Ca$_3$GeO$_4$Cl$_2$ with a norbergite-like structure

Günther J. Redhammer,[a]* Georg Roth[b] and Georg Amthauer[a]

[a]Department of Materials Science, Division of Mineralogy, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria, and [b]Institute of Crystallography, RWTH Aachen University, Jägerstrasse 17/19, D-52056 Aachen, Germany
Correspondence e-mail: guenther.redhammer@aon.at

The title compound, tricalcium monogermanate dichloride, is orthorhombic and consists of one distinct Ge site on special position 4c, site symmetry m, and two different Ca sites, Ca1 and Ca2, one on general position 8d, site symmetry 1, and the other on special position 4c. Two of the O atoms occupy the 4c position (symmetry m); the third O atom is situated on the general 8d position, symmetry 1, as is the one distinct Cl position. By sharing common edges, the distorted Ca1 octahedra form infinite crankshaft-like chains parallel to the b direction. Along a and c, these chains are connected to one another via common corners, thereby forming a three-dimensional framework of edge- and corner-sharing Ca1O$_4$Cl$_2$ octahedra. Triangular prisms of Ca2O$_4$Cl$_2$ polyhedra and GeO$_4$ tetrahedra fill the interstitial space within the Ca1 polyhedral framework. Relationships between the structures of the title compound and the humite-type materials norbergite (Mg$_3$SiO$_4$F$_2$) and Mn$_3$SiO$_4$F$_2$ are discussed.

Comment

As part of our investigations of Ca germanates with clino-pyroxene and olivine-type structures, the title compound was obtained during attempts to synthesize CaFeGeO$_4$ from a CaCl$_2$ flux. Ca$_3$GeO$_4$Cl$_2$ is, to the best of our knowledge, the first calcium–germanate–chloride compound reported so far; no corresponding entries were found in the Inorganic Crystal Structure Database (ICSD, 2006) or in the Powder Diffraction File (ICDD, 1999). Czaya & Bissert (1971) reported the crystal structure of Ca$_3$SiO$_4$Cl$_2$, representing the silicate analogue of the title compound in the chemical sense. The silicate compound, however, is monoclinic, P2$_1$/c, and forms a structure distinctly different to that found for the germanate reported here. The structure of Ca$_3$SiO$_4$Cl$_2$ can be described in terms of two different sheet systems (Czaya & Bissert, 1971), the first containing a two-dimensional network of corner- and edge-sharing irregularly shaped sixfold-coordinated Ca1O$_2$Cl$_4$ polyhedra within the bc plane. The second sheet system is built

up by infinite chains of edge-sharing triangular Ca3O$_6$ prisms, which are parallel to the b axis and which are connected laterally to one another via common corners by isolated SiO$_4$ tetrahedra. Perpendicular to the Ca3 polyhedral chain, the sevenfold-coordinated Ca2O$_4$Cl$_3$ polyhedra form a second chain via corner sharing; this is also part of the second sheet system within the bc plane and interconnects the two systems along a. The sheet-like structure of Ca$_3$SiO$_4$Cl$_2$ is fundamentally different from that of the title compound, described below. The topology of the title compound is, however, related to the structure of the humite-type mineral norbergite, Mg$_3$SiO$_4$F$_2$ (Gibbs & Ribbe, 1969; Camara, 1997), and synthetic Mn$_3$SiO$_4$F$_2$ (Zenser et al., 2000). This is further reflected by similar lattice parameters and the same space-group symmetry. Some basic structural parameters are included in Table 1.

