



Re-investigation and correct symmetry of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$

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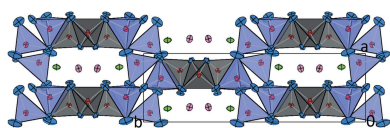
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Keywords: crystal structure; $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$; redetermination; symmetry analysis.**CCDC reference:** 1890066**Supporting information:** this article has supporting information at journals.iucr.org/e

A re-investigation of the crystal structure of tricalcium cobalt(II) tetra-aluminate, $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$, using single-crystal X-ray diffraction data, revealed orthorhombic (*Pbcm*) symmetry. The present contribution corrects the results of a previous X-ray powder diffraction study [Vazquez *et al.* (2002). *J. Solid State Chem.* **166**, 191–196] where this phase has been described in an unnecessarily low space-group symmetry (*Pbc2₁*). The compound belongs to the group of tetrahedral framework structures. The distribution of the aluminium and cobalt ions among the centres of the four different tetrahedra within the asymmetric unit has been studied in detail. Charge compensation is achieved by the incorporation of two symmetrically independent calcium ions located in voids of the tetrahedral framework. $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ is isotopic with $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$.

1. Chemical context

In a recent paper on the phase relationships in the system $\text{CaO-MgO-Al}_2\text{O}_3$, we reported the existence and the crystal structure of $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ (Kahlenberg *et al.*, 2018), a phase of interest for slags occurring in secondary refining processes in metallurgy or refractories, for example. In the course of this study it became obvious that the compound is closely related to the corresponding Zn and Co analogues that have already been reported in the literature (Barbanyagre *et al.*, 1997; Vazquez *et al.*, 2002). In fact Vazquez *et al.* (2002) used the coordinates from the Zn compound as a starting model for their Rietveld refinement of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$. The major difference from our investigation on $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ results from the fact that the previous study attributed $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ to the acentric space group *Pbc2₁*, while $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ crystallizes in the centrosymmetric space group *Pbcm*. However, for the former compound the description in an acentric space group has to be scrutinized. A detailed analysis of the atomic coordinates using the program *PSEUDO* (Kroumova *et al.*, 2001) indicated that the published model fulfills the symmetry requirements of *Pbcm*. Notably, Vazquez *et al.* (2002) reported problems during their structure analysis of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$, including unstable refinements and unrealistically short cation–oxygen distances. Both observations are typical features when a structure is refined in an unnecessarily low space-group symmetry (Baur & Tillmanns, 1986). Therefore, it was deemed appropriate to re-investigate the crystal structure of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ using single-crystal X-ray diffraction data obtained from melt-grown crystals.



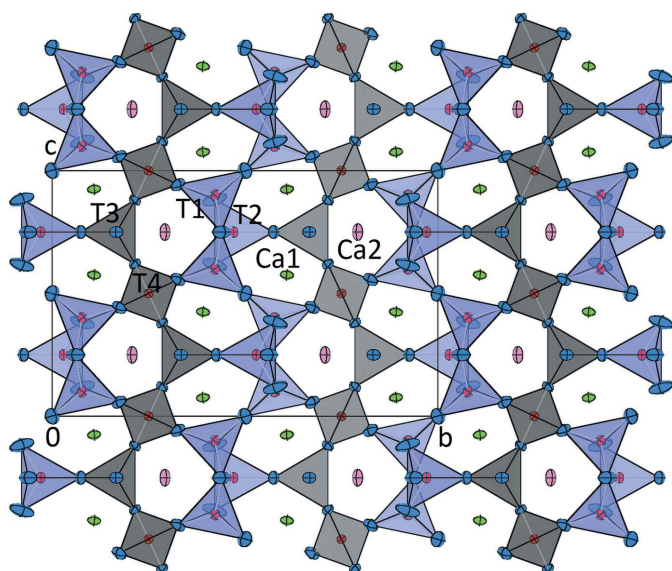


Figure 1
Projection of the crystal structure of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ in a view parallel to $[100]$. Displacement ellipsoids are shown at the 90% probability level. Colour codings for the atoms and polyhedra are as follows: blue: oxygen; red: aluminium/cobalt; Ca1: pink; Ca2: green; cobalt-containing tetrahedra ($[T1O_4]$ and $[T2O_4]$): lilac; pure aluminium tetrahedra ($[T3O_4]$ and $[T4O_4]$): grey.

