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Europium(II) bromide iodide

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Eu–Br) = 0.002 Å
R factor = 0.038
wR factor = 0.080
Data-to-parameter ratio = 28.7

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

Pink single crystals of EuBrI were grown from fluxes in Ta ampoules at 973 K and structurally characterized by X-ray diffraction. EuBrI crystallizes in the orthorhombic system with nine-coordinate divalent europium and adopts the ordered $PbCl_2$ structure type.

Comment

The first mixed-halide phase of divalent europium, EuFCl, was reported by Tanguy *et al.* in 1973. In the following years, the compounds Eu*FX* (*X* = Cl, Br, I) were synthesized and characterized by Brixner & Bierlein (1974,) and Brixner (1976), Lambrecht *et al.* (1974) and also Beck (1976). Clink & Eick (1979) studied the $EuBr_2$–$EuCl_2$ system and investigated the compositions $EuBr_{1.8}Cl_{0.2}$ and $EuBr_{1.5}Cl_{0.5}$. Hodorowicz *et al.* (1984) observed the formation of the pure phases EuClI and SrClI for the 1:1 composition in the MCl_2–MI_2 (M = Sr and Eu) systems. In addition, Hodorowicz *et al.* (1984) characterized the $EuBr_2$–EuI_2 system, which exhibits seven distinct regions ($EuBr_{2-x}I_x$ with $SrBr_2$ type for $0 \leq x \leq 0.2$, a two-phase region with $SrBr_2$ and $PbCl_2$ types for $0.2 < x < 0.4$, the $PbCl_2$ type for $0.4 \leq x \leq 1.2$, another two-phase region for $1.2 < x < 1.6$, the pure phase $EuBr_{0.4}I_{1.6}$, a third two-phase region for $1.6 < x < 1.8$, and the pure phase of $EuBr_{0.2}I_{1.8}$ type with $1.8 \leq x \leq 2$). These authors also mentioned the compound EuBrI crystallizing in *Pbnm* and refined its lattice parameters from

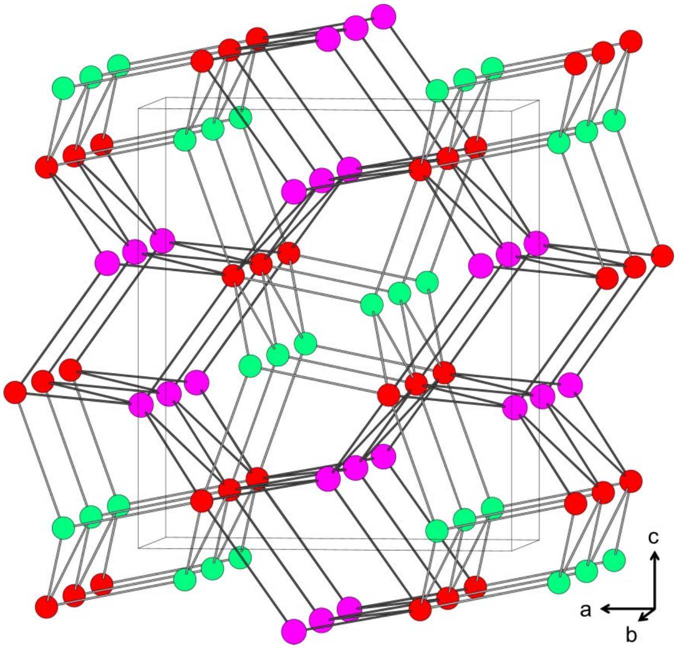

Figure 1
View of the crystal structure of EuBrI approximately along [010], with Eu given as red, Br as green and I as purple spheres.

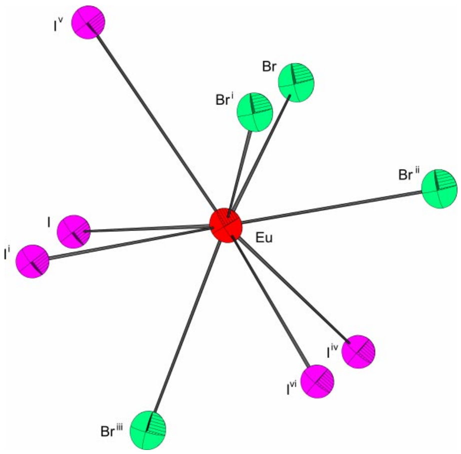

Figure 2
Coordination environment of Eu in EuBrI, with displacement ellipsoids drawn at the 50% probability level. Symmetry codes are as in Table 1.

X-ray powder diffraction data, but gave no further structural details. According to their work, such europium dihalides can be made from the oxide using the method of Taylor & Carter (1962). Here we present X-ray single-crystal data for EuBrI.

