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$PbCa_2[Al_8O_{15}]$ with a novel three-dimensional aluminate anion

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The asymmetric unit of the title compound, lead(II) dicalcium octaaluminate, contains one Pb, one Ca, four Al and eight O atoms, with the Pb atom and one O atom situated on mirror planes. Three Al atoms exhibit slightly distorted tetrahedral coordinations with a mean Al—O bond length of 1.76 Å. The fourth Al atom is in a considerably distorted trigonal–bipyramidal coordination with a mean Al—O bond length of 1.89 Å. One AlO_4 tetrahedron forms infinite chains parallel to [100] *via* corner-sharing. These chains are linked by parallel chains of edge-sharing AlO_5 trigonal bipyramids into layers *A* of six-membered double rings extending parallel to (010). The second layer *B* is made up of the remaining two AlO_4 tetrahedra. These tetrahedra share corners, resulting in likewise six-membered double rings. Finally, the parallel layers *A* and *B* are linked into a three-dimensional framework by common corners. Charge compensation is achieved by the Pb^{2+} and Ca^{2+} cations, which are situated in the cavities of the anionic framework, and which are surrounded by seven and six O atoms, respectively, both within highly irregular coordination polyhedra.

Comment

Compared with the high number of known silicates, the number of structurally characterized aluminates is significantly smaller. However, as well as the tetrahedral XO_4 group as the main structural motif and the less frequently found octahedral XO_6 group observed in the multifarious structural chemistry of silicates (Liebau, 1985), trigonal–bipyramidal XO_5 groups are also known in the crystal chemistry of aluminates (Santamaría-Pérez & Vegas, 2003), albeit with only a few representatives, *e.g.* in the structure of the mineral andalusite, Al_2SiO_5 (Burnham & Buerger, 1961). Such a trigonal–bipyramidal AlO_5 group is also present in the crystal structure of the title aluminate, $PbCa_2[Al_8O_{15}]$, which was obtained serendipitously from a lead oxide flux.

The crystal structure of $PbCa_2[Al_8O_{15}]$ contains the novel three-dimensional $[Al_8O_{15}]^{6-}$ aluminate anion. Although the phases $BaCa_2[Al_8O_{15}]$ (Brisi & Montorsi, 1962) and $CsCa_2[Al_8O_{15}]$ (van Hoek *et al.*, 1989) have also been reported with the same composition for the anion, their crystal structures remain undetermined. The anion in the title compound is composed of three different AlO_4 tetrahedra (Al1–Al3) and one trigonal–bipyramidal AlO_5 group (Al4). The $Al1O_4$ tetrahedra are linked into infinite zweier single chains (Liebau, 1985) parallel to [100] *via* corner-sharing. These chains are corner-linked above and below their propagation by parallel chains of edge-sharing $Al4O_5$ trigonal bipyramids into layers *A* of six-membered double rings extending parallel to (010) (Fig. 1). The second layer *B* consists of the remaining $Al2O_4$ and $Al3O_4$ tetrahedra. Each of them is likewise assembled into infinite zweier single chains that are further linked *via* corner-sharing to build up six-membered double rings (Fig. 2). Since atom O2 that links two single ring layers is situated on a special position with site symmetry *m*, layer *B* is bisected by a mirror plane. Finally, layers *A* and *B* are linked by common corners along [010] into a three-dimensional anionic framework structure. The Ca^{2+} and Pb^{2+} cations are situated in the cavities of the *A* and *B* layers, respectively (Fig. 3).

The three AlO_4 tetrahedra are distorted, with Al—O distances in the range 1.7214 (13)–1.7758 (13) Å (average =

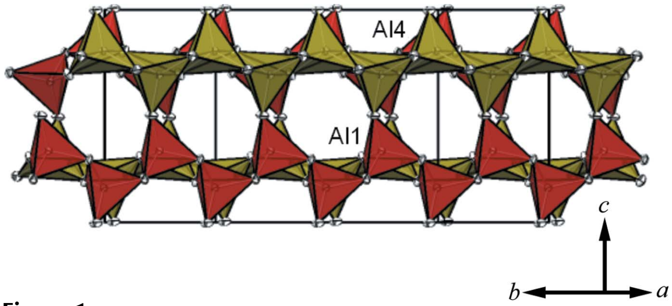

Figure 1
Layer *A*, composed of chains of corner-sharing $Al1O_4$ tetrahedra (light grey; red in the electronic version of the paper) and chains of edge-sharing $Al4O_5$ trigonal bipyramids (dark grey; yellow). Displacement ellipsoids are drawn at the 90% probability level.