2. Structural commentary

The crystal structure of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ can be described as a three-dimensional network with four symmetrically different corner-sharing $[(\text{Al},\text{Co})\text{O}_4]$ tetrahedra around the central atoms $T1$ – $T4$ (Fig. 1). The basic building units of the structure are chains of tetrahedra running parallel to $[001]$. Using the crystal chemical classification developed by Liebau (1985), these linear elements can be described as mixed-branched *vierer* single chains (Fig. 2). Condensation of adjacent chains along $[010]$ results in the formation of stepped layers parallel to (100) (Fig. 3). Within these layers, channels can be identified which host the additional calcium ions.

Site-occupancy refinements indicated that cobalt incorporation is limited to two of the four T sites within the asymmetric unit ($T1$ and $T2$). $T3$ and $T4$ are virtually cobalt free. The spread of the individual T – O bond lengths and the O – T – O angles follow expected crystallochemical trends. For the average T – O values, two groups can be distinguished: $T1$, $T2$: 1.808 Å and $T3$, $T4$: 1.758 Å. These values reflect the larger ionic radius of Co^{2+} for fourfold coordination [$r(\text{Co}^{2+}, [4])$: 0.58 Å] when compared to the corresponding value for Al^{3+} [$r(\text{Al}^{3+}, [4])$: 0.39 Å] (Shannon, 1976), and can be used as an indication that $T1$ and $T2$ have higher Co contents. This observation compares well with the site-population refinements. Quadratic elongations as defined by Robinson *et al.* (1971), which can be used as numerical descriptors for the distortions, take the following values for the individual $[(\text{Al},\text{Co})\text{O}_4]$ -groups: $T1$: 1.015, $T2$: 1.006, $T3$: 1.016, $T4$: 1.001.

Among the extra-framework cations, two crystallographically independent calcium sites (Ca1, Ca2) can be distinguished. They are coordinated by six and eight nearest

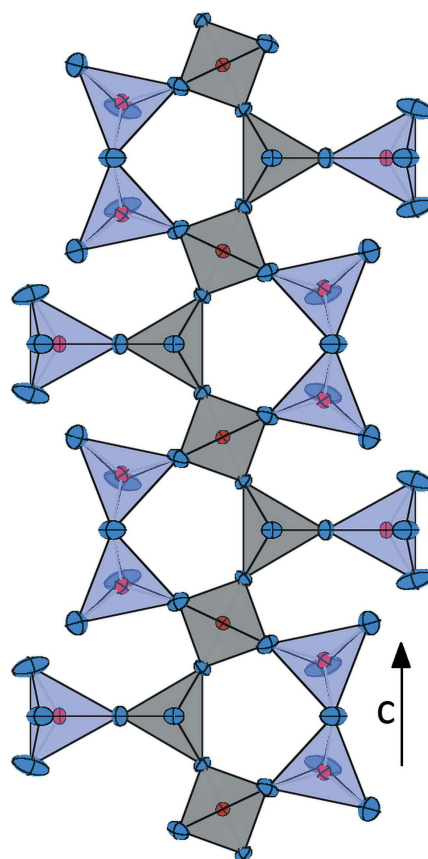


Figure 2
A single mixed-branched *vierer* single chain (running parallel to $[001]$) representing the backbone of the framework in $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$. Displacement ellipsoids as in Fig. 1.

oxygen neighbours. Their coordination polyhedra can be described as distorted octahedra and square antiprisms, respectively. Each two $[\text{Ca}1\text{O}_6]$ octahedra and a single $[\text{Ca}2\text{O}_8]$ square antiprism form a polyhedral unit by sharing edges.