The crystal structure of the title compound contains one distinct Ge site, two distinct Ca sites, three O-atom positions and one Cl position. An anisotropic displacement plot, containing the atomic nomenclature, is given in Fig. 1, while Figs. 2 and 3 are polyhedral representations. The structure can be described in terms of infinite crankshaft-like chains of edge-sharing Ca1 octahedra (Fig. 2). Along a, these chains are connected to each other via isolated GeO$_4$ tetrahedra and the isolated sixfold-coordinated Ca2 sites. Within the crankshaft-like chain, two different Ca1···Ca1 distances can be identified: the shorter is aligned parallel to b, with Ca1···Ca1^i = 3.513 (1) Å, while the longer forms an angle of ~120° with b and has Ca1···Ca1^{vi} = 4.385 (1) Å [symmetry codes: (i) x, −y + $\frac{1}{2}$, z; (vi) −x + 1, −y, −z + 1]. The next nearest Ca1 octahedral chains are displaced along the ⟨101⟩ directions by a/2 and c/2, the symmetry equivalents of Ca1 being Ca1^v and Ca1^{vii}, and the congeners of Ca1^i being Ca1^{iv} and Ca1^{viii}, respectively [symmetry codes: (iv) x + $\frac{1}{2}$, y, −z + $\frac{3}{2}$; (v) −x + $\frac{1}{2}$, −y, z − $\frac{1}{2}$; (vii) −x + $\frac{1}{2}$, −y, z + $\frac{1}{2}$; (viii) x + $\frac{1}{2}$, y, −z + $\frac{1}{2}$]. Thus, one central Ca1 chain has four nearest chains, which are connected to one another via common corners, thereby forming a dense framework of Ca1 polyhedra (Fig. 3a). The shortest interchain interatomic distance between neighboring Ca1 atoms of different chains (e.g. Ca1···Ca1^{iv} or Ca1···Ca1^v) is 3.871 (1) Å. The interstitial space is filled by GeO$_4$ tetra-
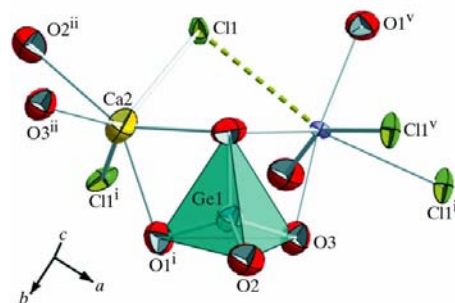

Figure 1
A view of the title compound, shown with 95% probability displacement ellipsoids. [Symmetry codes: (i) x, −y + $\frac{1}{2}$, z; (ii) x − $\frac{1}{2}$, −y + $\frac{1}{2}$, −z + $\frac{1}{2}$; (iii) x, y, z + 1; (iv) x + $\frac{1}{2}$, y, −z + $\frac{3}{2}$; (v) −x + $\frac{1}{2}$, −y, z − $\frac{1}{2}$.]

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hedra and sixfold-coordinated Ca2 sites. Viewed on their own, these two polyhedra form a chain parallel to the a direction and thus perpendicular to the Ca1 octahedral chain (Fig. 3b). Within this chain, the GeO$_4$ tetrahedra alternate with the Ca2 polyhedra; the connection of these polyhedra also alternates between edge and corner sharing.

The coordination polyhedron around the Ca1 site can be described as a distinctly distorted octahedron, having four short Ca—O and two long Ca—Cl bonds (Table 1). The next nearest Cl atom is 3.207 (2) Å away from Ca1 (the dashed line in Fig. 1). The two long bonds to Cl atoms are responsible for the distinct deviation from octahedral geometry, both the octahedral angle variance, OAV, and the quadratic octahedral elongation, OQE (Robinson *et al.*, 1971), being large (Table 2). Similarly large values can be found in the ScO$_6$ octahedra in the compound Cu$_2$Sc$_2$Ge$_4$O$_{13}$ (OAV $\simeq$ 211° and OQE $\simeq$ 1.056; Redhammer & Roth, 2004). The noteworthy point here is the remarkable topological similarity of the infinite Ca1 chain of the title compound and the ScO$_6$ chain in Cu$_2$Sc$_2$Ge$_4$O$_{13}$; both chains exhibit an identical crankshaft-like appearance with a *cis–trans* connection of individual edge-sharing octahedra, and four octahedra are needed to reach the next symmetry-equivalent octahedron along b (equal to the unit-cell dimension). When taking into account the size difference between Ca^{2+} [ionic radius $r = 1.00$ Å for sixfold coordination (Shannon & Prewitt, 1969)] and Sc^{3+} ($r = 0.73$ Å for sixfold coordination), the b axes in both compounds are comparable. However, it should be noted that the inter-chain connection is distinctly different in the two compounds, especially along c. While the title compound can be understood as a framework of Ca1 octahedra, Cu$_2$Sc$_2$Ge$_4$O$_{13}$ displays a sheet-like structure with Cu– and Sc–oxygen polyhedral sheets separated from each other by Ge$_4$O$_{13}$ units along c.

