

## Lutetium(III) oxide bromide, LuOBr

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Received 1 June 2007; accepted 6 June 2007

 Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{Lu}-\text{O}) = 0.001$  Å;  $R$  factor = 0.023;  $wR$  factor = 0.054; data-to-parameter ratio = 10.7.

Single crystals of lutetium oxide bromide, LuOBr, were obtained accidentally as a by-product of the reaction of lutetium metal, ruthenium powder and lutetium tribromide, LuBr<sub>3</sub>, in a sealed tantalum container. As is typical for rare-earth oxide halides of the type REOX (RE = rare-earth metal and X = halogen), LuOBr crystallizes in the tetragonal PbFCl structure type (matlockite), where Lu, O and Br are situated on positions with  $4mm$ ,  $\bar{4}m2$  and  $4mm$  symmetry, respectively.

### Related literature

For a previous powder study of LuOBr, see Mayer *et al.* (1965). Syntheses of lanthanide compounds have been compiled by Meyer (1991).

### Experimental

#### Crystal data

LuOBr	$Z = 2$
$M_r = 270.88$	Mo $K\alpha$ radiation
Tetragonal, $P4/nmm$	$\mu = 58.17$ mm <sup>-1</sup>
$a = 3.7646$ (13) Å	$T = 293$ (2) K
$c = 8.354$ (4) Å	$0.20 \times 0.10 \times 0.05$ mm
$V = 118.39$ (8) Å <sup>3</sup>	

#### Data collection

Stoe IPDS I diffractometer	1046 measured reflections
Absorption correction: numerical	107 independent reflections
[ <i>X-RED</i> (Stoe & Cie, 2001) and <i>X-SHAPE</i> (Stoe & Cie, 1999)]	107 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.004$ , $T_{\max} = 0.057$	$R_{\text{int}} = 0.099$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	10 parameters
$wR(F^2) = 0.054$	$\Delta\rho_{\max} = 1.55$ e Å <sup>-3</sup>
$S = 1.29$	$\Delta\rho_{\min} = -2.54$ e Å <sup>-3</sup>
107 reflections	

**Table 1**

Selected bond lengths (Å).

Lu—O	2.1847 (7)	Lu—Lu <sup>i</sup>	3.4650 (14)
Lu—Br	3.1228 (15)		

 Symmetry code: (i)  $-x, -y + 2, -z + 1$ .

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, 2005); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Deutsche Forschungsgemeinschaft (DFG), SFB 608 (Complex transition metal compounds with spin and charge degrees of freedom and disorder).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2121).

### References

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**supplementary materials**

*Acta Cryst.* (2007). E63, i156 [ doi:10.1107/S1600536807027821 ]

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### Comment

In conproportionation reactions of rare-earth trihalides  $REX_3$  with their respective metals (frequently with the addition of a transition metal), the oxide halides  $REOX$  often appear as a few single crystals as by-products. Except for impurities from the reaction containers, *e.g.* tantalum, this may be due to impure anhydrous rare-earth trihalides  $REX_3$  which are generated by the so-called ammonium halide route (Meyer, 1991).

LuOBr was obtained in a reaction of lutetium metal, ruthenium powder and nominally pure lutetium tribromide,  $LuBr_3$ , in a tantalum container at 1273 K. It crystallizes with the tetragonal  $PbFCI$ - (matlockite) type of structure, in which a central sheet of oxygen atoms is flanked by two sheets of bromine atoms. Between these  $Br-O-Br$  sheets,  $Lu^{3+}$  is surrounded by four oxygen and four bromine atoms in a distorted square antiprism with  $Lu-O$  distances of 2.1847 (7) Å and  $Lu-Br$  distances of 3.1228 (15) Å (Figs. 1, 2). There is an additional bromine atom capping one of the square faces at a distance of 3.851 (3) Å. The cell parameters obtained from the single-crystal study show no significant differences to those of a previous powder work ( $a = 3.770$ ,  $c = 8.387$  Å; Mayer *et al.*, 1965).

