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Tetrasamarium(II) oxide hexaiodide, Sm_4OI_6

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Black single crystals of tetrasamarium(II) oxide hexaiodide, Sm_4OI_6, were obtained from a reaction of SmI_3, SmOI, NaI, and Na in a sealed tantalum container. Sm_4OI_6 crystallizes in space group $P6_3mc$ and, like many M_4OX_6 type oxide halides of divalent metals, adopts the anti-K_6HgS_4/Na_6ZnO_4 type of structure, with $K_6HgS_4 \simeq I_6OSm_4$. A tetrahedron of samarium(II) that incorporates an oxide ion is surrounded by 18 iodide ions which are connected further into a three-dimensional non-centrosymmetric structure. The O atom and one of the Sm atoms occupy sites with $3m$ symmetry, whereas the second Sm atom and both I atoms are located at sites with m symmetry.

Comment

The divalent lanthanides, especially Eu^{II}, Sm^{II}, and Yb^{II} which are the most stable with their electronic configurations [Xe] $6s^05d^04f^n$ (n = 7, 6, 14, respectively), exhibit a structural behaviour very similar to that of the respective alkaline-earth elements Ba, Sr, and Ca. This is, for example, the case for many binary and ternary halides and also for the oxide halides M_4OX_6. These were first observed for M = Ba, Sr, Eu (Tanguy *et al.*, 1970). The crystal structure was first determined for Ba_4OCl_6 (Frit *et al.*, 1970). Later on, these oxide halides were obtained as single crystals either on purpose or as by-products, examples being Ca_4OCl_6 (Meyer *et al.*, 1991), Sr_4OCl_6 (Hagemann *et al.*, 1996; Reckeweg & Meyer, 1997), Sr_4OI_6 (Barker, Francesconi, Shutt & Wilson, 2001), Ba_4OI_6 (Barker, Francesconi & Wilson, 2001), Sm_4OCl_6 (Schleid & Meyer, 1987c), Eu_4OX_6 (X = Cl, Br) (Schleid & Meyer, 1987b), Eu_4OI_6 (Liao & Dronskowski, 2004) and Yb_4OCl_6 (Schleid & Meyer, 1987a).
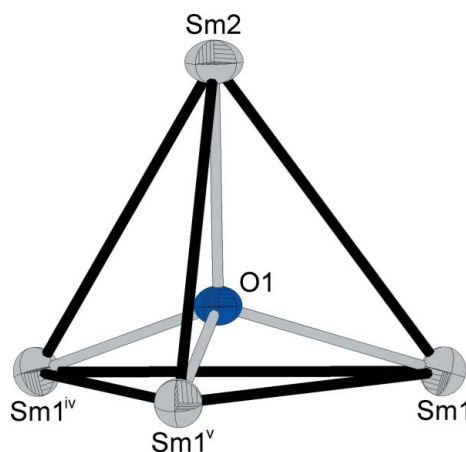

Figure 1
The Sm_4O tetrahedron in the crystal structure of Sm_4OI_6. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (iv) $-x + y, 1 - x, z$; (v) $1 - y, 1 + x$-y, z].
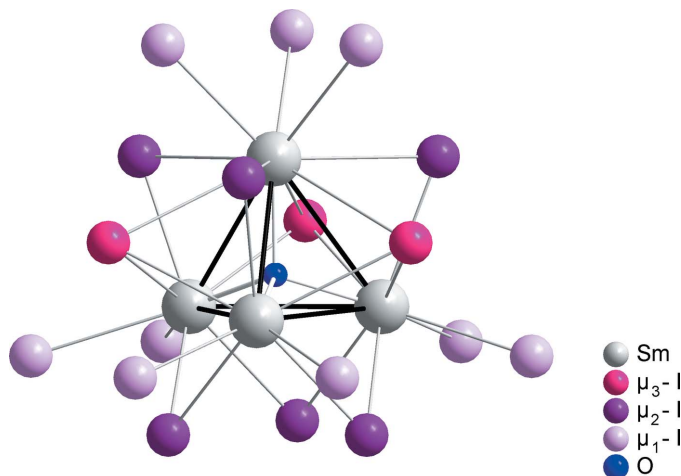
Figure 2
One $[Sm_4O]^{6+}$ tetrahedron surrounded by 18 iodide ions of which three are face-capping (μ_3), six edge-capping (μ_2), and nine terminal (μ_1).
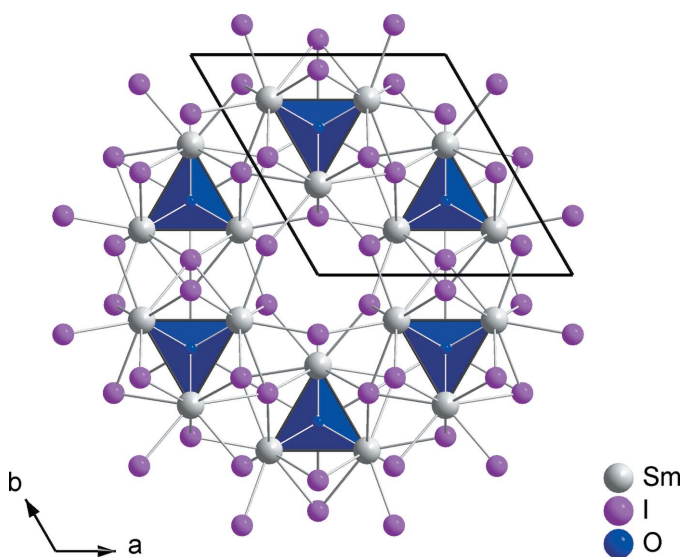

Figure 3
Projection of the crystal structure of Sm_4OI_6 in the direction of the hexagonal c axis.

