

O3	0.1784 (7)	0.253 (1)	0.116 (2)	0.0024 (5)
O4	0.1851 (6)	0.115 (1)	0.392 (1)	0.0024 (5)
O5	0.1911 (6)	0.635 (1)	0.368 (1)	0.0024 (5)
O6	0.3037 (7)	0.749 (1)	0.357 (2)	0.0024 (5)
O7	0.3119 (6)	0.370 (1)	0.123 (1)	0.0024 (5)
O8	0.3274 (6)	0.126 (1)	0.135 (1)	0.0024 (5)
O9	0.4385 (7)	0.128 (1)	0.056 (1)	0.0024 (5)
O10	0.4326 (7)	0.250 (1)	0.306 (1)	0.0024 (5)
O11	0.4405 (7)	0.372 (1)	0.053 (1)	0.0024 (5)
O12	0.068 (1)	0	0.196 (2)	0.0024 (5)
O13	0.2030 (9)	0	0.655 (2)	0.0024 (5)
O14	0.3148 (9)	0	0.386 (2)	0.0024 (5)
O15	0.313 (1)	0	0.885 (2)	0.0024 (5)
O16	0.429 (1)	0	0.304 (2)	0.0024 (5)

Table 2. Selected geometric parameters (\AA , °)

Ti4—O12	1.83 (2)	Ti5—O14	1.89 (2)
Ti4—O1	1.91 (1)	Ti5—O5 ⁱⁱ	1.96 (1)
Ti4—O1 ⁱ	1.91 (1)	Ti5—O5 ⁱⁱⁱ	1.96 (1)
Ti4—O4	1.95 (1)	Ti5—O4	2.10 (1)
Ti4—O4 ⁱ	1.95 (1)	Ti5—O4 ⁱ	2.10 (1)
Ti4—O13	2.66 (1)	Ti5—O13	2.10 (1)
O12—Ti4—O1	98.4 (5)	O1 ⁱ —Ti4—O13	90.7 (4)
O12—Ti4—O1 ⁱ	98.4 (5)	O1—Ti4—O4 ⁱ	164.7 (5)
O12—Ti4—O4	96.2 (5)	O1—Ti4—O4	88.9 (5)
O12—Ti4—O4 ⁱ	96.2 (5)	O1—Ti4—O13	90.7 (4)
O12—Ti4—O13	166.7 (7)	O4 ⁱ —Ti4—O4	84.7 (5)
O1 ⁱ —Ti4—O1	93.8 (5)	O4—Ti4—O13	74.2 (4)
O1 ⁱ —Ti4—O4 ⁱ	88.9 (5)	O4—Ti4—O13	74.2 (4)
O1 ⁱ —Ti4—O4	164.7 (5)		

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

Data collection was performed using *PC-APD* software (Philips Electronics, 1997). The measurement was carried out using programmable optics for the primary and secondary paths. The sample was spun during the measurement, and the irradiated area had a width and a length of 10 mm. For data reduction, and cell and structure refinement, the program *PC-Rietveld Plus* (Philips Electronics, 1993) was used. Cell parameters and atomic sites were taken from the isostructural compound Ba₄Al₂Ti₁₀O₂₇ (Schmachtel & Müller-Buschbaum, 1981). The profile shape was corrected for peak asymmetry up to $2\theta = 30.1^\circ$ (Rietveld, 1969). In addition, lattice and structure parameters, zero-point shift, six background parameters and the scale factor were refined. A refinement of the isotropic displacement parameters was possible for the barium sites. For the titanium sites, as well as for the oxygen sites, a common displacement parameter was refined. The structural graphics were created with *ATOMS* (Dowty, 1997).

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Calcium pyroborate, Ca₂B₂O₅

QI-SHENG LIN, WEN-DAN CHIENG, JIU-TONG CHEN AND JIN-SHUN HUANG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China. E-mail: cwd@ms.fjirsm.ac.cn

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Abstract

The title compound was synthesized by high-temperature solution reaction and its structure determined by X-ray diffraction techniques. The structure contains Ca₄O₁₉ tetramers which form double chains extending along the *a* direction. The double chains are linked to form layers and B₂O₅ groups bridge these adjacent chains and adjacent layers through O atoms to form a three-dimensional framework.

Comment

There are few papers on the CaO–B₂O₃ system in the literature. As examples, the detailed structures of Ca₃(BO₃)₂ (Schuckmann, 1969; Vegas *et al.*, 1975), Ca₂B₆O₁₁ (Zayakina & Brovkin, 1976) and CaB₄O₇ (Zayakina & Brovkin, 1977) have been reported.

CaB₂O₄ was found to be polymorphic under high pressure (Marezio *et al.*, 1963, 1969). The cell constants of Ca₂B₂O₅ have been determined previously by X-ray powder diffraction to be $a = 11.497(3)$, $b = 5.157(2)$, $c = 7.200(2)$ Å and $\beta = 92.91(2)^\circ$ (Schaefer, 1968), which are slightly different from those obtained by us. The detailed structure of Ca₂B₂O₅ determined by single-crystal X-ray techniques is reported here.