In Mg$_3$SiO$_4$F$_2$, the M1 site is also sixfold coordinated, forming a zigzag chain of edge-sharing MgO$_4$F$_2$ octahedra similar to that in the title compound but with polyhedral distortion parameters of approximately one-third of those

found in Ca$_3$GeO$_4$Cl$_2$ (Table 1). This is due to the close similarity between Mg—O and Mg—F bonds, while Ca—O and Ca—Cl bonds differ distinctly. In Mn$_3$SiO$_4$F$_2$ (Zenser *et al.*, 2000), the M1 octahedra are also regular (Table 1), forming the same wavelike chains passing through the structure along b; differences in average bond lengths clearly reflect the cationic size differences between Mg^{2+}, Mn^{2+} and Ca^{2+}. A comparison of the title compound with the olivine-type material Ca$_2$GeO$_4$ is also worthy of discussion. This germanate olivine contains a realization of a somewhat more regular octahedral coordination of Ca^{2+} (Redhammer *et al.*, 2007). Here, Ca^{2+} on the smaller M1 site has Ca—O bond lengths between 2.330 (1) and 2.407 (2) Å, while the larger M2 site has Ca—O values between 2.295 (2) and 2.458 (2) Å (Redhammer & Roth, 2007), and the polyhedral distortion parameters are distinctly smaller than those of the title compound (Table 2). It is evident that the Ca—O bonds in the title compound are similar to those in Ca$_2$GeO$_4$, while the Ca—Cl bonds are quite different from these values (owing to the larger size of Cl$^-$) and cause the large polyhedral distortion.

In Ca$_3$GeO$_4$Cl$_2$, the Ca1 octahedron is characterized by a high degree of edge and corner sharing with neighboring polyhedra. It shares two of its edges with two neighboring Ca1 sites (thus forming the Ca1 chain along b), while two out of the four O-atom corners are common to two Ca1 octahedra from two different chains. One edge is common to the Ca1 and Ca2 polyhedra, while four corners of Ca1O$_6$ are also corners of four neighboring Ca2O$_6$ polyhedra. Finally, one edge is common to the Ca1 octahedron and the GeO$_4$ tetrahedron. This common O1–O3 edge is the shortest among the octahedral edges [2.755 (1) Å], while the longest is the Cl1^{iv}–Cl1^v edge [3.565 (1) Å]. The bond-valence sums, S (Brese & O'Keeffe, 1991), are ideal for the Ca1 site [$S = 2.00$ valence units (v.u.)].

The Ca2 site is also sixfold coordinated, the coordination polyhedron being close to a triangular prism. Three short bonds connect atom Ca2 to O atoms of the O1/O1^i/O3^{ii} triangular face [symmetry codes: (i) x, $-y + \frac{1}{2}$, z; (ii) $x - \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$], which defines the lower base of the triangular prism, having common corners with octahedra of one and the same crankshaft-like Ca1 chain. However, this lower base shares one of its edges with a neighboring GeO$_4$ tetrahedron. The upper triangular face of the Ca2 prism is formed by Cl1/Cl1^i/O2^{ii} and shows distinctly longer bond lengths to Ca2 (Table 1). This upper triangular face fits into a triangular area between two edge-sharing Ca1 octahedra of the next higher crankshaft-like Ca1 chain along the c direction. Thus, the upper triangular face of the Ca2 prism shares two edges with two neighboring Ca1 polyhedra. The Ca2 triangular prisms are isolated from each other but connect individual crankshaft-like Ca1 chains to one another along the a axis. The bond-valence sum for Ca2 is lower than expected ($S = 1.85$).

For the Ca2 (M2) site, some more evident differences do exist between the structure of the title compound and the norbergite-type structures of Mg$_3$SiO$_4$F$_2$ and Mn$_3$SiO$_4$F$_2$. Here, the M2 site is in a true octahedral coordination. Similar to the olivine-type structure, M2 in norbergite is somewhat
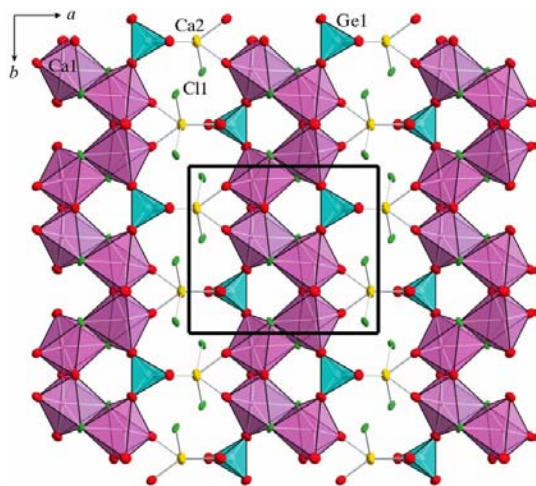

