	0.0115 (6)	−0.0004 (5)	−0.0031 (5)	0.0037 (5)
O4	0.0152 (6)	0.0110 (6)	0.0111 (6)	−0.0003 (5)	−0.0018 (5)	−0.0002 (5)
O5	0.0172 (6)	0.0082 (6)	0.0096 (6)	−0.0005 (5)	−0.0016 (5)	−0.0004 (5)
O6	0.0270 (7)	0.0093 (6)	0.0108 (6)	−0.0036 (5)	−0.0029 (5)	0.0029 (5)
O7	0.0153 (6)	0.0127 (6)	0.0108 (6)	0.0022 (5)	−0.0022 (5)	0.0006 (5)
O8	0.0133 (6)	0.0115 (6)	0.0126 (6)	0.0020 (5)	0.0008 (5)	−0.0026 (5)
O9	0.0154 (6)	0.0116 (6)	0.0142 (6)	0.0027 (5)	0.0016 (5)	0.0039 (5)
O10	0.0199 (7)	0.0110 (6)	0.0150 (6)	0.0052 (5)	−0.0014 (5)	−0.0032 (5)
O11	0.0295 (7)	0.0152 (6)	0.0085 (6)	0.0080 (6)	0.0053 (5)	0.0013 (5)
O12	0.0185 (6)	0.0098 (6)	0.0095 (6)	0.0028 (5)	0.0014 (5)	0.0024 (5)
O13	0.0193 (7)	0.0092 (6)	0.0096 (6)	0.0051 (5)	0.0026 (5)	0.0015 (5)
O14	0.0161 (6)	0.0120 (6)	0.0088 (6)	0.0022 (5)	0.0024 (5)	−0.0006 (5)
O15	0.0236 (7)	0.0125 (6)	0.0092 (6)	0.0029 (5)	−0.0010 (5)	0.0009 (5)
O16	0.0206 (7)	0.0088 (6)	0.0108 (6)	0.0020 (5)	0.0022 (5)	0.0016 (5)
O17	0.0171 (7)	0.0154 (7)	0.0123 (6)	−0.0029 (5)	−0.0003 (6)	−0.0010 (5)
O18	0.0175 (7)	0.0242 (8)	0.0178 (7)	0.0091 (6)	0.0042 (6)	0.0068 (6)
O19	0.0143 (7)	0.0103 (7)	0.0247 (7)	0.0012 (6)	0.0002 (6)	−0.0026 (5)
O20	0.0164 (7)	0.0133 (6)	0.0116 (6)	0.0024 (5)	0.0001 (5)	−0.0013 (5)
O21	0.0323 (8)	0.0115 (7)	0.0108 (7)	−0.0053 (6)	−0.0008 (6)	0.0016 (5)
O22	0.0384 (9)	0.0119 (7)	0.0127 (7)	−0.0064 (6)	0.0073 (6)	−0.0008 (5)
O23	0.0165 (7)	0.0166 (7)	0.0128 (7)	0.0001 (6)	−0.0001 (6)	0.0041 (5)
O24	0.0285 (8)	0.0130 (7)	0.0132 (6)	0.0013 (6)	0.0066 (6)	0.0013 (6)
O25	0.0204 (7)	0.0112 (7)	0.0114 (7)	0.0028 (5)	−0.0005 (5)	−0.0005 (5)
O26	0.0158 (7)	0.0117 (6)	0.0255 (7)	0.0033 (6)	−0.0026 (6)	−0.0011 (6)
O27	0.0145 (7)	0.0110 (6)	0.0204 (7)	0.0026 (5)	0.0013 (5)	0.0024 (5)
O28	0.0222 (8)	0.0179 (7)	0.0239 (7)	0.0028 (6)	0.0040 (6)	−0.0008 (6)
O29	0.0337 (9)	0.0179 (7)	0.0101 (7)	0.0007 (6)	−0.0029 (6)	0.0014 (5)
Ca1	0.01094 (16)	0.00795 (16)	0.00727 (16)	0.00073 (13)	0.00000 (12)	−0.00028 (12)
Ca2	0.01122 (17)	0.00735 (16)	0.00825 (16)	−0.00045 (13)	0.00028 (12)	0.00033 (12)
Ca3	0.01280 (17)	0.00742 (16)	0.00802 (16)	0.00195 (13)	0.00126 (13)	0.00085 (12)

