Acta Cryst E
CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of calcium perchlorate anhydrate, $Ca(ClO_4)_2$, from laboratory powder X-ray diffraction data

Dongmin Lee, Hyeri Bu, Dohwan Kim, Jooeun Hyoung and Seung-Tae Hong*

Daegu Gyeongbuk Institute of Science and Technology (DGIST), Daegu 42988, Republic of Korea. *Correspondence e-mail: st.hong@dgist.ac.kr

Received 6 February 2018
Accepted 7 March 2018

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; powder X-ray diffraction; calcium perchlorate anhydrate; $Ca(ClO_4)_2$; isotypism.

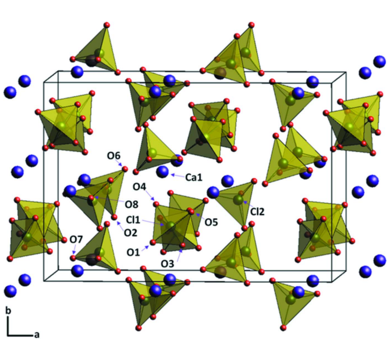
CCDC reference: 1827999

Supporting information: this article has supporting information at journals.iucr.org/e

The crystal structure of calcium perchlorate anhydrate was determined from laboratory X-ray powder diffraction data. The title compound was obtained by heating hydrated calcium perchlorate [$Ca(ClO_4)_2{\cdot}xH_2O$] at 623 K in air for 12 h. It crystallizes in the orthorhombic space group *Pbca* and is isotypic with $Ca(AlD_4)_2$. The asymmetric unit contains one Ca, two Cl and eight O sites, all on general sites (Wyckoff position 8*c*). The crystal structure consists of isolated ClO_4^- tetrahedra and Ca^{2+} cations. The Ca^{2+} cation is coordinated by eight O atoms of eight symmetry-related ClO_4^- tetrahedra within a distorted square-antiprismatic environment.

1. Chemical context

Recently, the alkaline earth metals, in particular magnesium and calcium, have received attention because of their incorporation in multivalent-ion batteries that can replace Li-ion batteries (Wang *et al.*, 2013; Datta *et al.*, 2014; Amatucci *et al.*, 2001). Calcium has several merits, such as low cost and abundance in nature (Padigi *et al.*, 2015; Rogosic *et al.*, 2014). In addition, the standard reduction potential of the calcium electrode is −2.87 V, which is only about 0.18 V higher than that of lithium (Muldoon *et al.*, 2014). Thus, calcium perchlorate is mainly used as a salt next to organic electrolytes in Ca-ion batteries (Hayashi *et al.*, 2003). Nevertheless, the crystal structure of anhydrous calcium perchlorate was



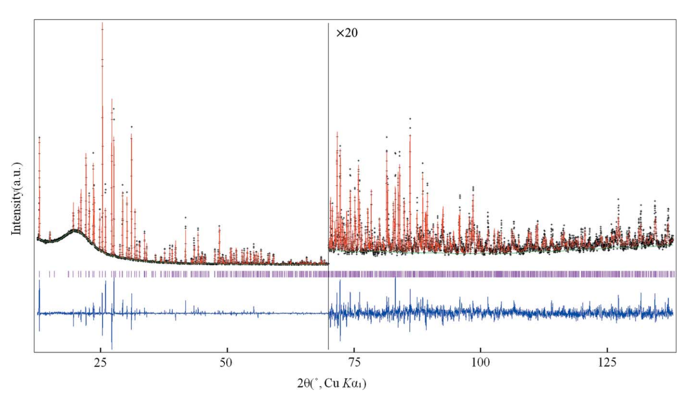


Figure 1
PXRD Rietveld refinement profiles for anhydrous $Ca(ClO_4)_2$ measured at ambient temperature. Crosses mark experimental data (black), the solid red line represents the calculated profile (red) and the solid green line is the background. The bottom trace represents the difference curve (blue) and the ticks denote the positions of expected Bragg reflections (magenta).