A detailed analysis of the topological features of the tetrahedral network including coordination sequences and extended point symbols has been already presented for isotopic $\text{Ca}_3\text{MgAl}_4\text{O}_{10}$ (Kahlenberg *et al.*, 2018) and will not be duplicated here. However, it is interesting to note that the framework consists of three ($T3$), four ($T4$) and five ($T1$, $T2$)-connected tetrahedra. Notably, the net contains an $\text{O}^{[3]}$ -type bridging oxygen ($\text{O}3$), simultaneously linking three tetrahedra (one $[T2O_4]$ - and two $[T1O_4]$ -units). In oxo-silicates that are

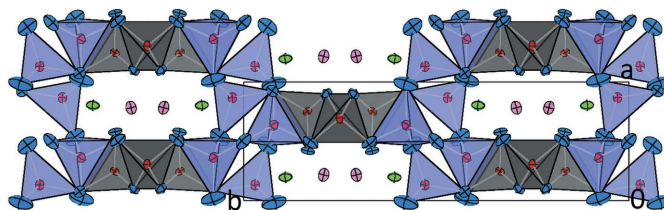


Figure 3
Projection of the crystal structure of $\text{Ca}_3\text{CoAl}_4\text{O}_{10}$ in a view parallel to $[001]$. Displacement ellipsoids as in Fig. 1.

based on [SiO₄] units, for example, only terminal (O^[1]) and simple bridging (O^[2]) oxygen atoms have been observed so far. In the present structure, the oxygen atoms O1 and O2, O4, O5, O6, O7 belong to these two groups. Notably, O3 is solely involved in O–T bonds with the two tetrahedra showing an Al/Co substitution.

3. Database survey

As mentioned above, the title compound is isotypic with Ca₃MgAl₄O₁₀. For the calculation of several quantitative descriptors for the characterization of the degree of similarity between the crystal structures of Ca₃CoAl₄O₁₀ and Ca₃MgAl₄O₁₀, the program *COMPSTRU* (de la Flor *et al.*, 2016) was employed. For the given two structures, the degree of lattice distortion *S*, *i.e.* the spontaneous strain obtained from the eigenvalues of the finite Lagrangian strain tensor calculated in a Cartesian reference system, has a value of *S* = 0.0010. The structure of Ca₃CoAl₄O₁₀ was transformed to the most similar configuration of Ca₃MgAl₄O₁₀. The calculations revealed the following atomic displacements (in Å) between the corresponding atoms in Ca₃CoAl₄O₁₀ and Ca₃MgAl₄O₁₀: Ca1: 0.036; Ca2: 0.028; T1: 0.044; T2: 0.010; T3: 0.027; T4: 0.031; O1: 0.026; O2: 0.030; O3: 0.019; O4: 0.024; O5: 0.000; O6: 0.031; O7: 0.040, *i.e.* the maximum displacement is lower than 0.05 Å. The measure of similarity (Δ) as defined by Bergerhoff *et al.* (1999) has a value of 0.007. Notably, for both structures the divalent cations Co²⁺ and Mg²⁺ are enriched in the tetrahedral positions T1 and T2.

The distribution of the cobalt and aluminium ions on the different *T* sites is another difference between the new centrosymmetric model in *Pbcm* (this work) and the previous acentric model in *Pbc2₁* (Vazquez *et al.*, 2002). Actually, in the latter case five different tetrahedral positions have to be distinguished. The authors considered four of them to be exclusively occupied with Al while the remaining fifth position was attributed to be a pure cobalt site. This distribution, however, was derived from the crystal-structure refinement of the zinc analog (Barbanyagre *et al.*, 1997) and not determined by site-occupancy refinements.