Geometric parameters (Å, º)

C1—O2	1.256 (2)	C28—O15	1.255 (2)
C1—O1	1.274 (2)	C28—O16	1.256 (2)
C1—C2	1.486 (2)	N1—H2	0.86 (2)
C1—Ca2^{i}	2.8519 (17)	N2—Ca1^{ii}	2.5069 (14)
C2—C3	1.372 (2)	N3—H4	0.86 (2)

C2—N1	1.379 (2)	N4—Ca3	2.5460 (14)
C3—C4	1.415 (2)	O1—Ca2^{i}	2.4812 (12)
C3—H3	0.9500	O2—Ca2^{i}	2.5279 (12)
C4—C12	1.405 (2)	O4—Ca1^{ii}	2.5928 (12)
C4—C5	1.445 (2)	O5—Ca1^{ii}	2.3784 (12)
C5—O3	1.217 (2)	O8—Ca1	2.3137 (12)
C5—C6	1.538 (2)	O12—Ca3	2.5703 (12)
C6—O4	1.216 (2)	O13—Ca3	2.3963 (12)
C6—C7	1.500 (2)	O14—Ca1	2.2514 (12)
C7—N2	1.334 (2)	O15—Ca2	2.3522 (12)
C7—C11	1.411 (2)	O17—Ca1	2.3694 (13)
C8—N2	1.337 (2)	O17—H171	0.85 (3)
C8—C9	1.393 (2)	O17—H172	0.86 (3)
C8—C13	1.520 (2)	O18—Ca1	2.3145 (14)
C9—C10	1.392 (2)	O18—H181	0.88 (3)
C9—H9A	0.9500	O18—H182	0.84 (3)
C10—C11	1.414 (2)	O19—Ca2	2.3894 (14)
C10—C14	1.529 (2)	O19—H191	0.81 (3)
C11—C12	1.458 (2)	O19—H192	0.85 (3)
C12—N1	1.350 (2)	O20—Ca2	2.4382 (13)
C13—O6	1.244 (2)	O20—H201	0.82 (3)
C13—O5	1.262 (2)	O20—H202	0.84 (3)
C14—O7	1.241 (2)	O21—Ca2	2.3824 (14)
C14—O8	1.260 (2)	O21—H211	0.80 (3)
C15—O10	1.255 (2)	O21—H212	0.85 (3)
C15—O9	1.261 (2)	O22—Ca2	2.3383 (14)
C15—C16	1.491 (2)	O22—H221	0.76 (3)
C16—C17	1.369 (2)	O22—H222	0.87 (3)
C16—N3	1.380 (2)	O23—Ca3	2.4362 (14)
C17—C18	1.416 (2)	O23—H231	0.76 (3)
C17—H17	0.9500	O23—H232	0.83 (3)
C18—C26	1.413 (2)	O24—Ca3	2.3607 (13)
C18—C19	1.425 (2)	O24—H241	0.81 (3)
C19—O11	1.229 (2)	O24—H242	0.82 (3)
C19—C20	1.530 (2)	O25—Ca3	2.5787 (14)
C20—O12	1.210 (2)	O25—H251	0.85 (3)
C20—C21	1.497 (2)	O25—H252	0.81 (3)
C21—N4	1.331 (2)	O26—Ca3	2.3962 (14)
C21—C25	1.414 (2)	O26—H261	0.86 (3)
C22—N4	1.336 (2)	O26—H262	0.80 (3)
C22—C23	1.391 (2)	O27—Ca3	2.4924 (14)
C22—C27	1.517 (2)	O27—H271	0.85 (3)
C23—C24	1.399 (2)	O27—H272	0.83 (3)
C23—H23	0.9500	O28—H281	0.89 (4)
C24—C25	1.416 (2)	O28—H282	0.83 (4)
C24—C28	1.531 (2)	O29—H291	0.84 (3)
C25—C26	1.468 (2)	O29—H292	0.79 (3)
C26—N3	1.349 (2)	Ca2—H212	2.77 (3)

C27—O14	1.241 (2)	Ca3—H242	2.79 (3)
C27—O13	1.270 (2)		
O2—C1—O1	122.57 (16)	Ca2—O20—H202	108.7 (19)
O2—C1—C2	119.37 (15)	H201—O20—H202	111 (3)
O1—C1—C2	118.05 (15)	Ca2—O21—H211	131.1 (19)