Figure 2
A polyhedral representation of the structure of the title compound, viewed along c. Polyhedra for the Ca2 site are not shown in order to highlight the crankshaft-like chains of Ca1 polyhedra.

larger in size and polyhedral distortion (Table 1), but clearly less distorted than the $M2$ site in both the title compound and the olivine Ca_2GeO_4 (Redhammer & Roth, 2007). The $M2$ site in $Mg_3SiO_4F_2$ is laterally attached to the zigzag chain of $M1$ *via* three common edges, while in the title compound the Ca2 site is attached to the Ca1 chain only *via* two common corners (Fig. 2). It should also be noted that the $M2$ octahedron in norbergite only shares common corners with the next higher and lower zigzag chains along c, while the title compound shares common edges through the upper triangular face Cl1^i/Cl1^i/O2^{ii} of the Ca2 prism. Additionally, no common edge, but only one common corner with the neighboring tetrahedral site, is found in the norbergite structure, while the title compound shares a common edge with the GeO_4 tetrahedron. All these differences are due to the distinct distortion of the structure as a consequence of the Cl^- incorporation.

The GeO_4 tetrahedra in $Ca_3GeO_4Cl_2$ are not connected to one another. Two of their edges are common to the tetrahedron and neighboring Ca1 polyhedra (O1–O1^i and O1–O3), and two are common to neighboring Ca2 sites (O1–O2). Bond angles opposite the common edges are smaller than the ideal $O-T-O$ values (Table 1), while those opposite the non-common edges are larger. As a consequence, the tetrahedron

suffers a trigonal C_{3v} distortion and is stretched towards atom O2. Thus, the tetrahedral distortion parameters are quite large (Table 2). In olivine-type Ca_2GeO_4, the basal plane edges of the isolated GeO_4 tetrahedra also are common to two $M1$ and one $M2$ sites, and the tetrahedron exhibits the same prolate aspect of basal plane $O-T-O$ bond angles, with a trigonal C_{3v} distortion and an elongation towards the apex O atom. As the number of common edges is lower in the olivine-type compound, the tetrahedral distortion parameters for the Ge site in that compound are lower (Table 2). For comparison, regular GeO_4 tetrahedra are realized in the compound $Ca_{7.96}Cu_{0.04}Ge_5O_{18}$. There, the isolated Ge3 site has no common edges with neighboring polyhedra and thus exhibits low tetrahedral angle variance and tetrahedral quadratic elongation values of $11.7°$ and 1.0034, respectively (Redhammer *et al.*, 2006).

As noted above, the structure of the title compound bares some remote similarities to the orthorhombic olivine-type structure of Ca_2GeO_4, which also shows *Pnma* symmetry at room temperature (Redhammer & Roth, 2007). The olivine $M1$ polyhedra (Ca1) form infinite stretched chains of edge-sharing CaO_6 octahedra parallel to the b axis. They are located at the center of the unit cell and at its corners, in close relation to the structure of the title compound, except that in $Ca_3GeO_4Cl_2$ these chains display a crankshaft character. The kinking of the Ca1 chain is presumably responsible for the differences in b lattice parameters compared with Ca_2GeO_4, where b is smaller by about one-third, while a and c are of similar size (Redhammer *et al.*, 2007). Owing to the elongation of the Ca1 polyhedra towards the Cl atoms in the title compound, individual Ca1 chains are connected to a framework, while the more regular Ca1 polyhedra in Ca_2GeO_4 form isolated chains. The incorporation of Cl atoms in the structure of the title compound also causes the Ca2 polyhedron to become a triangular prism without any connections to next-nearest Ca2 polyhedra, while the Ca2 sites in the olivine form a framework of corner-sharing $Ca2O_6$ octahedra. However, the spatial distribution of Ca2 sites within the unit cell is similar in the two compounds, as is the distribution of GeO_4 tetrahedra.

