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Tricaesium undecalanthanum dodecaselenate(IV) dodecachloride

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(e–O) = 0.006 Å
R factor = 0.044
wR factor = 0.095
Data-to-parameter ratio = 26.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of the title compound, $Cs_3La_{11}(SeO_3)_{12}Cl_{12}$, consists of complex slabs of composition $[La_{22}(SeO_3)_{24}]$ that are stacked along the *a* axis and are separated by sublayers of either chloride anions or caesium chloride. All SeO_3 groups show the typical pyramidal shape. The Se—O bond distances vary from 1.672 (6) to 1.747 (6) Å.

Comment

Inorganic compounds with various anions attract attention because of the features of their crystal chemistry (Berdonosov *et al.*, 2000; Ruck & Schmidt, 2003; Lipp & Schleid, 2005; Ben Hamida & Wickleder, 2005). Therefore, we have systematically investigated the structural peculiarities of halide–selenates(IV) with complex cation compositions.

A view of the crystal structure of $Cs_3La_{11}(SeO_3)_{12}Cl_{12}$, (I), is shown in Fig. 1. Compound (I) contains six crystallographically independent La atoms, three Cs atoms, six Se atoms, 18 O atoms and nine Cl atoms. Atoms La1 and La2 are surrounded by four O atoms and four chloride anions, forming a distorted square antiprism (4 + 4 coordination) (Fig. 2); this is similar to the coordination of La in LaOCl (Hölsä *et al.*, 1997). Other La atoms in (I) have oxygen-only coordination, with shortest interatomic distances of ~2.49 Å and other O atoms at distances ranging from ~2.55 to 2.80 Å (Table 1). The bond-valence-sum approach (Brese & O'Keeffe, 1991) was used to determine the coordination around atoms La3–La6. The bond-valence sum v_i for La6 is ~3 if eight O atoms are included in the coordination polyhedron. For the other La atoms (La3–La5), 10 O atoms should be considered (Fig. 2). All Se atoms have three O atom neighbors. The SeO_3^{2-} ions exhibit a typical pyramidal shape due to the electron lone pair of the Se atom. Cs atoms have only chlorine neighbours at distances of 3.424 (6)–3.649 (3) Å (Table 1).

The $La4O_{10}$ and $La5O_{10}$ polyhedra form infinite chains along the *b* axis by sharing common edges. The $La3O_{10}$ and $La6O_8$ polyhedra form a similar set of chains that are also parallel to *b*. Both types of chains are linked *via* common edges of the $La6O_8$ and $La4O_{10}$ polyhedra as well as common faces of the $La3O_{10}$ and $La5O_{10}$ polyhedra, forming a layer parallel to the *bc* plane (Fig. 2). A set of such layers forms pairs connected to each other by the $La1O_4Cl_4$ antiprisms. The bases of these antiprisms are formed by O atoms originating from the top and bottom layers. The antiprisms are arranged along the *a* axis in opposite directions. The bases of the $La1O_4Cl_4$ antiprisms, formed by Cl atoms from different layers, are directed towards each other, and one of their edges is shared with the 'upper' $La1O_4Cl_4$ polyhedron. The La2 atoms are situated above and below such double blocks. The $La2O_4Cl_4$ antiprisms share their oxygen vertices with different

La–O blocks formed by La3, La4, La5 and La6 polyhedra, whereas the La1O$_4$Cl$_4$ antiprisms are connected by Cl atoms only.

The SeO$_3$ pyramids may be considered as additional links between the lanthanum oxide layers. They share common edges with one polyhedron and common vertices with other polyhedra from this layer.

Along the *a* axis, the double layers are separated by layers of Cs atoms. The bases of the La2O$_4$Cl$_4$ antiprisms that are made up of Cl atoms are situated above and below the layers. According to the bond-valence calculations, the suggested coordination number is 6 (distorted triangular prism) for Cs1 and 8 (distorted cube) for Cs2 and Cs3 (Table 1). The Cs1Cl$_6$ prism is connected with the CsCl$_8$ cubes through common edges. Two Cs2Cl$_8$ and two Cs3Cl$_8$ units form a group of four polyhedra with common faces. Such quadruplets are joined by sharing edges with four other [2Cs2Cl$_8$2Cs3Cl$_8$] quadruplets and four Cs1Cl$_6$ prisms. As a result, the described polyhedra form a layer which shares Cl—Cl edges with the La2O$_4$Cl$_4$ antiprisms, thus forming a framework structure (Fig. 2).