O2—C1—Ca2^{i}	62.38 (9)	Ca2—O21—H212	108.2 (18)
O1—C1—Ca2^{i}	60.30 (9)	H211—O21—H212	104 (2)
C2—C1—Ca2^{i}	174.96 (12)	Ca2—O22—H221	122 (2)
C3—C2—N1	108.35 (15)	Ca2—O22—H222	133.1 (18)
C3—C2—C1	131.39 (16)	H221—O22—H222	105 (3)
N1—C2—C1	120.24 (15)	Ca3—O23—H231	115.6 (19)
C2—C3—C4	106.75 (15)	Ca3—O23—H232	116.1 (18)
C2—C3—H3	126.6	H231—O23—H232	108 (3)
C4—C3—H3	126.6	Ca3—O24—H241	125.7 (19)
C12—C4—C3	107.73 (15)	Ca3—O24—H242	113.0 (19)
C12—C4—C5	122.41 (15)	H241—O24—H242	104 (3)
C3—C4—C5	129.85 (15)	Ca3—O25—H251	114.2 (18)
O3—C5—C4	126.34 (16)	Ca3—O25—H252	106 (2)
O3—C5—C6	118.97 (15)	H251—O25—H252	106 (3)
C4—C5—C6	114.67 (14)	Ca3—O26—H261	131 (2)
O4—C6—C7	120.52 (15)	Ca3—O26—H262	115.5 (19)
O4—C6—C5	120.10 (15)	H261—O26—H262	105 (3)
C7—C6—C5	119.34 (14)	Ca3—O27—H271	122.3 (18)
N2—C7—C11	124.30 (15)	Ca3—O27—H272	112.4 (17)
N2—C7—C6	113.14 (14)	H271—O27—H272	107 (2)
C11—C7—C6	122.55 (15)	H281—O28—H282	103 (3)
N2—C8—C9	121.27 (15)	H291—O29—H292	107 (3)
N2—C8—C13	115.32 (14)	O14—Ca1—O8	110.58 (4)
C9—C8—C13	123.41 (15)	O14—Ca1—O18	83.93 (5)
C10—C9—C8	120.33 (15)	O8—Ca1—O18	160.87 (5)
C10—C9—H9A	119.8	O14—Ca1—O17	81.08 (5)
C8—C9—H9A	119.8	O8—Ca1—O17	84.33 (5)
C9—C10—C11	118.83 (15)	O18—Ca1—O17	110.98 (5)
C9—C10—C14	115.60 (14)	O14—Ca1—O5^{ii}	147.08 (4)
C11—C10—C14	125.56 (15)	O8—Ca1—O5^{ii}	92.68 (4)
C7—C11—C10	116.10 (15)	O18—Ca1—O5^{ii}	79.85 (5)
C7—C11—C12	115.64 (14)	O17—Ca1—O5^{ii}	78.35 (4)
C10—C11—C12	128.24 (15)	O14—Ca1—N2^{ii}	139.18 (5)
N1—C12—C4	106.95 (15)	O8—Ca1—N2^{ii}	80.01 (4)
N1—C12—C11	127.93 (15)	O18—Ca1—N2^{ii}	80.87 (5)
C4—C12—C11	125.07 (15)	O17—Ca1—N2^{ii}	139.74 (5)
O6—C13—O5	126.02 (15)	O5^{ii}—Ca1—N2^{ii}	65.71 (4)
O6—C13—C8	117.71 (14)	O14—Ca1—O4^{ii}	79.80 (4)
O5—C13—C8	116.27 (14)	O8—Ca1—O4^{ii}	80.92 (4)
O7—C14—O8	126.49 (15)	O18—Ca1—O4^{ii}	89.87 (5)
O7—C14—C10	116.37 (15)	O17—Ca1—O4^{ii}	149.89 (4)
O8—C14—C10	117.05 (14)	O5^{ii}—Ca1—O4^{ii}	128.25 (4)

O10—C15—O9	126.01 (16)	N2^{ii}—Ca1—O4^{ii}	62.59 (4)
O10—C15—C16	115.89 (15)	O22—Ca2—O15	148.18 (5)
O9—C15—C16	118.07 (15)	O22—Ca2—O21	78.62 (5)
C17—C16—N3	108.57 (14)	O15—Ca2—O21	77.75 (5)
C17—C16—C15	129.10 (15)	O22—Ca2—O19	81.60 (5)