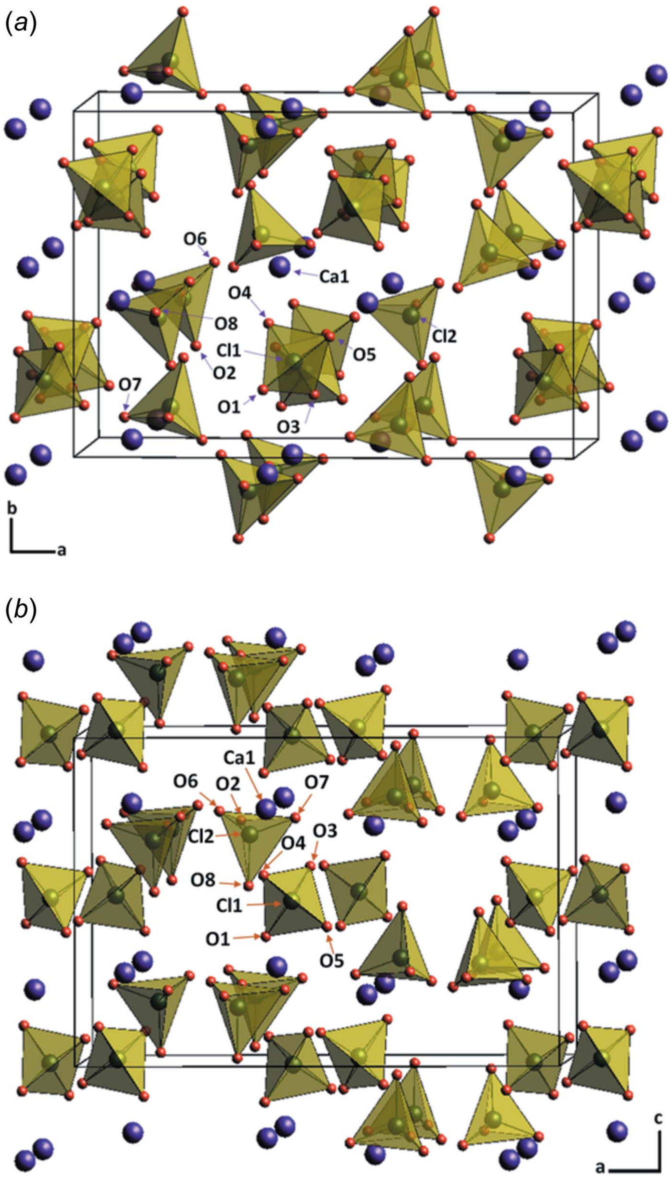


Figure 2
The crystal structure of $Ca(ClO_4)_2$ with ClO_4^- tetrahedra (yellow) and Ca^{2+} cations (purple), showing (*a*) a view approximately along [001] and (*b*) approximately along [010].

unknown until now (Pearse & Pflaum, 1959) because of the lack of single crystals. Calcium perchlorate is strongly hygroscopic, and growing single crystals of a size sufficient for X-ray structure analysis has not been successful up to date. On the other hand, the crystal structures of the perchlorates of magnesium, barium and other alkaline earth metals have been determined for both hydrated and anhydrous phases (Gallucci & Gerkin, 1988; Lee *et al.*, 2015; Lim *et al.*, 2011; Robertson & Bish, 2010). However, for calcium perchlorate only the hydrated forms were structurally determined (Hennings *et al.*, 2014).

We present here the crystal structure of calcium perchlorate anhydrate, using laboratory powder X-ray diffraction (PXRD) data (Fig. 1).

Table 1
Selected bond lengths (Å).