Furthermore, the new model in *Pbcm* results in considerably less distorted tetrahedra. Although soft constraints on the Al–O and Co–O bond lengths had been applied, individual *T*–O distances and O–*T*–O angles in the *Pbc2₁* structure model showed a pronounced variation between 1.68 and 2.05 Å and 92.9 and 124.6°, respectively. The corresponding values in the present model are in the ranges from 1.719 (4) to 1.847 (2) Å and from 98.95 (16) to 120.38 (18)°, respectively. Finally, the displacement parameters in *Pbcm* are all well behaved, while the overall isotropic temperature factor for the oxygen atoms reported in the study of Vazquez *et al.* (2002) takes a physically unrealistic value of *U*_{iso} = 0.001 (2) Å².

4. Synthesis and crystallization

Single crystals of Ca₃CoAl₄O₁₀ were obtained during a series of synthesis experiments in the system CaO–CoO–Al₂O₃.

Table 1
Experimental details.

Crystal data	
Chemical formula	Al ₄ Ca ₃ CoO ₁₀
<i>M_r</i>	447.09
Crystal system, space group	Orthorhombic, <i>Pbcm</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.1324 (6), 16.7550 (19), 10.6822 (12)
<i>V</i> (Å ³)	918.60 (18)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	3.97
Crystal size (mm)	0.12 × 0.09 × 0.06
Data collection	
Diffractometer	Rigaku Oxford Diffraction Xcalibur, Ruby, Gemini ultra
Absorption correction	Analytical (<i>CrysAlis PRO</i> ; Rigaku OD, 2015). Analytical numeric absorption correction using a multifaceted crystal model based on expressions published by Clark & Reid (1995).
<i>T</i> _{min} – <i>T</i> _{max}	0.759, 0.898
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	5719, 973, 791
<i>R</i> _{int}	0.065
(sin θ/λ) _{max} (Å ⁻¹)	0.621
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.061, 1.07
No. of reflections	973
No. of parameters	96
No. of restraints	1
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.6, –0.64

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXL2017/1* (Sheldrick, 2015), *VESTA3* (Momma & Izumi, 2011), *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

1.35 g of the educts consisting of CaCO₃, CoO and Al₂O₃ in the molar ratio 14:6:5 were homogenized in an agate mortar, transferred into a platinum crucible and covered with a lid. The container was fired in a resistance-heated furnace from 590 to 1623 K with a ramp of 100 K h⁻¹. The target temperature was held for 1 h. Subsequently, the sample was cooled down to 1273 K at a rate of 7.5 K h⁻¹ and, finally, the temperature was reduced to 473 K at a rate of 100 K h⁻¹. After removal of the crucible, the solidified melt cake was immediately crushed in an agate mortar and transferred to a glass slide under a polarizing binocular. A first inspection revealed the presence of two crystalline phases: larger colourless optically isotropic crystals of Ca₃Al₂O₆ (up to 500 μm in size) and considerably smaller, intensively blue birefringent crystals of Ca₃CoAl₄O₁₀. A platy fragment of the latter compound showing sharp extinction under crossed polarizers was selected for further structural studies and mounted on the tip of a glass fibre using fingernail hardener as glue.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Starting parameters for the atomic

coordinates were taken from the crystal structure of $\text{Ca}_3\text{Al}_4\text{MgO}_{10}$ (Kahlenberg *et al.*, 2018). Initially, mixed cobalt–aluminium populations were considered for all four *T* sites. However, the resulting values of the site occupancies for *T3* and *T4* indicated pure Al populations (within two standard uncertainties each). In the final cycles a restraint was introduced, fixing the total amount of cobalt distributed among the remaining *T1* and *T2* sites to four atoms per unit cell.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: coordinates from isotypic structure; program(s) used to refine structure: *SHELXL2017/1* (Sheldrick, 2015); molecular graphics: *VESTA3* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010) and *WinGX* (Farrugia, 2012).