N3—C16—C15	122.28 (15)	O15—Ca2—O19	87.27 (5)
C16—C17—C18	106.85 (15)	O21—Ca2—O19	110.91 (5)
C16—C17—H17	126.6	O22—Ca2—O20	98.71 (5)
C18—C17—H17	126.6	O15—Ca2—O20	98.27 (5)
C26—C18—C17	107.48 (14)	O21—Ca2—O20	80.94 (5)
C26—C18—C19	122.96 (15)	O19—Ca2—O20	167.84 (5)
C17—C18—C19	129.55 (15)	O22—Ca2—O1^{iii}	127.21 (5)
O11—C19—C18	127.61 (16)	O15—Ca2—O1^{iii}	81.48 (4)
O11—C19—C20	118.19 (15)	O21—Ca2—O1^{iii}	151.55 (5)
C18—C19—C20	114.20 (14)	O19—Ca2—O1^{iii}	87.10 (5)
O12—C20—C21	121.02 (15)	O20—Ca2—O1^{iii}	83.06 (4)
O12—C20—C19	118.84 (15)	O22—Ca2—O2^{iii}	75.46 (5)
C21—C20—C19	120.12 (14)	O15—Ca2—O2^{iii}	133.97 (4)
N4—C21—C25	124.89 (15)	O21—Ca2—O2^{iii}	145.39 (5)
N4—C21—C20	112.30 (14)	O19—Ca2—O2^{iii}	87.61 (5)
C25—C21—C20	122.68 (15)	O20—Ca2—O2^{iii}	80.74 (4)
N4—C22—C23	121.19 (15)	O1^{iii}—Ca2—O2^{iii}	52.58 (4)
N4—C22—C27	114.53 (14)	O22—Ca2—C1^{iii}	101.03 (5)
C23—C22—C27	124.27 (15)	O15—Ca2—C1^{iii}	107.87 (5)
C22—C23—C24	120.98 (15)	O21—Ca2—C1^{iii}	162.54 (5)
C22—C23—H23	119.5	O19—Ca2—C1^{iii}	86.13 (5)
C24—C23—H23	119.5	O20—Ca2—C1^{iii}	81.88 (5)
C23—C24—C25	118.04 (15)	O1^{iii}—Ca2—C1^{iii}	26.49 (4)
C23—C24—C28	115.57 (14)	O2^{iii}—Ca2—C1^{iii}	26.12 (4)
C25—C24—C28	126.36 (14)	O22—Ca2—H212	94.6 (6)
C21—C25—C24	115.99 (15)	O15—Ca2—H212	60.7 (6)
C21—C25—C26	114.23 (14)	O21—Ca2—H212	17.0 (6)
C24—C25—C26	129.67 (15)	O19—Ca2—H212	107.9 (6)
N3—C26—C18	106.92 (14)	O20—Ca2—H212	84.2 (6)
N3—C26—C25	127.74 (15)	O1^{iii}—Ca2—H212	137.7 (6)
C18—C26—C25	125.34 (15)	O2^{iii}—Ca2—H212	160.4 (6)
O14—C27—O13	124.61 (15)	C1^{iii}—Ca2—H212	160.5 (6)
O14—C27—C22	118.79 (14)	O24—Ca3—O26	83.48 (5)
O13—C27—C22	116.58 (14)	O24—Ca3—O13	161.79 (5)
O15—C28—O16	125.31 (15)	O26—Ca3—O13	85.73 (5)
O15—C28—C24	114.92 (14)	O24—Ca3—O23	82.50 (5)
O16—C28—C24	119.76 (14)	O26—Ca3—O23	144.90 (5)
C12—N1—C2	110.20 (15)	O13—Ca3—O23	98.26 (5)
C12—N1—H2	124.5 (14)	O24—Ca3—O27	96.15 (5)
C2—N1—H2	124.9 (14)	O26—Ca3—O27	75.13 (5)
C7—N2—C8	119.04 (14)	O13—Ca3—O27	95.21 (4)
C7—N2—Ca1^{ii}	123.03 (11)	O23—Ca3—O27	138.35 (5)
C8—N2—Ca1^{ii}	117.70 (11)	O24—Ca3—N4	132.11 (5)

C26—N3—C16	110.18 (14)	O26—Ca3—N4	137.02 (5)