Ca1—O1^{i}	2.451 (6)	Cl1—O2	1.411 (6)
Ca1—O2^{ii}	2.412 (6)	Cl1—O6	1.414 (6)
Ca1—O3	2.448 (6)	Cl1—O7	1.421 (6)
Ca1—O4^{iii}	2.370 (6)	Cl1—O8	1.423 (6)
Ca1—O5^{ii}	2.429 (6)	Cl2—O1	1.456 (6)
Ca1—O6^{iv}	2.512 (6)	Cl2—O3	1.408 (6)
Ca1—O7^{i}	2.519 (6)	Cl2—O4	1.453 (6)
Ca1—O8	2.413 (6)	Cl2—O5	1.442 (6)

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

2. Structural commentary

The crystal structure of anhydrous calcium perchlorate, $Ca(ClO_4)_2$, is isotypic with that of $Ca(AlD_4)_2$ (Sato *et al.*, 2009), but is different from barium or magnesium perchlorates (Lee *et al.*, 2015; Lim *et al.*, 2011). Different viewing directions of the crystal structure of $Ca(ClO_4)_2$ are presented in Fig. 2, using ClO_4^- tetrahedra and Ca^{2+} cations. The unit cell contains one Ca (on general positions 8*c*), two Cl (8*c*), and eight O (8*c*) sites. The ClO_4^- tetrahedra are slightly distorted [mean Cl—O distance 1.43 (2) Å, angular range 103.5 (4)–114.6 (4)°] and isolated from each other. The local environment around the Ca^{2+} cation is presented in Fig. 3. It is coordinated by eight isolated ClO_4^- tetrahedra with an apex oxygen atom of each tetrahedron bonded to the Ca^{2+} cation. The resulting coordination sphere can be considered as a distorted square antiprism. The average Ca—O distance is 2.476 Å (Table 1), which is intermediate between those of comparable Mg—O (2.098 Å) and Ba—O (2.989 Å) polyhedra (Lee *et al.*, 2015; Lim *et al.*, 2011), and consistent with the sum of the ionic radii of the alkaline earth metals and oxygen (Shannon, 1976). The coordination number of the

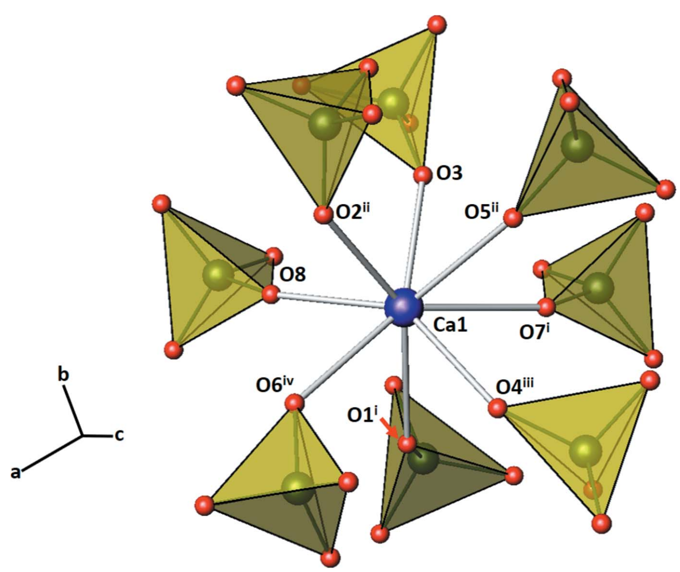


Figure 3
The local environment of the Ca^{2+} cation (purple sphere) surrounded by ClO_4^- tetrahedra (yellow). [Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (iv) $-x+\frac{1}{2}, -y+1, z+\frac{1}{2}$.]

Table 2
Experimental details.

Crystal data	
Chemical formula	$Ca(ClO_4)_2$
M_r	238.98
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	295
a, b, c (Å)	13.75102 (8), 9.50887 (5), 9.06168 (5)
V (Å^3)	1184.88 (1)
Z	8
Radiation type	Cu $K\alpha_1$, λ = 1.5405 Å
Specimen shape, size (mm)	Flat sheet, 24.9 × 24.9
Data collection	
Diffractometer	PANalytical Empyrean
Specimen mounting	Packed powder
Data collection mode	Reflection
Scan method	Step
2θ values (°)	$2\theta_{min}$ = 5.001 $2\theta_{max}$ = 139.993 $2\theta_{step}$ = 0.013
Refinement	
R factors and goodness of fit	R_p = 0.068, R_{wp} = 0.104, R_{exp} = 0.055, $R(F^2)$ = 0.151, χ^2 = 3.610
No. of parameters	44

Computer programs: *X'Pert Data Collector* and *X'Pert HighScore Plus* (PANalytical, 2011), *GSAS* (Larson & Von Dreele, 2000), *SHELXS97* (Sheldrick, 2008), *CRYSTALS* (Betteridge *et al.*, 2003) and *ATOMS* (Dowty, 2000).