### Experimental

Light-orange, transparent plates of LuOBr were obtained in this special case as a major by-product (35%) from the reaction of lutetium powder (0.092 g, 0.5 mmol; Smart Elements, 99.99%), ruthenium powder (0.022 g, 0.2 mmol; Merck, 99%) and nominally pure  $LuBr_3$  (0.150 g, 0.4 mmol). Except for excess starting materials, other products were not identified so far.  $LuBr_3$  was prepared by the reaction of  $Lu_2O_3$  (Chempur, 99.9%) with  $NH_4Br$  (KMF, 99.5%) (Meyer, 1991), followed by the decomposition of the resulting  $(NH_4)_3LuBr_6$  at 693 K and subsequent sublimation. The reaction was carried out in a He-arc welded tantalum container within a silica jacket at 1273 K for 3 d and tempering at 1073 K for 10 d. Due to their moisture and air sensitivity, reagents and products were handled in an argon-filled glove box (M. Braun, Garching, Germany).

### Refinement

For the present refinement, origin choice 2 for space group  $P4/nmm$  was chosen. The highest peak in the final difference Fourier map is 1.03 Å from atom Lu and the deepest hole is 1.14 Å from the same atom.

Figures

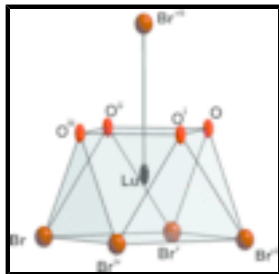


Fig. 1. The surrounding of  $\text{Lu}^{3+}$  in LuOBr with displacement ellipsoids drawn at the 75% (O, Br) and 80% (Lu) probability level. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $x, y + 1, z$ ; (iii)  $-x - 1, -y + 1, -z + 1$ ; (iv)  $x - 1, y - 1, z$ ; (v)  $x - 1, y, z$ ; (vi)  $x, y - 1, z$ ; (vii)  $-x, -y + 2, -z + 1$ ].

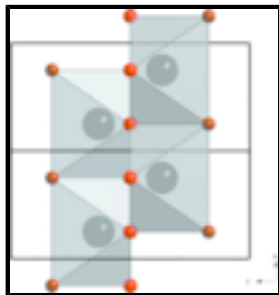


Fig. 2. Part of the crystal structure of LuOBr, viewed along the  $a$  axis. Lu atoms are represented as grey, O as red and Br as brown spheres.

Lutetium(III) oxide bromide

Crystal data

LuOBr	$Z = 2$
$M_r = 270.88$	$F_{000} = 228$
Tetragonal, $P4/nmm$	$D_x = 7.598 \text{ Mg m}^{-3}$
Hall symbol: $-P 4a 2a$	Melting point: no K
$a = 3.7646 (13) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 3.7646 (13) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 8.354 (4) \text{ \AA}$	Cell parameters from 1168 reflections
$\alpha = 90^\circ$	$\theta = 1.9\text{--}28.2^\circ$
$\beta = 90^\circ$	$\mu = 58.17 \text{ mm}^{-1}$
$\gamma = 90^\circ$	$T = 293 (2) \text{ K}$
$V = 118.39 (8) \text{ \AA}^3$	Plate, light-orange
	$0.20 \times 0.10 \times 0.05 \text{ mm}$

Data collection

Stoe IPDS I diffractometer	107 independent reflections
Radiation source: fine-focus sealed tube	107 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.099$
$T = 293(2) \text{ K}$	$\theta_{\text{max}} = 27.7^\circ$
$\varphi$ scans	$\theta_{\text{min}} = 4.9^\circ$
Absorption correction: numerical [X-RED (Stoe & Cie, 2001) and X-SHAPE (Stoe & Cie, 1999)]	$h = -4 \rightarrow 4$

$T_{\min} = 0.004$ ,  $T_{\max} = 0.057$   
1046 measured reflections

$k = -4 \rightarrow 4$   
 $l = -10 \rightarrow 10$

### Refinement

Refinement on  $F^2$

$$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 0.8289P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

Least-squares matrix: full

$$(\Delta/\sigma)_{\max} < 0.001$$

$$R[F^2 > 2\sigma(F^2)] = 0.023$$

$$\Delta\rho_{\max} = 1.55 \text{ e } \text{\AA}^{-3}$$

$$wR(F^2) = 0.054$$

$$\Delta\rho_{\min} = -2.54 \text{ e } \text{\AA}^{-3}$$

$S = 1.29$

Extinction correction: SHELXL97,  
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

107 reflections

Extinction coefficient: 0.019 (3)

10 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

### Special details

**Experimental.** The absorption correction (*X-RED*; Stoe & Cie, 2001) was performed after optimizing the crystal shape using *X-SHAPE* (Stoe & Cie, 1999).