C26—N3—H4	119.6 (16)	O13—Ca3—N4	64.53 (4)
C16—N3—H4	129.8 (16)	O23—Ca3—N4	73.39 (5)
C21—N4—C22	118.67 (14)	O27—Ca3—N4	77.41 (5)
C21—N4—Ca3	122.66 (11)	O24—Ca3—O12	70.98 (4)
C22—N4—Ca3	118.65 (11)	O26—Ca3—O12	134.27 (5)
C1—O1—Ca2^{i}	93.21 (10)	O13—Ca3—O12	126.46 (4)
C1—O2—Ca2^{i}	91.50 (10)	O23—Ca3—O12	69.44 (4)
C6—O4—Ca1^{ii}	120.35 (11)	O27—Ca3—O12	70.85 (4)
C13—O5—Ca1^{ii}	124.78 (10)	N4—Ca3—O12	62.01 (4)
C14—O8—Ca1	146.93 (11)	O24—Ca3—O25	81.28 (5)
C20—O12—Ca3	121.20 (11)	O26—Ca3—O25	73.38 (5)
C27—O13—Ca3	125.58 (10)	O13—Ca3—O25	81.59 (4)
C27—O14—Ca1	161.86 (11)	O23—Ca3—O25	72.78 (5)
C28—O15—Ca2	139.74 (11)	O27—Ca3—O25	148.49 (5)
Ca1—O17—H171	115.5 (18)	N4—Ca3—O25	127.07 (4)
Ca1—O17—H172	125.2 (16)	O12—Ca3—O25	135.26 (4)
H171—O17—H172	107 (2)	O24—Ca3—H242	15.8 (6)
Ca1—O18—H181	117.1 (16)	O26—Ca3—H242	98.7 (6)
Ca1—O18—H182	129 (2)	O13—Ca3—H242	168.8 (6)
H181—O18—H182	113 (3)	O23—Ca3—H242	72.2 (6)
Ca2—O19—H191	125.4 (19)	O27—Ca3—H242	95.9 (6)
Ca2—O19—H192	123.7 (18)	N4—Ca3—H242	116.6 (6)
H191—O19—H192	109 (3)	O12—Ca3—H242	56.6 (6)
Ca2—O20—H201	112 (2)	O25—Ca3—H242	89.7 (6)

O2—C1—C2—C3	4.2 (3)	C27—C22—C23—C24	179.30 (15)
O1—C1—C2—C3	−177.26 (18)	C22—C23—C24—C25	−2.2 (2)
O2—C1—C2—N1	−174.51 (15)	C22—C23—C24—C28	175.81 (15)
O1—C1—C2—N1	4.0 (2)	N4—C21—C25—C24	−3.8 (2)
N1—C2—C3—C4	−0.1 (2)	C20—C21—C25—C24	171.68 (15)
C1—C2—C3—C4	−178.94 (18)	N4—C21—C25—C26	179.55 (15)
C2—C3—C4—C12	−0.2 (2)	C20—C21—C25—C26	−5.0 (2)
C2—C3—C4—C5	179.25 (18)	C23—C24—C25—C21	4.9 (2)
C12—C4—C5—O3	177.69 (17)	C28—C24—C25—C21	−172.84 (15)
C3—C4—C5—O3	−1.7 (3)	C23—C24—C25—C26	−179.05 (16)
C12—C4—C5—C6	−3.6 (2)	C28—C24—C25—C26	3.2 (3)
C3—C4—C5—C6	176.96 (17)	C17—C18—C26—N3	0.23 (19)
O3—C5—C6—O4	7.4 (3)	C19—C18—C26—N3	−179.13 (15)
C4—C5—C6—O4	−171.33 (16)	C17—C18—C26—C25	−179.41 (15)
O3—C5—C6—C7	−174.98 (16)	C19—C18—C26—C25	1.2 (3)
C4—C5—C6—C7	6.2 (2)	C21—C25—C26—N3	−179.48 (16)
O4—C6—C7—N2	−5.9 (2)	C24—C25—C26—N3	4.4 (3)
C5—C6—C7—N2	176.54 (14)	C21—C25—C26—C18	0.1 (2)
O4—C6—C7—C11	173.13 (16)	C24—C25—C26—C18	−176.01 (16)
C5—C6—C7—C11	−4.4 (2)	N4—C22—C27—O14	176.56 (15)
N2—C8—C9—C10	−3.1 (3)	C23—C22—C27—O14	−4.9 (2)