Mg^{2+}, Ca^{2+}, and Ba^{2+} cations in the anhydrous perchlorates increases from 6, 8, and to 12, respectively.

3. Synthesis and crystallization

In order to prepare calcium perchlorate anhydrate, $Ca(ClO_4)_2{\cdot}xH_2O$ (reagent grade, Alfa Aesar) was placed in 75 ml glass vials. The vials were placed into a box furnace, heated at 623 K for 12 h with a heating rate of 3 K min^{-1}, cooled down to 423 K, and transferred to a glove box under an Ar atmosphere. The exposed time in a normal atmosphere during the transfer was about 10 s. The sample was ground using an agate mortar, and placed in a dome-type PXRD sample holder that was sealed tightly to prevent atmospheric exposure during the data collection.

4. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 2. The powder XRD data of anhydrous calcium perchlorate were collected using a Bragg–Brentano diffractometer (PANalytical Empyrean) with Cu $K\alpha_1$ radiation (λ = 1.5406 Å) at 40 kV and 30 mA, using a graphite monochromator and a Pixcel3D 2×2 detector. X-ray intensities were measured for 12 h at 0.013° intervals in the angular range of $5° \leq 2\theta \leq 140°$. X-ray diffraction data were indexed by the *TREOR90* algorithm (Werner, 1990) in the *CRYSFIRE* program suite (Shirley, 2002), with 22 indexed reflections starting from the smallest angle. An orthorhombic unit cell was revealed suggesting *Pbca* as the most probable space group. Based on these results, the refinement process was performed using the *GSAS* program (Larson & Von Dreele, 2000) and the *CRYSTALS* program (Betteridge *et al.*, 2003). The process was started with the assumption that there is one dummy atom at an arbitrary position. Then direct methods were applied to calculate the initial solution of the crystal structure using *SHELXS97* (Sheldrick, 2008), which yielded a Ca site as a starting postition. The initial model was then replaced with the partial model, and this data was used for a LeBail fit in *GSAS*. Then, improved structure factors were calculated, which were used for the refinement in *CRYSTALS*. These processes were repeated until a complete and sufficient structural model converged. Based on these results, the *MCE* programme (Rohlíček & Hušák, 2007) was used to draw the calculated Fourier-density map in three dimensions. For the final Rietveld refinement with *GSAS*, an overall displacement parameter was used, and Cl—O bond lengths were restrained with a tolerance value of 25% from the distances determined from *CRYSTALS*, where the distances matched well with Shannon's radii sum. Pseudovoigt profile coefficients as parameterized in Thompson *et al.* (1987), asymmetry correction of Finger *et al.* (1994) and microstrain broadening of Stephens (1999).

Funding information

This work was supported by Samsung Research Funding & Incubation Center of Samsung Electronics under Project No. SRFC-MA1601–04.