In monoclinic Ca₂B₂O₅, there are two crystallographically different Ca atoms. Ca1 is seven-coordinated in a monocapped distorted trigonal prism arrangement and Ca2 is six-coordinated in a distorted octahedral arrangement. The Ca1—O distances vary from 2.282(4) to 2.649(4) Å and the Ca2—O distances vary from 2.290(3) to 2.415(4) Å. Two Ca1O₇ polyhedra and two Ca2O₆ polyhedra share four O—O edges to form Ca₄O₁₉ tetramers (Fig. 1), which results in an infinite double chain extending along the a direction. These double chains are connected to form layers in the ac plane by sharing O atoms. Furthermore, these layers are stacked along the b direction to form a three-dimensional framework by sharing atoms O3, O4 and O5. The B₂O₅ groups bridge adjacent double chains and adjacent layers. The O atoms of each B₂O₅ group are not quite coplanar; the dihedral angle between the two slanting trigonal-planar BO₃ groups is 13.26°. Except for O1, which bonds to one Ca atom and two B atoms, the other O atoms bond to three Ca atoms and one B atom.

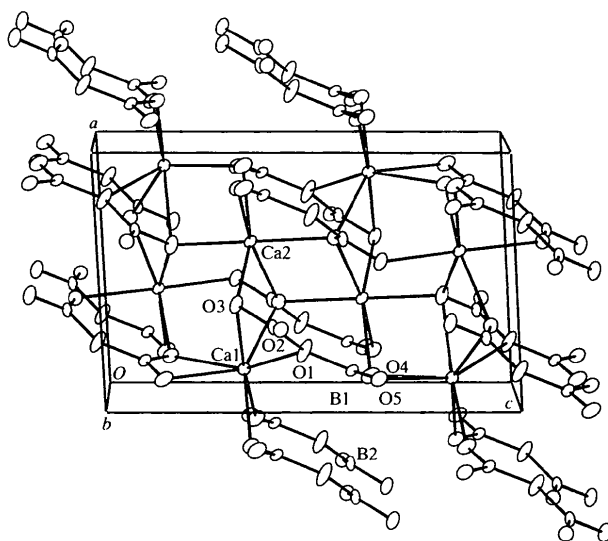


Fig. 1. Packing diagram viewed along the b direction. Displacement ellipsoids are drawn at the 80% probability level. The solid lines show a double chain.

The very anisotropic character of the displacement parameters of O1 is due to its coplanarity with the coordinating atoms; the anisotropy is perpendicular to the B—O—B plane.

Experimental

Crystals of the title compound were unexpectedly grown from an appropriate mixture of CaF₂, H₃BO₃ and Na₂CO₃ to produce fluoroborate. The mixture was preheated and thoroughly milled several times, then progressively heated in a platinum crucible in air to 1023 K for 6 h and then slowly cooled to 973 K at a rate of 10 K d⁻¹. Finally, the melt was cooled to room temperature whereupon colorless crystals were obtained.

Crystal data

Ca₂B₂O₅
 $M_r = 181.78$
 Monoclinic
 $P2_1/c$
 $a = 7.212(2)$ Å
 $b = 5.177(1)$ Å
 $c = 11.498(3)$ Å
 $\beta = 93.11(2)^\circ$
 $V = 428.6(4)$ Å³
 $Z = 4$
 $D_x = 2.82$ Mg m⁻³
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 7-13^\circ$
 $\mu = 2.51$ mm⁻¹
 $T = 293$ K
 Rectangular prism
 $0.50 \times 0.05 \times 0.05$ mm
 Colorless

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.422$, $T_{\max} = 0.862$
 3019 measured reflections
 2859 independent reflections

1407 reflections with $I > 3\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 40^\circ$
 $h = 0 \rightarrow 12$
 $k = 0 \rightarrow 9$
 $l = -20 \rightarrow 20$
 3 standard reflections every 200 reflections
 intensity decay: none

Refinement

Refinement on F
 $R = 0.0561$
 $wR = 0.0710$
 $S = 1.42$
 1407 reflections
 82 parameters
 $w = 1/[\sigma^2(F) + (0.020F)^2 + 1.0]$

$(\Delta/\sigma)_{\max} = 0.0002$
 $\Delta\rho_{\max} = 1.15$ e Å⁻³
 $\Delta\rho_{\min} = -1.89$ e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Ca1	0.8764 (1)	0.1011 (2)	0.16419 (8)	0.0058 (1)
Ca2	0.3819 (1)	0.0643 (2)	0.13299 (7)	0.0055 (1)
O1	0.7711 (5)	0.0931 (6)	0.5159 (3)	0.0107 (6)
O2	0.6437 (5)	-0.1785 (6)	0.0708 (3)	0.0077 (6)
O3	0.5909 (5)	0.4209 (7)	0.1744 (3)	0.0093 (6)
O4	1.1077 (5)	-0.1926 (7)	0.1418 (3)	0.0096 (6)
O5	0.8523 (4)	-0.1451 (6)	0.3430 (3)	0.0075 (6)
B1	0.8449 (6)	0.076 (1)	0.4044 (4)	0.0055 (8)
B2	0.6631 (7)	-0.061 (1)	0.5886 (4)	0.0060 (8)