Experimental

The title compound was obtained during the synthesis of olivine-type $CaFeGeO_4$. For this synthesis, a homogeneous mixture (1 g) of $CaCO_3$, Fe, Fe_2O_3 and GeO_2, weighted in the molar ratio of $CaFe^{2+}GeO_4$, was placed in a platinum crucible together with $CaCl_2$ (2.5 g), serving as the high-temperature solution. This assemblage was transferred to a chamber furnace, heated to 1273 K at a rate of 100 K h^{-1}, held at this temperature for 12 h to ensure complete melting and decomposition of $CaCO_3$, and then cooled slowly to 1073 K at a rate of 6 K h^{-1}. After dissolving the flux with hot water, the experimental yield consisted of hematite flakes up to 3 mm in diameter, colorless crystals of the title compound, bordeaux-red crystals of an as yet unidentified phase, black idiomorphic cubes of up to 150 μm, which transpired to be Ge- and Pt-containing brown millerite-type $Ca_2Fe_2O_5$ (Redhammer *et al.*, 2004), and a fine-grained powder of Ge andradite, $Ca_3Fe_2Ge_3O_{12}$.
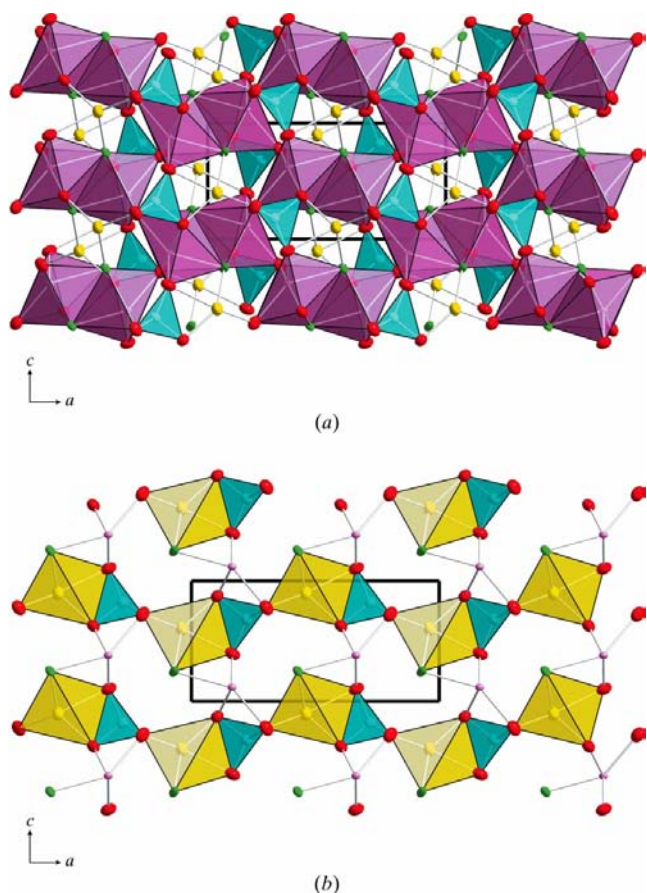
Figure 3
Polyhedral representations of the structure of the title compound, viewed along b. In (a), Ca2 polyhedra are not shown, while in (b), Ca1 polyhedra have been omitted to highlight chains of Ca2 polyhedra and GeO_4 tetrahedra along the a direction.

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Crystal data

Ca$_3$GeO$_4$Cl$_2$
$M_r = 327.73$
Orthorhombic, $Pnma$
$a = 11.7045$ (8) Å
$b = 10.3432$ (7) Å
$c = 5.7082$ (4) Å

$V = 691.05$ (8) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 7.37$ mm^{-1}
$T = 295$ (2) K
$0.19 \times 0.17 \times 0.11$ mm

Data collection

Bruker SMART APEX
  diffractometer
Absorption correction: numerical
  (*via* equivalents using *X-SHAPE*;
  Stoe & Cie, 1996)
  $T_{min} = 0.27$, $T_{max} = 0.44$

7796 measured reflections
908 independent reflections
880 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.057$
$S = 1.15$
908 reflections

53 parameters
$\Delta\rho_{max} = 1.05$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ge1—O2	1.742 (2)	Ca1—Cl1^v	2.8084 (8)
Ge1—O1	1.7570 (17)	Ca1—Cl1^{iv}	2.8429 (9)
Ge1—O3	1.767 (2)	Ca2—O3^{ix}	2.277 (2)
Ca1—O1^{vii}	2.2764 (18)	Ca2—O1	2.3967 (18)
Ca1—O3	2.3549 (16)	Ca2—O2^{ix}	2.667 (3)
Ca1—O2^{iii}	2.3703 (16)	Ca2—Cl1^i	2.7903 (8)
Ca1—O1	2.5638 (19)		
O2—Ge1—O1	120.11 (7)	O2—Ge1—O3	106.40 (11)
O1^i—Ge1—O1	102.07 (11)	O1—Ge1—O3	102.83 (7)