References

Amatucci, G. G., Badway, F., Singhal, A., Beaudoin, B., Skandan, G., Bowmer, T., Plitz, I., Pereira, N., Chapman, T. & Jaworski, R. (2001). *J. Electrochem. Soc.* **148**, A940–A950.
Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
Datta, D., Li, J. & Shenoy, V. B. (2014). *Appl. Mater. Interfaces*, **6**, 1788–1795.
Dowty, E. (2000). *ATOMS for Windows*. Shape Software, Kingsport, Tennessee, USA.
Finger, L. W., Cox, D. E. & Jephcoat, A. P. (1994). *J. Appl. Cryst.* **27**, 892–900.
Gallucci, J. C. & Gerkin, R. E. (1988). *Acta Cryst.* C**44**, 1873–1876.
Hayashi, M., Arai, H., Ohtsuka, H. & Sakurai, Y. (2003). *J. Power Sources*, **119–121**, 617–620.
Hennings, E., Schmidt, H. & Voigt, W. (2014). *Acta Cryst.* E**70**, 510–514.
Larson, A. C. & Von Dreele, R. B. (2000). *General Structure Analysis System (GSAS)*. Los Alamos National Laboratory Report LAUR 86-748, USA.
Lee, J. H., Kang, J. H., Lim, S.-C. & Hong, S.-T. (2015). *Acta Cryst.* E**71**, 588–591.
Lim, H.-K., Choi, Y. S. & Hong, S.-T. (2011). *Acta Cryst.* C**67**, i36–i38.
Muldoon, J., Bucur, C. B. & Gregory, T. (2014). *Chem. Rev.* **114**, 11683–11720.
Padigi, P., Goncher, G., Evans, D. & Solanki, R. (2015). *J. Power Sources*, **273**, 460–464.
PANalytical (2011). *X'Pert Data Collector* and *X'Pert Highscore-Plus*. PANalytical BV, Almelo, The Netherlands.
Pearse, G. A. Jr & Pflaum, R. T. (1959). *J. Am. Chem. Soc.* **81**, 6505–6508.
Robertson, K. & Bish, D. (2010). *Acta Cryst.* B**66**, 579–584.

Rogosic, J. (2014). *Towards the Development of Calcium Ion Batteries*. Ph D Thesis, Massachusetts Institute of Technology, USA.
Rohlíček, J. & Hušák, M. (2007). *J. Appl. Cryst.* **40**, 600–601.
Sato, T., Sørby, M. H., Ikeda, K., Sato, S., Hauback, B. C. & Orimo, S. (2009). *J. Alloys Compd.* **487**, 472–478.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Shirley, R. (2002). *The Crysfire 2002 System for Automatic Powder Indexing: User's Manual.* Guildford: The Lattice Press.
Stephens, P. W. (1999). *J. Appl. Cryst.* **32**, 281–289.
Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.
Wang, R. Y., Wessells, C. D., Huggins, R. A. & Cui, Y. (2013). *Nano Lett.* **13**, 5748–5752.
Werner, P. E. (1990). *TREOR90.* Stockholm, Sweden.

supporting information

Acta Cryst. (2018). E**74**, 514-517   [https://doi.org/10.1107/S2056989018003936]

Crystal structure of calcium perchlorate anhydrate, $Ca(ClO_4)_2$, from laboratory powder X-ray diffraction data

Dongmin Lee, Hyeri Bu, Dohwan Kim, Jooeun Hyoung and Seung-Tae Hong

Computing details

Data collection: *X'Pert Data Collector* (PANalytical, 2011); cell refinement: *GSAS* (Larson & Von Dreele, 2000); data reduction: *X'Pert HighScore Plus* (PANalytical, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *CRYSTALS* (Betteridge *et al.*, 2003); program(s) used to refine structure: *GSAS* (Larson & Von Dreele, 2000); molecular graphics: *ATOMS* (Dowty, 2000); software used to prepare material for publication: *GSAS* (Larson & Von Dreele, 2000).

Calcium bis(perchlorate)

Crystal data

$Ca(ClO_4)_2$
$M_r = 238.98$
Orthorhombic, *Pbca*
Hall symbol: -P_2ac_2ab
$a = 13.75102$ (8) Å
$b = 9.50887$ (5) Å
$c = 9.06168$ (5) Å
$V = 1184.88$ (1) Å^3
$Z = 8$
$F(000) = 944.0$
$D_x = 2.680$ Mg m^{-3}
Cu $K\alpha_1$ radiation, $\lambda = 1.5405$ Å
$T = 295$ K
white
flat_sheet, 24.9 × 24.9 mm
Specimen preparation: Prepared at 295 K

Data collection

PANalytical Empyrean diffractometer
Radiation source: sealed X-ray tube, PANalytical Cu Ceramic X-ray tube
Specimen mounting: packed powder
Data collection mode: reflection
Scan method: step
$2\theta_{min} = 5.001°$, $2\theta_{max} = 139.993°$, $2\theta_{step} = 0.013°$

Refinement

Least-squares matrix: full
$R_p = 0.068$
$R_{wp} = 0.104$
$R_{exp} = 0.055$
$R(F^2) = 0.15096$
10385 data points
Excluded region(s): 5 to 12.5 degrees are excluded due to background scattering at low angles, in addition there are no peaks in this region.

