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Europium(II) oxyiodide

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Yellow single crystals of Eu_4OI_6 were grown from fluxes in Ta ampoules and structurally characterized by X-ray diffraction. Eu_4OI_6 crystallizes in a hexagonal system and is isotypic with the corresponding chloride and bromide compounds. The O atom and one Eu atom lie on sites with $3m$ symmetry; the other Eu atom and the two unique I atoms are at sites with m symmetry. The structure is characterized by O-centered tetrahedra of divalent europium cations [Eu—O = 2.391 (15) and 2.416 (5) Å, and mean Eu—Eu = 3.94 Å] and hexagonal channels along [001] filled with iodide anions.

Comment

Europium oxyhalides of general formula Eu_4OX_6 (X = Cl and Br) were first referred to by Tanguy *et al.* (1970), who indexed their X-ray patterns on the basis of the pattern of Ba_4OCl_6. The formation of single crystals has been observed as a by-product from oxygen-containing melts (Meyer & Schleid, 1987), and a systematic route based on reaction mixtures incorporating EuX_3 (X = Cl and Br), Eu_2O_3 and lithium succeeded in growing pale-yellow single crystals of good quality (Schleid & Meyer, 1987*a*). The synthesis and structure determination of the iodide phase Eu_4OI_6, however, have not yet been reported. The present contribution is part of a project targeted at synthesizing rare-earth cyanamides/carbodiimides, during which, by accident, we found a simple way to grow single crystals of Eu_4OX_6 (X = Cl, Br and I).

Eu_4OI_6 crystallizes in a hexagonal system in space group $P6_3mc$ and is isotypic with Eu_4OCl_6 and Eu_4OBr_6. The most important structural feature of Eu_4OI_6 is the tetrahedral $[Eu_4O]^{6+}$ unit (Fig. 1) containing divalent europium. The O atom resides at the center of the tetrahedron, the Eu—O distances being similar [Eu1—O = 2.391 (15) Å and Eu2—O = 2.416 (5) Å; Table 1]. The Eu—Eu distances are 3.8900 (16) (Eu1—Eu2) and 3.9796 (14) Å (Eu2—Eu2), and the tetrahedral angles are very close to their ideal values, namely 108.0 (3)° for Eu1—O—Eu2 and 110.9 (3)° for Eu2—O—Eu2. The average Eu—O [2.41 (1) Å] and Eu—Eu [3.92 (2) Å] distances in Eu_4OI_6 are only slightly larger than those in Eu_4OCl_6 (2.36 and 3.86 Å, respectively) and Eu_4OBr_6 (2.39 and 3.90 Å, respectively).

The Eu coordination is augmented by neighboring iodide anions, with interatomic distances ranging from 3.3891 (16) to 3.5794 (12) Å (Eu1, six bonds) and from 3.2905 (15) to 3.5458 (11) Å (Eu2, seven bonds). On the basis of the tabulated bond-valence parameter for the Eu^{II}—O (r_0 = 2.147 Å; Brese & O'Keeffe, 1991) and Eu^{II}—I bonds (r_0 = 2.869 Å; generated from the crystal structure of EuI_2; Sanchez *et al.*, 1985), the empirical valences of atoms Eu1 and Eu2 sum to 1.69 and 2.11, respectively. Even including the three very long Eu1—O distances (3.96 Å) in the calculation, the Eu1 valence sum does not fully match the divalent state. We note that a similar effect is missing in Ba_4OCl_6, thereby indicating the possibility of weak metal–metal bonding in the rare-earth tetrahedron through residual electron density. In fact, the Eu^{II}—Eu^{II} distances in Eu_4OI_6 are almost identical to those in elemental Eu (3.99 Å; Sutton, 1965), and similar effects of metal–metal bonding in less than fully oxidized rare-earth metal compounds have been described in corresponding quantum-chemical investigations of extended solids (Landrum *et al.*, 1999).

When projected along [001] (Fig. 2), the crystal structure of Eu_4OI_6 exhibits one-dimensional hexagonal channels of approximate diameter 4.86 Å (atom-to-atom distance), which can be compared with the corresponding channel diameters in both Eu_4OBr_6 (4.70 Å) and Eu_4OCl_6 (4.62 Å). Analogous

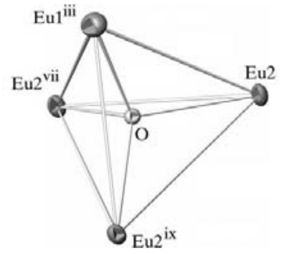

Figure 1
The tetrahedral $[Eu_4O]^{6+}$ unit in Eu_4OI_6, with displacement ellipsoids drawn at the 50% probability level. The symmetry codes are as in Table 2, with the addition of (ix) $1 - x + y, -x, z$.