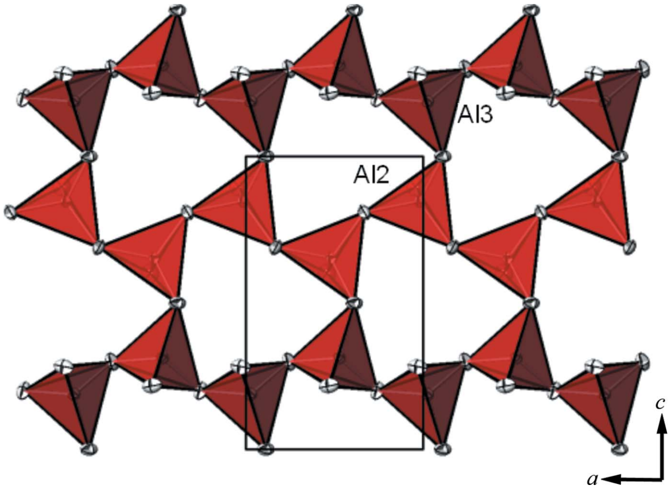

Figure 2
Layer *B*, composed of corner-sharing $Al2O_4$ and $Al3O_4$ tetrahedra. Displacement ellipsoids are drawn at the 90% probability level.

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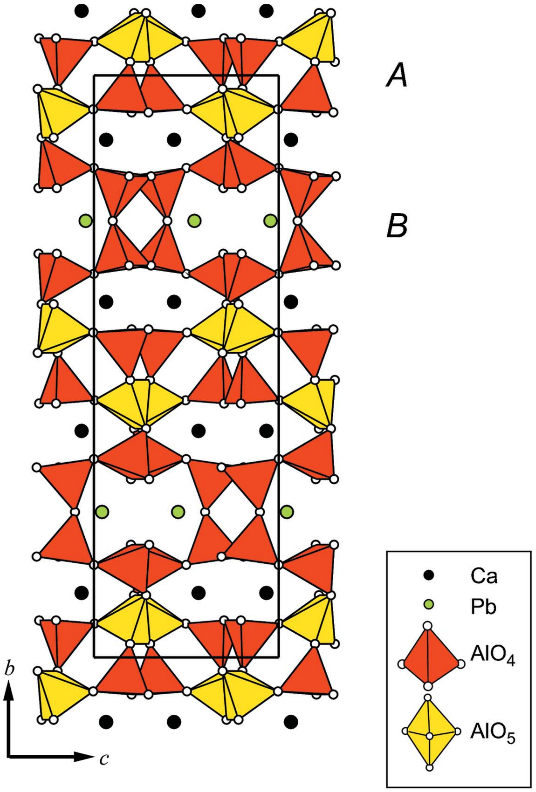

Figure 3
The structure of $PbCa_2[Al_8O_{15}]$ in a projection along [100].

1.76 Å) and O—Al—O angles between 101.27 (6)–119.09 (8)°. The AlO_5 group likewise shows a distortion, with three short Al4—O distances in the equatorial plane (average = 1.76 Å) and two longer but very different Al—O distances (Table 1) to the apices of the polyhedron, with an overall mean of 1.89 Å. A displacement of the Al atom by 0.230 (1) Å from the equatorial plane towards the more tightly bonded of the two apical O atoms is observed. The spread of interatomic distances and angles within the aluminate framework are in normal ranges (Santamaría-Pérez & Vegas, 2003) and match other structures where different AlO_x coordination polyhedra are present. For example, AlO_4, AlO_5 and AlO_6 polyhedra coexist in $Ca_4Al_6O_{13}$, which was prepared under high-pressure conditions (Kahlenberg *et al.*, 2000). In that structure, mean values of 1.78 Å for the Al—O distances in two AlO_4 tetrahedra, 1.86 Å in two AlO_5 trigonal bipyramids and 1.93 Å in three AlO_6 octahedra are observed. The ideal values for these polyhedra, calculated using the corresponding ionic radii for Al^{3+} and O^{2-} (Shannon, 1976), are 1.75, 1.84 and 1.90 Å, respectively.

Another structural aspect that has been used to classify aluminates is the distribution of Al···Al distances, which show two distinct maxima (Isea *et al.*, 1998). One sharp maximum is observed around 2.86 Å, which represents the Al···Al distance in elementary aluminium (face-centred cubic) and corresponds to the separation between two Al atoms which occupy edge-sharing AlO_6 octahedra. The second, broader, maximum is around 3.3 Å and coincides with the distribution of distances between two tetracoordinated Al atoms bridged by one O atom. In $PbCa_2[Al_8O_{15}]$, the Al4···Al4 distance of 2.8644 (8) Å between the two edge-sharing AlO_5 groups is in agreement with this concept, as are the Al1···Al1 and Al2···Al3 separations between two corner-sharing AlO_4 tetrahedra of 3.0980 (8) and 3.1323 (8) Å, respectively. However, the very short Al3···Al3 distance of 2.9040 (8) Å between two AlO_4 tetrahedra is too short with respect to this simple concept.