Tricalcium cobalt(II) tetraaluminate

Crystal data

$\text{Ca}_3\text{CoAl}_4\text{O}_{10}$

$M_r = 447.09$

Orthorhombic, *Pbcm*

Hall symbol: -P 2c 2b

$a = 5.1324$ (6) Å

$b = 16.7550$ (19) Å

$c = 10.6822$ (12) Å

$V = 918.60$ (18) Å³

$Z = 4$

$F(000) = 876$

$D_x = 3.233$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 939 reflections

$\theta = 5.0\text{--}28.4^\circ$

$\mu = 3.97$ mm⁻¹

$T = 293$ K

Fragment, colourless

$0.12 \times 0.09 \times 0.06$ mm

Data collection

Rigaku Oxford Diffraction Xcalibur, Ruby,

Gemini ultra

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.3575 pixels mm⁻¹

ω scans

Absorption correction: analytical

(*CrysAlisPro*; Rigaku OD, 2015). Analytical

numeric absorption correction using a

multifaceted crystal model based on expressions

published by Clark & Reid (1995).

$T_{\min} = 0.759$, $T_{\max} = 0.898$

5719 measured reflections

973 independent reflections

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

$R_{\text{int}} = 0.065$

$\theta_{\max} = 26.2^\circ$, $\theta_{\min} = 3.8^\circ$

$h = -5 \rightarrow 6$

$k = -20 \rightarrow 15$

$l = -12 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.061$

$S = 1.07$

973 reflections

96 parameters

1 restraint

$w = 1/[\sigma^2(F_o^2) + (0.0197P)^2 + 0.4838P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.6$ e Å⁻³

$$\Delta\rho_{\min} = -0.64 \text{ e } \text{\AA}^{-3}$$

Extinction correction: SHELXL-2017/1
(Sheldrick 2015),
 $F_c^* = kF_c [1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0014 (4)

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Al1	0.63528 (15)	−0.07769 (4)	0.59968 (7)	0.0076 (2)	0.6196 (19)
Co1	0.63528 (15)	−0.07769 (4)	0.59968 (7)	0.0076 (2)	0.3804 (19)
Al2	0.1321 (2)	−0.02939 (7)	0.75	0.0068 (4)	0.761 (4)
Co2	0.1321 (2)	−0.02939 (7)	0.75	0.0068 (4)	0.239 (4)
Al3	0.2463 (3)	0.16550 (9)	0.75	0.0043 (3)	
Al4	0.3045 (3)	0.25	0.5	0.0062 (4)	
Ca1	0.80287 (14)	0.10873 (4)	0.57559 (7)	0.0093 (2)	
Ca2	0.7833 (2)	0.20768 (6)	0.25	0.0131 (3)	
O1	0.5811 (6)	0.1666 (2)	0.75	0.0085 (8)	
O2	0.0758 (7)	0.0742 (2)	0.75	0.0102 (8)	
O3	0.4655 (8)	−0.0615 (2)	0.75	0.0192 (10)	
O4	0.1005 (5)	0.21476 (14)	0.6201 (2)	0.0084 (6)	
O5	0.5	0	0.5	0.0174 (9)	
O6	0.4916 (5)	−0.17398 (15)	0.5570 (2)	0.0130 (6)	
O7	−0.0172 (5)	−0.07854 (19)	0.8828 (2)	0.0249 (7)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0068 (4)	0.0079 (5)	0.0082 (4)	−0.0011 (3)	−0.0006 (3)	−0.0001 (3)
Co1	0.0068 (4)	0.0079 (5)	0.0082 (4)	−0.0011 (3)	−0.0006 (3)	−0.0001 (3)
Al2	0.0072 (7)	0.0052 (7)	0.0080 (7)	0.0001 (5)	0	0
Co2	0.0072 (7)	0.0052 (7)	0.0080 (7)	0.0001 (5)	0	0
Al3	0.0042 (8)	0.0054 (8)	0.0034 (7)	−0.0015 (6)	0	0
Al4	0.0072 (8)	0.0058 (8)	0.0056 (8)	0	0	0.0003 (6)
Ca1	0.0080 (4)	0.0119 (4)	0.0080 (4)	−0.0004 (3)	−0.0010 (3)	−0.0005 (3)
Ca2	0.0116 (6)	0.0077 (6)	0.0200 (6)	−0.0011 (5)	0	0
O1	0.0035 (19)	0.013 (2)	0.0085 (17)	0.0022 (15)	0	0
O2	0.009 (2)	0.010 (2)	0.0120 (18)	0.0015 (15)	0	0
O3	0.021 (2)	0.026 (3)	0.011 (2)	0.0087 (19)	0	0
O4	0.0083 (13)	0.0085 (15)	0.0083 (12)	−0.0018 (10)	−0.0007 (11)	0.0021 (10)
O5	0.017 (2)	0.017 (2)	0.018 (2)	−0.0078 (17)	0.0023 (18)	0.0007 (17)
O6	0.0126 (15)	0.0155 (16)	0.0109 (13)	0.0068 (12)	−0.0013 (11)	−0.0033 (11)
O7	0.0163 (16)	0.043 (2)	0.0152 (14)	−0.0090 (14)	−0.0037 (13)	0.0088 (14)