C13—C8—C9—C10	177.06 (15)	N4—C22—C27—O13	−2.0 (2)

C8—C9—C10—C11	3.0 (2)	C23—C22—C27—O13	176.54 (15)
C8—C9—C10—C14	−175.77 (15)	C23—C24—C28—O15	−28.3 (2)
N2—C7—C11—C10	−2.8 (3)	C25—C24—C28—O15	149.54 (17)
C6—C7—C11—C10	178.32 (15)	C23—C24—C28—O16	150.92 (16)
N2—C7—C11—C12	178.55 (15)	C25—C24—C28—O16	−31.3 (2)
C6—C7—C11—C12	−0.4 (2)	C4—C12—N1—C2	−0.58 (19)
C9—C10—C11—C7	−0.2 (2)	C11—C12—N1—C2	−178.32 (16)
C14—C10—C11—C7	178.43 (15)	C3—C2—N1—C12	0.5 (2)
C9—C10—C11—C12	178.31 (16)	C1—C2—N1—C12	179.42 (15)
C14—C10—C11—C12	−3.1 (3)	C11—C7—N2—C8	2.7 (3)
C3—C4—C12—N1	0.49 (19)	C6—C7—N2—C8	−178.26 (14)
C5—C4—C12—N1	−179.02 (16)	C11—C7—N2—Ca1^{ii}	−171.66 (12)
C3—C4—C12—C11	178.31 (16)	C6—C7—N2—Ca1^{ii}	7.34 (19)
C5—C4—C12—C11	−1.2 (3)	C9—C8—N2—C7	0.3 (2)
C7—C11—C12—N1	−179.28 (16)	C13—C8—N2—C7	−179.89 (15)
C10—C11—C12—N1	2.2 (3)	C9—C8—N2—Ca1^{ii}	175.00 (12)
C7—C11—C12—C4	3.4 (2)	C13—C8—N2—Ca1^{ii}	−5.19 (19)
C10—C11—C12—C4	−175.13 (17)	C18—C26—N3—C16	−0.16 (19)
N2—C8—C13—O6	−175.07 (15)	C25—C26—N3—C16	179.48 (16)
C9—C8—C13—O6	4.7 (3)	C17—C16—N3—C26	0.02 (19)
N2—C8—C13—O5	4.8 (2)	C15—C16—N3—C26	177.55 (15)
C9—C8—C13—O5	−175.37 (16)	C25—C21—N4—C22	−0.5 (2)
C9—C10—C14—O7	−42.5 (2)	C20—C21—N4—C22	−176.42 (14)
C11—C10—C14—O7	138.90 (17)	C25—C21—N4—Ca3	177.66 (12)
C9—C10—C14—O8	134.37 (16)	C20—C21—N4—Ca3	1.78 (18)
C11—C10—C14—O8	−44.3 (2)	C23—C22—N4—C21	3.7 (2)
O10—C15—C16—C17	−8.1 (3)	C27—C22—N4—C21	−177.79 (14)
O9—C15—C16—C17	170.08 (16)	C23—C22—N4—Ca3	−174.62 (12)
O10—C15—C16—N3	174.93 (15)	C27—C22—N4—Ca3	3.93 (18)
O9—C15—C16—N3	−6.9 (2)	O2—C1—O1—Ca2^{i}	3.95 (18)
N3—C16—C17—C18	0.13 (18)	C2—C1—O1—Ca2^{i}	−174.56 (14)
C15—C16—C17—C18	−177.18 (16)	O1—C1—O2—Ca2^{i}	−3.87 (17)
C16—C17—C18—C26	−0.22 (19)	C2—C1—O2—Ca2^{i}	174.62 (14)
C16—C17—C18—C19	179.08 (17)	C7—C6—O4—Ca1^{ii}	1.8 (2)
C26—C18—C19—O11	−178.07 (17)	C5—C6—O4—Ca1^{ii}	179.39 (11)
C17—C18—C19—O11	2.7 (3)	O6—C13—O5—Ca1^{ii}	177.84 (13)
C26—C18—C19—C20	2.1 (2)	C8—C13—O5—Ca1^{ii}	−2.1 (2)
C17—C18—C19—C20	−177.06 (16)	O7—C14—O8—Ca1	97.5 (2)
O11—C19—C20—O12	−7.9 (2)	C10—C14—O8—Ca1	−79.0 (2)
C18—C19—C20—O12	171.94 (15)	C21—C20—O12—Ca3	−10.8 (2)