The crystal structure of (I) may be considered to be similar to those of $Bi_8(SeO_3)_9Br_6$ or $Sm_{21}Cs(SeO_3)_{24}Br_{16}$, described by Ruck & Schmidt (2003). In (I), CsCl slabs separate blocks of composition $M_8(SeO_3)_9X_6$, where X = Br in the $Bi_8(SeO_3)_9Br_6$ structure. Another related compound is $Rb_6LiNd_{11}Cl_{16}(SeO_3)_{12}$ (Lipp & Schleid 2005). It contains only RbCl slabs which separate blocks with composition $[Nd_{29}Li_4O_8(SeO_3)_{24}]$, analogous to the 'triple sublayers' in Fig. 2. In the $Rb_6LiNd_{11}Cl_{16}(SeO_3)_{12}$ structure, small Li atoms are regularly situated in metal–selenium–O-atom blocks, whereas in the case of $Sm_{21}Cs(SeO_3)_{24}Br_{16}$, the Cs atom is statistically distributed in similar blocks.

Experimental

The title compound was obtained in an evacuated silica ampoule from a mixture of high purity LaOCl, SeO$_2$ and CsCl in a 1:1:1 molar ratio. The reaction mixture was heated to 923 K and was then cooled to 473 K at a rate of 2 K h^{-1}. The product was washed with distilled water and ethanol. Small plate-shaped colorless, transparent crystals were selected from the washed and dried product.

Crystal data

$Cs_3La_{11}(SeO_3)_{12}Cl_{12}$
M_r = 3875.66
Orthorhombic, *Cmca*
a = 43.176 (8) Å
b = 16.073 (2) Å
c = 16.037 (2) Å
V = 11129 (3) Å^3
Z = 8
D_x = 4.626 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 7054 reflections
θ = 2.5–28.2°
μ = 18.69 mm^{-1}
T = 173 (2) K
Block, colorless
0.09 × 0.08 × 0.05 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.245, T_{max} = 0.393
30595 measured reflections
6572 independent reflections
4369 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 28.3°
$h = -55 \rightarrow 52$
$k = -20 \rightarrow 21$
$l = -14 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.095
S = 1.00
6572 reflections
253 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0334P)^2 + 133.1504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.20 e Å^{-3}
$\Delta\rho_{min}$ = −2.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

La1—O6^{i}	2.416 (6)	La5—O15	2.597 (6)
La1—O4	2.416 (6)	La5—O1	2.616 (6)
La1—O18^{i}	2.478 (6)	La5—O2	2.621 (7)
La1—O3	2.519 (6)	La5—O3	2.679 (6)
La1—Cl3	2.999 (2)	La5—O18^{iv}	2.702 (6)
La1—Cl9	3.0263 (16)	La6—O17	2.444 (6)
La1—Cl8	3.051 (2)	La6—O7	2.451 (7)
La1—Cl2	3.1077 (6)	La6—O10	2.478 (7)
La2—O11	2.492 (6)	La6—O12	2.493 (6)
La2—O5	2.496 (6)	Se1—O17	1.691 (6)
La2—O2	2.526 (6)	Se1—O13	1.714 (6)
La2—O1	2.538 (6)	Se1—O1	1.733 (6)
La2—Cl4	2.862 (3)	Se2—O12	1.681 (6)
La2—Cl7	2.865 (3)	Se2—O16	1.699 (6)
La2—Cl6	2.944 (3)	Se2—O18	1.747 (6)
La2—Cl1	2.9855 (15)	Se3—O4	1.706 (6)
La3—O9	2.488 (6)	Se3—O6	1.708 (6)
La3—O8^{ii}	2.490 (6)	Se3—O15	1.711 (7)
La3—O5	2.507 (6)	Se4—O7	1.679 (6)
La3—O6	2.563 (6)	Se4—O8	1.708 (6)
La3—O17	2.589 (6)	Se4—O2	1.741 (6)
La3—O1	2.614 (6)	Se5—O5	1.697 (6)
La3—O12	2.645 (6)	Se5—O11^{i}	1.705 (6)
La3—O18	2.664 (6)	Se5—O14	1.721 (6)
La3—O14	2.755 (6)	Se6—O10	1.672 (6)
La3—O15	2.776 (6)	Se6—O9	1.705 (6)
La4—O11	2.510 (6)	Se6—O3	1.729 (6)
La4—O16^{iii}	2.521 (6)	Cs1—Cl7^{v}	3.424 (3)
La4—O4	2.575 (6)	Cs1—Cl4^{vi}	3.428 (3)
La4—O7	2.591 (7)	Cs1—Cl1^{vi}	3.446 (2)
La4—O2	2.602 (7)	Cs1—Cl6^{vii}	3.649 (3)
La4—O10	2.618 (6)	Cs2—Cl7^{vii}	3.458 (3)
La4—O3	2.644 (6)	Cs2—Cl6^{vii}	3.502 (3)
La4—O15	2.765 (6)	Cs2—Cl5^{viii}	3.545 (3)
La4—O14^{iv}	2.790 (6)	Cs2—Cl4^{iv}	3.634 (3)
La5—O8	2.531 (6)	Cs3—Cl4^{vii}	3.457 (3)
La5—O13	2.535 (6)	Cs3—Cl6^{vii}	3.502 (3)
La5—O14^{iv}	2.561 (6)	Cs3—Cl5^{ix}	3.545 (3)
La5—O9	2.567 (6)	Cs3—Cl7^{v}	3.632 (3)
La5—O16^{iv}	2.572 (6)		
O17—Se1—O13	103.6 (3)	O7—Se4—O8	103.4 (3)
O17—Se1—O1	93.7 (3)	O7—Se4—O2	93.3 (3)
O13—Se1—O1	94.5 (3)	O8—Se4—O2	94.9 (3)
O12—Se2—O16	104.4 (3)	O5—Se5—O11^{i}	106.6 (3)
O12—Se2—O18	94.8 (3)	O5—Se5—O14	95.0 (3)
O16—Se2—O18	95.2 (3)	O11^{i}—Se5—O14	96.1 (3)
O4—Se3—O6	106.9 (3)	O10—Se6—O9	105.4 (3)
O4—Se3—O15	96.3 (3)	O10—Se6—O3	95.0 (3)
O6—Se3—O15	95.3 (3)	O9—Se6—O3	95.9 (3)