Geometric parameters (Å, °)

T1—O7 ⁱ	1.794 (3)	T4—O4 ^v	1.758 (2)
T1—O5	1.8194 (7)	Ca1—O6 ^{iv}	2.342 (3)
T1—O6	1.831 (3)	Ca1—O1	2.389 (2)
T1—O3	1.847 (2)	Ca1—O7 ^{vi}	2.389 (3)
T2—O2	1.759 (4)	Ca1—O4 ^{vii}	2.391 (3)
T2—O3	1.794 (4)	Ca1—O2 ^{vii}	2.402 (2)
T2—O7	1.810 (3)	Ca1—O5	2.5273 (8)
T2—O7 ⁱⁱ	1.810 (3)	Ca2—O1 ^v	2.348 (4)
T3—O1	1.719 (4)	Ca2—O4 ^{viii}	2.503 (3)
T3—O2	1.762 (4)	Ca2—O4 ^{ix}	2.503 (3)
T3—O4 ⁱⁱ	1.780 (3)	Ca2—O6 ^{vi}	2.561 (3)
T3—O4	1.780 (3)	Ca2—O6 ^{iv}	2.561 (3)
T4—O6 ⁱⁱⁱ	1.758 (3)	Ca2—O3 ^{iv}	2.762 (4)
T4—O6 ^{iv}	1.758 (3)	Ca2—O7 ^{iv}	2.852 (3)
T4—O4	1.758 (2)	Ca2—O7 ^{vi}	2.852 (3)
O7 ⁱ —T1—O5	116.51 (11)	O2 ^{vii} —Ca1—O5	115.65 (9)
O7 ⁱ —T1—O6	114.80 (13)	O1 ^v —Ca2—O4 ^{viii}	79.73 (9)
O5—T1—O6	109.33 (9)	O1 ^v —Ca2—O4 ^{ix}	79.73 (9)
O7 ⁱ —T1—O3	112.30 (14)	O4 ^{viii} —Ca2—O4 ^{ix}	67.34 (11)
O5—T1—O3	102.92 (12)	O1 ^v —Ca2—O6 ^{vi}	87.38 (8)
O6—T1—O3	98.95 (16)	O4 ^{viii} —Ca2—O6 ^{vi}	156.79 (9)
O2—T2—O3	116.90 (19)	O4 ^{ix} —Ca2—O6 ^{vi}	91.52 (8)
O2—T2—O7	112.29 (13)	O1 ^v —Ca2—O6 ^{iv}	87.38 (8)
O3—T2—O7	105.50 (13)	O4 ^{viii} —Ca2—O6 ^{iv}	91.52 (8)
O2—T2—O7 ⁱⁱ	112.29 (13)	O4 ^{ix} —Ca2—O6 ^{iv}	156.79 (9)
O3—T2—O7 ⁱⁱ	105.50 (13)	O6 ^{vi} —Ca2—O6 ^{iv}	107.20 (12)
O7—T2—O7 ⁱⁱ	103.2 (2)	O1 ^v —Ca2—O3 ^{iv}	126.24 (12)
O1—T3—O2	120.38 (18)	O4 ^{viii} —Ca2—O3 ^{iv}	139.56 (7)
O1—T3—O4 ⁱⁱ	114.55 (12)	O4 ^{ix} —Ca2—O3 ^{iv}	139.56 (7)