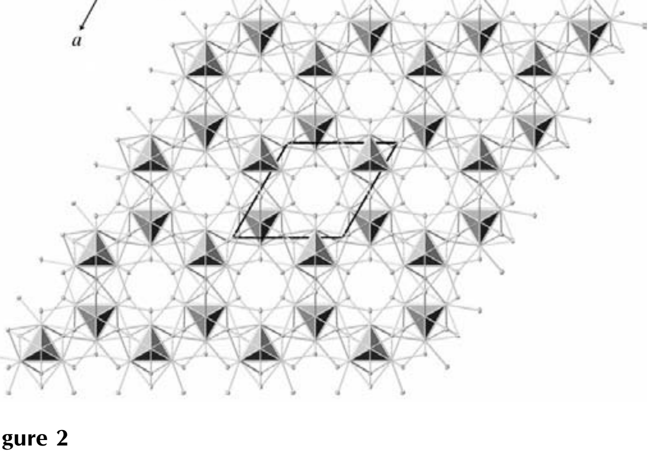

Figure 2
A projection of the crystal structure of Eu_4OI_6 along [001].

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channels are also observed in related rare-earth oxyhalides, such as Sm_4OCl_6 [4.61 Å; calculated with the data given by Schleid & Meyer (1987*b*)] and Yb_4OCl_6 (4.37 Å; Schleid & Meyer, 1987*c*). It is not yet known whether these channels can provide enough empty space for the inclusion of other chemical species. To the best of our knowledge, hexagonal channels filled with only halide anions are exclusively found in the rare-earth oxyhalides. For related oxoselenate or phosphate compounds, similar hexagonal channels have been described in combination with electron 'lone pairs' on the Se and P atoms (Morris *et al.*, 1994; Wontcheu & Schleid, 2003). In $Tb_3O_2Cl[SeO_3]_2$ (Wontcheu & Schleid, 2002), two chloride anions in diametrically opposed positions around the hexagon are involved in channel formation.

Experimental

Because of the extraordinary affinity of europium towards oxygen, all chemical manipulations were performed in a glove-box under dry argon, with oxygen and moisture levels below 1 p.p.m. The accidental synthesis of Eu_4OI_6 resulted from a 1:1 mixture of EuI_2 (Aldrich, 99.9%) and $Li_2(NCN)$ [synthesized according to Liu (2002)], which was placed in a tantalum ampoule that was sealed with an arc welder and jacketed with quartz, both under argon. The sample was heated to 1073 K for two days and then cooled slowly (6 K min^{-1}) to room temperature. As a result of slight oxygen contamination (probably as LiOH) of the X-ray pure $Li_2(NCN)$, yellow prisms of Eu_4OI_6 (~3 × 0.5 × 0.5 mm in size) were obtained. The phase seemingly acts as a getter for traces of oxygen, in agreement with independent observations (Meyer & Schleid, 1987). The title compound can also be synthesized by deliberately introducing oxygen-containing educts (*e.g.* Eu_2O_3), and crystals of Eu_4OCl_6 and Eu_4OBr_6 can be grown under identical conditions. The halide/cyanamide melts seemingly catalyze the growth of single crystals, which are difficult to obtain otherwise. Because of their sensitivity to oxygen and moisture, the single crystals were mounted in glass capillaries inside a glove-box for the X-ray measurements.

Crystal data

Eu_4OI_6
$M_r = 1385.24$
Hexagonal, $P6_3mc$
$a = 10.404$ (2) Å
$c = 7.996$ (3) Å
$V = 749.5$ (3) Å^3
$Z = 2$
$D_x = 6.138$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9730 reflections
$\theta = 2.3$–28.3°
$\mu = 28.82$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.15 × 0.10 × 0.09 mm

Table 1
Selected geometric parameters (Å, °).

Eu1—O	2.391 (15)	Eu2—I2$^{\text{iv}}$	3.3757 (12)
Eu1—I2$^{\text{i}}$	3.3891 (16)	Eu2—I1$^{\text{v}}$	3.4032 (9)
Eu1—I1$^{\text{ii}}$	3.5794 (12)	Eu2—I2$^{\text{vi}}$	3.5458 (11)
Eu1—Eu2$^{\text{ii}}$	3.8900 (16)	Eu2—Eu1$^{\text{iii}}$	3.8900 (16)
Eu2—O$^{\text{iii}}$	2.416 (5)	Eu2—Eu2$^{\text{vii}}$	3.9796 (14)
Eu2—I1	3.2905 (15)		
Eu2$^{\text{ii}}$—Eu1—Eu2$^{\text{i}}$	61.53 (3)	Eu1—O—Eu2$^{\text{i}}$	108.0 (3)
Eu1$^{\text{iii}}$—Eu2—Eu2$^{\text{vii}}$	59.235 (15)	Eu2$^{\text{ii}}$—O—Eu2$^{\text{i}}$	110.9 (3)

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

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.479$, $T_{\max} = 1.0$
9730 measured reflections
727 independent reflections
704 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.056$
$\theta_{\max} = 28.3°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.067$
$S = 1.09$
727 reflections
24 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 11.61P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.86$ e Å^{-3}
$\Delta\rho_{\min} = -1.73$ e Å^{-3}
Absolute structure: Flack (1983), 336 Friedel pairs
Flack parameter = 0.07 (4)

The refinement was started using the structure of the isotypic chloride phase, with anisotropic displacement parameters for Eu and I atoms and an isotropic displacement parameter for the O atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1033). Services for accessing these data are described at the back of the journal.

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