O11—C19—C20—C21	173.47 (15)	C19—C20—O12—Ca3	170.58 (11)
C18—C19—C20—C21	−6.7 (2)	O14—C27—O13—Ca3	−179.65 (12)
O12—C20—C21—N4	6.0 (2)	C22—C27—O13—Ca3	−1.2 (2)
C19—C20—C21—N4	−175.40 (14)	O13—C27—O14—Ca1	−135.4 (3)
O12—C20—C21—C25	−170.03 (15)	C22—C27—O14—Ca1	46.2 (4)

C19—C20—C21—C25	8.6 (2)	O16—C28—O15—Ca2	−14.3 (3)
N4—C22—C23—C24	−2.3 (3)	C24—C28—O15—Ca2	164.88 (12)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H2···O8	0.86 (2)	2.01 (2)	2.7232 (19)	139.6 (19)
N3—H4···O16	0.86 (2)	1.83 (2)	2.6163 (19)	151 (2)
O17—H171···O10^{iv}	0.85 (3)	1.91 (3)	2.7543 (18)	170 (3)
O17—H172···O1	0.86 (3)	2.08 (3)	2.9287 (19)	170 (2)
O18—H181···O28	0.88 (3)	1.82 (3)	2.681 (2)	166 (2)
O18—H182···O1^{iii}	0.84 (3)	1.97 (3)	2.8107 (19)	176 (3)
O19—H191···O20^{i}	0.81 (3)	2.10 (3)	2.8789 (19)	161 (3)
O19—H192···O5^{ii}	0.85 (3)	1.89 (3)	2.7350 (18)	174 (3)
O20—H201···O11^{v}	0.82 (3)	2.00 (3)	2.8221 (18)	173 (3)
O20—H202···O2^{vi}	0.84 (3)	1.94 (3)	2.7620 (18)	169 (3)
O21—H211···O29^{iv}	0.80 (3)	2.05 (3)	2.845 (2)	173 (3)
O21—H212···O16	0.85 (3)	1.90 (3)	2.7320 (18)	163 (3)
O22—H221···O19^{vi}	0.76 (3)	2.26 (3)	2.958 (2)	152 (3)
O22—H222···O6^{vii}	0.87 (3)	1.83 (3)	2.6985 (19)	175 (3)
O23—H231···O3^{viii}	0.76 (3)	2.10 (3)	2.8398 (19)	164 (3)
O23—H232···O9^{iv}	0.83 (3)	1.90 (3)	2.7217 (19)	169 (3)
O24—H241···O7^{ix}	0.81 (3)	2.03 (3)	2.8040 (19)	163 (3)
O24—H242···O29	0.82 (3)	1.93 (3)	2.750 (2)	172 (3)
O25—H251···O13^{ix}	0.85 (3)	2.02 (3)	2.8578 (18)	168 (3)
O25—H252···O3^{viii}	0.81 (3)	2.41 (3)	3.0258 (19)	133 (2)
O25—H252···O4^{viii}	0.81 (3)	2.28 (3)	3.0405 (18)	155 (3)
O26—H261···O27^{x}	0.86 (3)	2.11 (3)	2.9018 (19)	154 (3)
O26—H262···O13^{ix}	0.80 (3)	2.06 (3)	2.8506 (19)	170 (3)
O27—H271···O25^{iii}	0.85 (3)	2.08 (3)	2.9022 (19)	164 (3)
O27—H272···O9^{v}	0.83 (3)	1.99 (3)	2.8125 (18)	171 (2)
O28—H281···O10^{v}	0.89 (4)	1.88 (4)	2.721 (2)	159 (3)
O28—H282···O26^{x}	0.83 (4)	2.59 (3)	3.098 (2)	121 (3)
O29—H291···O6^{ix}	0.84 (3)	1.85 (3)	2.6582 (19)	160 (3)
O29—H292···O11	0.79 (3)	2.27 (3)	3.021 (2)	159 (3)
O29—H292···O12	0.79 (3)	2.40 (3)	2.7789 (19)	110 (2)

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