O2—T3—O4 ⁱⁱ	101.18 (12)	O6 ^{vi} —Ca2—O3 ^{iv}	63.24 (7)
O1—T3—O4	114.55 (12)	O6 ^{iv} —Ca2—O3 ^{iv}	63.24 (7)
O2—T3—O4	101.18 (12)	O1 ^v —Ca2—O7 ^{iv}	150.06 (6)
O4 ⁱⁱ —T3—O4	102.48 (17)	O4 ^{viii} —Ca2—O7 ^{iv}	113.33 (9)
O6 ⁱⁱⁱ —T4—O6 ^{iv}	106.90 (19)	O4 ^{ix} —Ca2—O7 ^{iv}	81.05 (8)
O6 ⁱⁱⁱ —T4—O4	110.19 (11)	O6 ^{vi} —Ca2—O7 ^{iv}	70.38 (8)
O6 ^{iv} —T4—O4	111.36 (12)	O6 ^{iv} —Ca2—O7 ^{iv}	117.70 (9)
O6 ⁱⁱⁱ —T4—O4 ^v	111.36 (12)	O3 ^{iv} —Ca2—O7 ^{iv}	61.43 (9)
O6 ^{iv} —T4—O4 ^v	110.19 (11)	O1 ^v —Ca2—O7 ^{vi}	150.06 (6)
O4—T4—O4 ^v	106.90 (18)	O4 ^{viii} —Ca2—O7 ^{vi}	81.05 (8)
O6 ^{iv} —Ca1—O1	88.56 (9)	O4 ^{ix} —Ca2—O7 ^{vi}	113.33 (9)
O6 ^{iv} —Ca1—O7 ^{vi}	82.78 (10)	O6 ^{vi} —Ca2—O7 ^{vi}	117.70 (9)
O1—Ca1—O7 ^{vi}	167.86 (11)	O6 ^{iv} —Ca2—O7 ^{vi}	70.38 (8)
O6 ^{iv} —Ca1—O4 ^{vii}	100.70 (9)	O3 ^{iv} —Ca2—O7 ^{vi}	61.43 (9)
O1—Ca1—O4 ^{vii}	81.24 (10)	O7 ^{iv} —Ca2—O7 ^{vi}	59.64 (11)
O7 ^{vi} —Ca1—O4 ^{vii}	91.99 (9)	T2—O2—T3	140.8 (2)

O6 ^{iv} —Ca1—O2 ^{vii}	163.33 (10)	T2—O3—T1 ⁱⁱ	119.61 (11)
O1—Ca1—O2 ^{vii}	76.74 (10)	T2—O3—T1	119.61 (11)
O7 ^{vi} —Ca1—O2 ^{vii}	110.44 (10)	T1 ⁱⁱ —O3—T1	120.8 (2)
O4 ^{vii} —Ca1—O2 ^{vii}	69.64 (11)	T4—O4—T3	118.32 (15)
O6 ^{iv} —Ca1—O5	75.31 (7)	T1—O5—T1 ^{iv}	180.00 (4)
O1—Ca1—O5	104.40 (9)	T4 ^{iv} —O6—T1	119.00 (15)
O7 ^{vi} —Ca1—O5	81.67 (7)	T1 ^x —O7—T2	119.94 (16)
O4 ^{vii} —Ca1—O5	172.84 (7)		

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