Profile function: CW Profile function number 4 with 18 terms Pseudovoigt profile coefficients as parameterized in P. Thompson, D.E. Cox & J.B. Hastings (1987). J. Appl. Cryst.,20,79-83. Asymmetry correction of L.W. Finger, D.E. Cox & A. P. Jephcoat (1994). J. Appl. Cryst.,27,892-900. Microstrain broadening by P.W. Stephens, (1999). J. Appl. Cryst.,32,281-289. #1(GU) = 9.638 #2(GV) = -11.095 #3(GW) = 2.275 #4(GP) = 4.393 #5(LX) = 0.935 #6(ptec) = 0.00 #7(trns) = 0.00 #8(shft) = -4.2154 #9(sfec) = 0.00 #10(S/L) = 0.0005 #11(H/L) = 0.0005 #12(eta) = 0.7500 #13(S400) = 0.0E+00 #14(S040) = 0.0E+00 #15(S004) = 0.0E+00 #16(S220) = 0.0E+00 #17(S202) = 0.0E+00 #18(S022) = 0.0E+00 Peak tails are ignored where the intensity is below 0.0100 times the peak Aniso. broadening axis 0.0 0.0 1.0
44 parameters
0 restraints
$(\Delta/\sigma)_{max} = 0.04$
Background function: GSAS Background function number 1 with 36 terms. Shifted Chebyshev function of 1st kind 1: 396.859 2: -606.961 3: 459.581 4: -240.760 5: 60.9683 6: 66.1787 7: -127.055 8: 123.403 9: -80.0454 10: 22.9955 11: 31.6319 12: -68.9521 13: 82.3967 14: -74.9306 15: 52.4628 16: -22.9755 17: -7.07207 18: 29.6007 19: -41.2483 20: 39.7866 21: -28.2300 22: 12.3296 23: 2.74056 24: -14.4441 25: 20.2978 26: -20.5325 27: 15.0728 28: -6.57858 29: -1.96745 30: 7.61710 31: -10.5263 32: 10.4139 33: -6.95249 34: 2.74624 35: 0.930279 36: -1.93129

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ca1	0.39788 (14)	0.5357 (2)	0.7164 (2)	0.0110 (2)*
Cl1	0.34080 (17)	0.6066 (3)	0.3157 (3)	0.0110 (2)*
Cl2	0.55928 (18)	0.7776 (3)	0.4961 (3)	0.0110 (2)*
O1	0.6154 (4)	0.7025 (6)	0.3850 (6)	0.0110 (2)*
O2	0.3176 (4)	0.7464 (6)	0.2773 (6)	0.0110 (2)*
O3	0.5240 (4)	0.6775 (7)	0.5973 (7)	0.0110 (2)*
O4	0.6137 (4)	0.8834 (6)	0.5773 (6)	0.0110 (2)*
O5	0.4842 (4)	0.8546 (7)	0.4199 (6)	0.0110 (2)*
O6	0.2815 (4)	0.5078 (6)	0.2414 (6)	0.0110 (2)*
O7	0.4359 (4)	0.5744 (6)	0.2647 (7)	0.0110 (2)*
O8	0.3387 (4)	0.5833 (6)	0.4708 (7)	0.0110 (2)*

Geometric parameters (Å, º)