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

Structure solution using Patterson methods yielded the Ge and Ca positions, as well as an initially unidentified peak, which was identified as chlorine during the later refinement procedure. O-atom positions were located in a residual electron-density analysis. After full anisotropic refinement on F^2, the occupation factors of the cations were refined (while fixing the anisotropic atomic displacement parameters to avoid infinite correlations) and refined to values corresponding to full occupation within one standard deviation. In the final refinement cycles, site-occupation factors were again fixed to ideal values.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.70.01; Farrugia, 1999).

Table 2
Selected structural parameters of Ca$_3$GeO$_4$Cl$_2$ in comparison with Ca$_2$GeO$_4$ (Redhammer *et al.*, 2007), norbergite (Mg$_3$SiO$_4$F$_2$; Gibbs & Ribbe, 1969) and Mn$_3$SiO$_4$F$_2$ (Zenser *et al.*, 2000).

	Ca$_3$GeO$_4$Cl$_2$	Ca$_2$GeO$_4$	Mg$_3$SiO$_4$F$_2$	Mn$_3$SiO$_4$F$_2$
T site				
$\langle T-O \rangle$ (Å)	1.756	1.765	1.630	1.630
$\langle O-O \rangle$ (Å)	2.853	2.873	2.654	2.654
BLD^a (%)	0.40	0.57	0.56	0.72
Volume (Å^3)	2.705	2.779	2.193	2.196
TAV^b (°)	75.72	47.74	41.32	35.55
TQE^c	1.0179	1.0108	1.0093	1.0079
S^d (v.u.)	3.92	3.83	4.01	3.95
*M*1 site				
$\langle M1-X \rangle$ (Å)	2.535	2.362	2.068	2.170
$\langle X-X \rangle$ (Å)	3.506	3.324	2.915	3.055
BLD^a (%)	7.97	1.25	3.03	2.67
Volume (Å^3)	19.348	16.529	11.515	13.169
OAV^e (°)	232.84	149.57	56.50	79.77
OQE^f	1.0894	1.0422	1.0174	1.0240
S^d (v.u.)	2.01	2.07	2.00	2.00
*M*2 site				
$\langle M2-X \rangle$ (Å)	2.553	2.397	2.104	2.203
$\langle X-X \rangle$ (Å)	3.358	3.368	2.958	3.091
BLD$_a$ (%)	7.69	2.34	4.31	5.17
Volume (Å^3)	16.825	17.413	12.029	13.628
OAV^e (°)	–	129.76	75.64	106.13
OQE^f	–	1.0368	1.0236	1.0324
S^d (v.u.)	1.85	1.90	1.89	1.89

Notes: (*a*) bond length distortion, BLD $= (100/n)\sum_{i=1}^{n}\{[(X-O)_i - \langle X-O \rangle]/\langle X-O \rangle\}$, where *n* is the number of bonds, $(X-O)_i$ is the central cation-to-oxygen length and $\langle X-O \rangle$ is the average cation–oxygen bond length (Renner & Lehmann, 1986); (*b*) tetrahedral angle variance, TAV $= \sum_{i=1}^{n}(\Theta_i - 109.47)^2/5$ (Robinson *et al.*, 1971); (*c*) tetrahedral quadratic elongation, TQE $= \sum_{i=1}^{4}(l_i/l_t)^2/4$, where l_t is the center-to-vertex distance for a regular tetrahedron whose volume is equal to that of the undistorted tetrahedron with bond length l_i (Robinson *et al.*, 1971); (*d*) bond-valence sum, *S* (Brese & O'Keeffe, 1991); (*e*) octahedral angle variance, OAV $= \sum_{i=1}^{n}(\Theta_i - 90)^2/11$ (Robinson *et al.*, 1971); (*f*) octahedral quadratic elongation, OQE $= \sum_{i=1}^{6}(l_i/l_o)^2/6$, where l_o is the center-to-vertex distance for a regular octahedron whose volume is equal to that of the undistorted octahedron with bond length l_i (Robinson *et al.*, 1971).

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