The cations Sr^{2+} and Eu^{2+} are known to exhibit very similar structural features in the solid state. Not surprisingly, EuBrI is structurally very close to SrBrI (Hodorowicz & Eick, 1983). Thus, both compounds adopt the $PbCl_2$ structure type with a layer-like structural motif parallel to the *ac* plane (Fig. 1). Nine anions coordinate the metal cation in a tricapped trigonal prismatic arrangement (Fig. 2), and the two different anionic positions have been labelled as *X*1 and *X*2, respectively (Braekken, 1932). Position *X*1, surrounded by four cations in a tetrahedral manner (3.10–3.20 Å), is taken by the smaller bromide anion whereas position *X*2, coordinated by five cations in a square pyramidal configuration (3.48–3.55 Å), is occupied by the iodide anion. This is consistent with the results of theoretical powder diffraction patterns by Hodorowicz *et al.* (1984), showing that the intensities obtained for selected reflections which are most sensitive to the anionic positions clearly indicate full ordering. In the SrBrI phase, however, the anion occupancy is random, even throughout the entire $SrBr_2$–SrI_2 system. In the simplest model, this pronounced difference between the Eu and Sr phases might be attributed to different cationic polarizabilities but other factors must complicate these systems. For comparison, Clink & Eick (1979) reported structural details for $EuBr_{1.5}Cl_{0.5}$, also with an ordered $PbCl_2$-type structure. Additionally, a study of the $SrBr_2$–$SrCl_2$ system (Hodorowicz & Eick, 1982) resulted in two phases with compositions $SrBr_{1.60}Cl_{0.40}$ and $SrBr_{1.40}Cl_{0.60}$, with ordered anionic arrangements but also one phase, $SrBr_{0.30}Cl_{1.70}$, with a random arrangement of Br and Cl. Both EuClI and SrClI exhibit ordered $PbCl_2$-type structures as for EuBrI.

Experimental

EuBrI was obtained as a by-product upon exploratory research targeted at synthesizing complex rare-earth carbodiimides from halide fluxes (Liao *et al.*, 2004) optimized for carbodiimide crystal growth. Owing to the extraordinary affinity of europium towards oxygen, all chemical manipulations were performed in a glove-box under dry argon, with oxygen and moisture levels well below 1 p.p.m. The accidental synthesis of EuBrI resulted from a 2:1:1:1 mixture of EuI_2 (Aldrich, 99.9%), $CuBr_2$ (Aldrich, 99.999%) and the two carbodiimide precursors NaCN (95%, Merck) and NaN_3 (99%, Alfa). The reaction mixture was introduced into a tantalum ampoule which was sealed with an arc welder and jacketed with quartz, both under argon. The sample was heated to 973 K and slowly cooled down within a week (6 K min^{-1}). Because of the reductive nature of cyanamide/carbodiimide to the transition metals (Gibson *et al.*, 2003), pink single crystals of EuBrI, elemental copper and a black solid of unknown composition were obtained. The single crystals of EuBrI were mounted in glass capillaries inside a glovebox for the X-ray measurements.

Crystal data

EuBrI
$M_r = 358.77$
Orthorhombic, *Pnma*
$a = 8.3723\ (18)$ Å
$b = 4.7404\ (11)$ Å
$c = 9.799\ (2)$ Å
$V = 388.89\ (15)$ Å^3
$Z = 4$
$D_x = 6.128$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 4924 reflections
$\theta = 3.2$–$28.4°$
$\mu = 34.08$ mm^{-1}
$T = 293\ (2)$ K
Block, pink
0.08 × 0.06 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.100$, $T_{max} = 0.360$
4924 measured reflections

546 independent reflections
429 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 28.4°$
$h = -11 \rightarrow 11$
$k = -6 \rightarrow 6$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.080$
$S = 1.08$
546 reflections
19 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 11.5746P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.58$ e Å^{-3}
$\Delta\rho_{min} = -2.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Eu—Br^{i}	3.1049 (15)	Eu—I^{i}	3.4772 (12)
Eu—Br^{ii}	3.166 (2)	Eu—I^{iv}	3.5261 (12)
Eu—Br^{iii}	3.204 (2)	Eu—I^{v}	3.5544 (15)
Br^{i}—Eu—Br	99.52 (6)	Br^{ii}—Eu—I^{iv}	69.38 (3)
Br^{i}—Eu—Br^{ii}	70.27 (5)	Br^{iii}—Eu—I^{iv}	67.96 (3)
Br^{i}—Eu—Br^{iii}	130.24 (3)	I^{i}—Eu—I^{iv}	137.56 (3)
Br^{ii}—Eu—Br^{iii}	121.14 (5)	I—Eu—I^{iv}	79.73 (2)
Br^{i}—Eu—I^{i}	72.99 (4)	I^{iv}—Eu—I^{vi}	84.47 (3)
Br—Eu—I^{i}	138.42 (5)	Br^{i}—Eu—I^{v}	68.60 (4)
Br^{ii}—Eu—I^{i}	136.960 (18)	Br^{ii}—Eu—I^{v}	114.11 (5)
Br^{iii}—Eu—I^{i}	69.61 (3)	Br^{iii}—Eu—I^{v}	124.75 (5)
I^{i}—Eu—I	85.94 (4)	I^{i}—Eu—I^{v}	70.74 (3)
Br^{i}—Eu—I^{iv}	138.84 (5)	I^{iv}—Eu—I^{v}	137.587 (19)
Br—Eu—I^{iv}	74.14 (4)		

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

The structure was solved using the parameters of SrBrI (Hodorowicz & Eick, 1983) and refined with anisotropic displacement parameters for all atoms. The highest peak and the deepest hole in

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the difference map are located 0.65 Å from Eu and 0.49 Å from Br, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; 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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