Ca1—Cl1	3.776 (3)	Cl2—Ca1	3.769 (3)
Ca1—Cl1^{i}	3.605 (3)	Cl2—Ca1^{v}	3.808 (3)
Ca1—Cl1^{ii}	3.662 (3)	Cl2—Ca1^{iii}	3.596 (3)
Ca1—Cl1^{iii}	3.851 (3)	Cl2—Ca1^{vii}	3.627 (3)
Ca1—Cl2	3.769 (3)	Cl2—O1	1.456 (6)
Ca1—Cl2^{i}	3.808 (3)	Cl2—O3	1.408 (6)
Ca1—Cl2^{iii}	3.596 (3)	Cl2—O4	1.453 (6)
Ca1—Cl2^{iv}	3.627 (3)	Cl2—O5	1.442 (6)
Ca1—O1^{iii}	2.451 (6)	O1—Ca1^{iii}	2.451 (6)
Ca1—O2^{i}	2.412 (6)	O1—Cl2	1.456 (6)
Ca1—O3	2.448 (6)	O2—Ca1^{v}	2.412 (6)
Ca1—O4^{iv}	2.370 (6)	O2—Cl1	1.411 (6)
Ca1—O5^{i}	2.429 (6)	O3—Ca1	2.448 (6)
Ca1—O6^{ii}	2.512 (6)	O3—Cl2	1.408 (6)
Ca1—O7^{iii}	2.519 (6)	O4—Ca1^{vii}	2.370 (6)
Ca1—O8	2.413 (6)	O4—Cl2	1.453 (6)
Cl1—Ca1	3.776 (3)	O5—Ca1^{v}	2.429 (6)
Cl1—Ca1^{v}	3.605 (3)	O5—Cl2	1.442 (6)
Cl1—Ca1^{vi}	3.662 (3)	O6—Ca1^{vi}	2.512 (6)
Cl1—Ca1^{iii}	3.851 (3)	O6—Cl1	1.414 (6)
Cl1—O2	1.411 (6)	O7—Ca1^{iii}	2.519 (6)
Cl1—O6	1.414 (6)	O7—Cl1	1.421 (6)
Cl1—O7	1.421 (6)	O8—Ca1	2.413 (6)
Cl1—O8	1.423 (6)	O8—Cl1	1.423 (6)
O1^{iii}—Ca1—O2^{i}	147.7 (2)	O6^{ii}—Ca1—O8	77.5 (2)
O1^{iii}—Ca1—O3	113.4 (2)	O7^{iii}—Ca1—O8	116.53 (2)
O1^{iii}—Ca1—O5^{i}	135.9 (2)	O2—Cl1—O6	112.2 (4)
O1^{iii}—Ca1—O6^{ii}	79.0 (2)	O2—Cl1—O7	109.4 (4)
O1^{iii}—Ca1—O7^{iii}	73.10 (19)	O2—Cl1—O8	112.7 (4)
O1^{iii}—Ca1—O8	78.62 (18)	O6—Cl1—O7	103.5 (4)
O2^{i}—Ca1—O3	87.3 (2)	O6—Cl1—O8	110.8 (4)
O2^{i}—Ca1—O5^{i}	71.4 (2)	O7—Cl1—O8	107.8 (4)
O2^{i}—Ca1—O6^{ii}	70.80 (19)	O1—Cl2—O3	107.6 (4)
O2^{i}—Ca1—O7^{iii}	139.2 (2)	O1—Cl2—O4	114.6 (4)
O2^{i}—Ca1—O8	84.0 (2)	O1—Cl2—O5	107.3 (4)
O3—Ca1—O5^{i}	75.6 (2)	O3—Cl2—O4	108.4 (4)
O3—Ca1—O6^{ii}	145.7 (2)	O3—Cl2—O5	114.1 (4)
O3—Ca1—O7^{iii}	67.4 (2)	Ca1^{iii}—O1—Cl2	132.3 (4)
O3—Ca1—O8	74.3 (2)	Ca1^{v}—O2—Cl1	139.7 (4)
O5^{i}—Ca1—O6^{ii}	118.8 (2)	Ca1—O3—Cl2	154.6 (4)
O5^{i}—Ca1—O7^{iii}	71.6 (2)	Ca1^{v}—O5—Cl2	158.7 (4)
O5^{i}—Ca1—O8	141.7 (2)	Ca1^{vi}—O6—Cl1	135.9 (4)
O6^{ii}—Ca1—O7^{iii}	144.7 (2)	Ca1^{iii}—O7—Cl1	154.5 (4)

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