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

Note that, according to the latest edition of the International Tables for Crystallography (2002, 5th ed.), the Hermann–Maugin symbol for space group *Cmca* has been modified to *Cmce*. Except for the O atoms, all atoms were refined with anisotropic displacement parameters. The highest peak is located 3.13 Å from atom La2 and the deepest hole 0.92 Å from Cs2.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to

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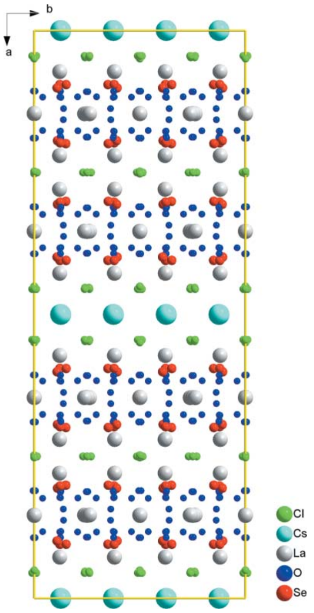

Figure 1
View of the crystal structure of (I), projected along the *c* axis.

refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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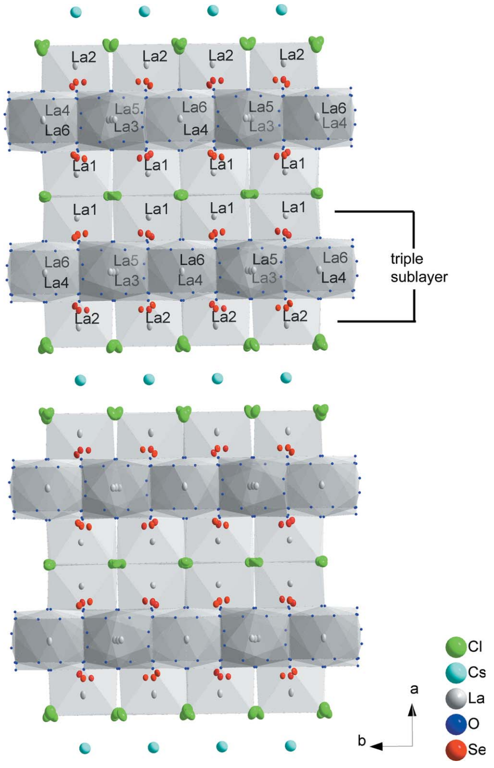

Figure 2
View of the polyhedra around the La atoms in (I), with the [$La_{22}(SeO_3)_{24}$] block outlined. Displacement ellipsoids are drawn at the 95% probability level.

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