In our effort to produce larger amounts of these oxide halides for further reactions, such as excision of the inner M_4O tetrahedron and its stabilization in solution with appropriate ligands, we have now obtained single crystals of Sm_4OI_6. These are isostructural with the above-mentioned oxide halides which have the structure type that occurs as an anti-type for Na_6ZnO_4 (Kastner & Hoppe, 1974) and K_6HgS_4 (Sommer & Hoppe, 1978) considering, for example, $K_6HgS_4 \simeq I_6OSm_4$. A purely ionic description, $\{(Sm^{2+})_4(O^{2-})\}^{6+}(I^-)_6$, excluding any metal–metal bonding, is the best approximation to the chemical bonding in this oxide iodide. The tetrahedra $[Sm_4O]^{6+}$, isolated from like tetrahedra (Fig. 1), are defined by Sm—Sm distances of 3.9068 (18) and 4.0133 (14) Å, only a little larger than the Eu—Eu distances in Eu_4OI_6 [3.8900 (16) and 3.9796 (14) Å], in accord with the lanthanide contraction effect. The Sm—O distances are 2.39 (2) and 2.436 (7) Å, respectively. The $[Sm_4O]^{6+}$ tetrahedra are surrounded by 18

iodide ions of which three are face-capping (μ_3), six edge-capping (μ_2), and nine terminal (μ_1) to this inner core of the crystal structure (Fig. 2). As there are only six halide ions per formula unit, this basic unit has to be connected to other units in accord with the formulation $\{Sm2Sm1_3O1\}I1_{6/4}I1_{3/2}I2_{3/6}$-$I2_{3/3}I2_{3/2}$ (Schleid & Meyer, 1987a). The $[Sm_4O]^{6+}$ tetrahedra are arranged in rows in the direction of the c axis (Fig. 3).

Experimental

SmI$_3$ was produced from the elements and purified by high-vacuum sublimation (Meyer, 1991). A mixture of SmI_3, SmOI, NaI and Na (molar ratio 3:1:1:4; SmOI was previously prepared from SmI_3 and Sm_2O_3; NaI and Na were used as purchased) was filled under dry-box conditions (M. Braun, Garching, Ar atmosphere) in a tantalum tube, which was He-arc welded and jacketed in a silica ampoule. The reaction mixture was heated to 903 K, kept there for 96 h, cooled to 773 K at a rate of 1 K h^{-1} and then cooled rapidly by turning off the furnace. Black columnar single crystals of Sm_4OI_6 were selected in a dry-box under a microscope and mounted in thin-walled glass capillaries.

Crystal data

Sm_4OI_6	Mo $K\alpha$ radiation
$M_r = 1378.80$	Cell parameters from 16703
Hexagonal, $P6_3mc$	reflections
$a = 10.4415$ (8) Å	$\theta = 2.3–32.2°$
$c = 8.0464$ (7) Å	$\mu = 27.38$ mm^{-1}
$V = 759.73$ (11) Å^3	$T = 293$ (2) K
$Z = 2$	Column, black
$D_x = 6.027$ Mg m^{-3}	$0.50 \times 0.10 \times 0.10$ mm

Data collection

Stoe IPDS-II diffractometer	957 independent reflections
ω and φ scans	917 reflections with $I > 2\sigma(I)$
Absorption correction: numerical	$R_{int} = 0.087$
[X-RED32 (Stoe & Cie, 2001)	$\theta_{max} = 32.2°$
and X-SHAPE (Stoe & Cie,	$h = -15 \rightarrow 15$
1999)]	$k = -15 \rightarrow 15$
$T_{min} = 0.029$, $T_{max} = 0.118$	$l = -9 \rightarrow 12$
17645 measured reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$\Delta\rho_{max} = 2.38$ e Å^{-3}
$wR(F^2) = 0.104$	$\Delta\rho_{min} = -1.61$ e Å^{-3}
$S = 1.09$	Extinction correction: SHELXL97
957 reflections	Extinction coefficient: 0.0108 (6)
26 parameters	Absolute structure: Flack (1983),
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2$	412 Friedel pairs
$+ 30.1615P]$	Flack parameter: 0.02 (6)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Sm1—O1	2.436 (7)	Sm2—O1	2.39 (2)
Sm1—I1	3.3061 (17)	Sm2—I2	3.4184 (19)
Sm1—I2^i	3.4013 (13)	Sm2—I2^{iv}	3.4184 (19)
Sm1—I1^{ii}	3.4078 (8)	Sm2—I1	3.5966 (13)
Sm1—I2^{iii}	3.5554 (11)	O1—Sm1^v	2.436 (7)
Sm1—Sm2	3.9068 (18)	O1—Sm1^{iv}	2.436 (7)
Sm1—Sm1^{iv}	4.0133 (14)		
Sm2—Sm1—Sm1^{iv}	59.094 (17)	Sm2—O1—Sm1	108.0 (5)
Sm1^{iv}—Sm1—Sm1^v	60.0	Sm1—O1—Sm1^{iv}	110.9 (5)

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

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The highest peak in the final difference Fourier map is 0.02 Å from atom Sm1 and the deepest hole 0.68 Å from the same atom.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

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