Table 2. Selected geometric parameters (Å, °)

Ca1—O1 ⁱ	2.419 (3)	Ca2—O3 ^{iv}	2.333 (3)
Ca1—O2	2.423 (3)	Ca2—O4 ^v	2.390 (4)
Ca1—O3	2.649 (4)	Ca2—O5 ^{vi}	2.290 (3)
Ca1—O4	2.282 (4)	B1—O1	1.416 (6)
Ca1—O4 ⁱⁱ	2.470 (4)	B1—O4 ⁱⁱ	1.361 (6)
Ca1—O5	2.434 (3)	B1—O5	1.349 (6)
Ca1—O5 ⁱⁱⁱ	2.362 (3)	B2—O1	1.420 (6)
Ca2—O2	2.409 (4)	B2—O2 ^{vii}	1.368 (6)
Ca2—O2 ⁱⁱⁱ	2.413 (3)	B2—O3 ^{viii}	1.353 (6)
Ca2—O3	2.415 (4)		
O1 ⁱ —Ca1—O2	84.0 (1)	O2—Ca2—O3	88.1 (1)
O1 ⁱ —Ca1—O3	53.7 (1)	O2—Ca2—O4 ^v	112.7 (1)
O1 ⁱ —Ca1—O4	124.1 (1)	O2—Ca2—O5 ^{vi}	166.8 (1)
O1 ⁱ —Ca1—O4 ⁱⁱ	110.6 (1)	O3—Ca2—O3 ^{iv}	92.1 (1)
O1 ⁱ —Ca1—O5	154.8 (1)	O3—Ca2—O4 ^v	157.9 (1)
O1 ⁱ —Ca1—O5 ⁱⁱⁱ	80.8 (1)	O3—Ca2—O5 ^{vi}	86.0 (1)
O2—Ca1—O3	82.6 (1)	O4 ^v —Ca2—O5 ^{vi}	75.1 (1)
O2—Ca1—O4	92.6 (1)	B1—O1—B2	138.0 (4)
O2—Ca1—O5	89.0 (1)	O1—B1—O4 ⁱⁱ	114.5 (4)
O3—Ca1—O4	174.8 (1)	O1—B1—O5	123.6 (4)
O3—Ca1—O5	101.4 (1)	O4 ⁱⁱ —B1—O5	121.7 (4)
O4—Ca1—O4 ⁱⁱ	113.0 (1)	O1—B2—O2 ^{vii}	121.4 (4)
O4—Ca1—O5	80.3 (1)	O1—B2—O3 ^{viii}	111.8 (4)
O5—Ca1—O5 ⁱⁱⁱ	114.7 (1)	O2 ^{vii} —B2—O3 ^{viii}	126.7 (4)
O2—Ca2—O2 ⁱⁱⁱ	81.9 (1)		

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

The title structure was solved by direct methods [MULTAN83 (Main *et al.*, 1983) in *MolEN* (Fair, 1990)]. The positions of the Ca atoms were located by direct methods and those of the other atoms were located from successive difference Fourier syntheses. The structure was refined anisotropically using full-matrix least-squares techniques. The largest residual peak of $1.15 \text{ e } \text{Å}^{-3}$ is 0.93 Å from the Ca2 atom. An extinction correction was applied to see if it reduced the difference density, but it did not help.

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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The double-anion salts $M_3[\text{ZnCl}_4]\text{NO}_3$ ($M = \text{K}^+$ and NH_4^+)

ROBERT L. CARTER AND LEVERETT J. ZOMPA

Department of Chemistry, University of Massachusetts Boston, Boston, MA 02125-3393, USA. E-mail: robert.carter@umb.edu

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Abstract

The title compounds, tripotassium tetrachlorozincate nitrate, $\text{K}_3[\text{ZnCl}_4]\text{NO}_3$, and triammonium tetrachlorozincate nitrate, $(\text{NH}_4)_3[\text{ZnCl}_4]\text{NO}_3$, are newly discovered double-anion salts containing ZnCl_4^{2-} and NO_3^- ions. The compounds are isomorphous and contain minimally distorted anions. Hydrogen bonds to both Cl and O atoms in the ammonium compound have negligible distorting influence on anion geometries and appear only to orient the NH_4^+ cations.

Comment

Zompa & Haidar (1996) reported the structure of the tetrachlorocadmiate salt of a binucleating ligand, tetrahydrogen 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane, which forms a doubly positive 1:1 cationic complex with zinc ions in aqueous solution. Subsequent X-ray studies of a salt of the 1:1 zinc complex with this ligand (Zompa, 1999) showed that the counter-ion was the trichloro(nitrato)zincate(II) ion, $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$, a previously unreported species in which the nitrate ion is bound to zinc through a single O atom. As a result of this discovery, we have been pursuing studies to determine if salts of $[\text{ZnCl}_3(\text{NO}_3)]^{2-}$ can be produced with simpler cations, and if so, to determine