The Ca^{2+} cation exhibits a coordination number of 6 within a very irregular coordination polyhedron. The Ca—O distances vary between 2.2925 (13) and 2.7121 (13) Å (mean = 2.43 Å), in good agreement with numerous other CaO_6 polyhedra and with the overall mean of the average Ca—O distances for CaO_x polyhedra of 2.46 Å (Chiari, 1990). The Pb^{2+} cation is situated on a mirror plane in the cavities of the *B* layer of the anionic framework and is bonded to seven O atoms, with Pb—O bond lengths ranging from 2.2925 (12) to 3.2809 (14) Å. The resulting PbO_7 polyhedron is heavily distorted and shows the typical influence of a stereochemically active electron lone pair (Galy *et al.*, 1975). Most probably, the electron lone pair points towards the layer voids, which are arranged parallel to the [301] direction.

Bond-valence sum (BVS) analysis (Brown, 2002) using the parameters of Brese & O'Keeffe (1991) revealed slight deviations from the expected values of 2 valence units (v.u.) for the Ca, Pb and O atoms and 3 v.u. for the Al atoms. The deviations reflect the distortions in the PbO_7, CaO_6 and AlO_x polyhedra: Pb1 (coordination number = 7; BVS = 1.88 v.u.), Ca1 (6; 1.86), Al1 (4; 2.80), Al2 (4; 2.71), Al3 (4; 2.74), Al4 (5, 2.75), O1 (3; 1.84), O2 (3; 1.78), O3 (3; 1.86), O4 (4; 1.71), O5 (3, 1.69), O6 (3; 1.93), O7 (4; 1.99), O8 (4, 1.89).

Experimental

Single crystals of the title compound grew accidentally from an attacked corundum crucible during attempts to synthesize phases with new compositions in the system CaO–PbO–TeO_3 using a lead oxide flux. A mixture of $2PbCO_3{\cdot}Pb(OH)_2$ (1.16 g), $CaCO_3$ (0.075 g) and TeO_2 (0.117 g) was thoroughly ground in an agate mortar and placed in a corundum crucible. The reaction mixture was heated over a period of 18 h to 1233 K, kept at this temperature for 6 h and cooled over a period of 18 h to room temperature. A few colourless crystals of the title compound grew on top of a brick-red microcrystalline matrix that mainly consisted of minium (Pb_3O_4). The crystals were manually separated and cleaned under a polarizing microscope.

Crystal data

$PbCa_2[Al_8O_{15}]$
$M_r = 743.19$
Orthorhombic, *Pnma*
$a = 5.3702$ (1) Å
$b = 27.9903$ (4) Å
$c = 8.8811$ (1) Å
$V = 1334.95$ (3) $Å^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 14.02$ mm^{-1}
$T = 296$ K
0.12 × 0.12 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
$T_{min} = 0.187$, $T_{max} = 0.246$
39453 measured reflections
5602 independent reflections
5068 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Table 1
Selected bond lengths (Å).

Al1—O6	1.7214 (13)	Al3—O7	1.7676 (13)
Al1—O8^{i}	1.7470 (13)	Al3—O7^{iv}	1.7738 (14)
Al1—O8	1.7690 (13)	Al3—O5	1.7740 (14)
Al1—O1^{ii}	1.7708 (13)	Al4—O6	1.7230 (13)
Al2—O3	1.7496 (13)	Al4—O1	1.7797 (13)
Al2—O2	1.7589 (7)	Al4—O5	1.7811 (14)
Al2—O4	1.7709 (13)	Al4—O1^{v}	1.8567 (14)
Al2—O4^{iii}	1.7758 (13)	Al4—O5^{iv}	2.2849 (16)
Al3—O3	1.7262 (14)		

Symmetry codes: (i) $x-\frac{1}{2}, y, -z+\frac{3}{2}$; (ii) $-x+\frac{1}{2}, -y, z-\frac{1}{2}$; (iii) $x+\frac{1}{2}, y, -z+\frac{3}{2}$; (iv) $x+\frac{1}{2}, y, -z+\frac{5}{2}$; (v) $x-\frac{1}{2}, y, -z+\frac{5}{2}$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.060$
$S = 1.06$
5602 reflections
121 parameters
$\Delta\rho_{\max} = 3.91$ e Å^{-3}
$\Delta\rho_{\min} = -3.21$ e Å^{-3}

The largest positive and negative residual electron densities are located 0.55 and 0.38 Å, respectively, from atom Pb1. Reflection 020 was affected by the beam stop and was omitted from the refinement.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3070). Services for accessing these data are described at the back of the journal.

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