A suitable single-crystal was carefully selected under a polarizing microscope and mounted in a glass capillary. The scattering intensities were collected on an imaging plate diffractometer (*IPDS I*, Stoe & Cie) equipped with a fine focus sealed tube X-ray source (Mo  $K_{\alpha}$ ,  $\lambda = 0.71073 \text{ \AA}$ ) operating at 50 kV and 40 mA. Intensity data for the title compound were collected at room temperature by  $\varphi$  scans in 100 frames ( $0 < \varphi < 200^\circ$ ,  $\Delta\varphi = 2^\circ$ , exposure time of 10 min) in the  $2\Theta$  range  $3.8$  to  $56.3^\circ$ . Structure solution and refinement were carried out using the programs *SIR92* (Altomare *et al.*, 1993) and *SHELXL97* (Sheldrick, 1997). A numerical absorption correction (*X-RED* (Stoe & Cie, 2001) was applied after optimization of the crystal shape (*X-SHAPE* (Stoe & Cie, 1999)). The last cycles of refinement included atomic positions and anisotropic parameters for all atoms. The final difference maps were free of any chemically significant features. The refinement was based on  $F^2$  for ALL reflections.

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Lu	-0.2500	0.7500	0.36724 (9)	0.0082 (4)
Br	0.2500	1.2500	0.1718 (3)	0.0158 (5)
O	-0.2500	0.2500	0.5000	0.009 (2)

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Lu	0.0034 (4)	0.0034 (4)	0.0178 (5)	0.000	0.000	0.000
Br	0.0142 (6)	0.0142 (6)	0.0190 (9)	0.000	0.000	0.000
O	0.005 (3)	0.005 (3)	0.016 (5)	0.000	0.000	0.000

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Lu—O <sup>i</sup>	2.1847 (7)	Lu—Lu <sup>i</sup>	3.4650 (14)
Lu—O <sup>ii</sup>	2.1847 (7)	Lu—Lu <sup>viii</sup>	3.4650 (13)
Lu—O <sup>iii</sup>	2.1847 (7)	Lu—Lu <sup>iii</sup>	3.4650 (14)
Lu—O	2.1847 (7)	Br—Lu <sup>ix</sup>	3.1228 (15)
Lu—Br <sup>iv</sup>	3.1228 (15)	Br—Lu <sup>ii</sup>	3.1228 (15)
Lu—Br	3.1228 (15)	Br—Lu <sup>x</sup>	3.1228 (15)
Lu—Br <sup>v</sup>	3.1228 (15)	O—Lu <sup>i</sup>	2.1847 (7)
Lu—Br <sup>vi</sup>	3.1228 (15)	O—Lu <sup>vi</sup>	2.1847 (7)
Lu—Lu <sup>vii</sup>	3.4650 (14)	O—Lu <sup>iii</sup>	2.1847 (7)
O <sup>i</sup> —Lu—O <sup>ii</sup>	75.07 (2)	O—Lu—Lu <sup>i</sup>	37.533 (10)
O <sup>i</sup> —Lu—O <sup>iii</sup>	118.99 (4)	Br <sup>iv</sup> —Lu—Lu <sup>i</sup>	109.55 (3)
O <sup>ii</sup> —Lu—O <sup>iii</sup>	75.07 (2)	Br—Lu—Lu <sup>i</sup>	109.55 (3)
O <sup>i</sup> —Lu—O	75.07 (2)	Br <sup>v</sup> —Lu—Lu <sup>i</sup>	171.72 (5)
O <sup>ii</sup> —Lu—O	118.99 (4)	Br <sup>vi</sup> —Lu—Lu <sup>i</sup>	71.33 (5)
O <sup>iii</sup> —Lu—O	75.07 (2)	Lu <sup>vii</sup> —Lu—Lu <sup>i</sup>	65.81 (3)
O <sup>i</sup> —Lu—Br <sup>iv</sup>	141.696 (9)	O <sup>i</sup> —Lu—Lu <sup>viii</sup>	98.23 (4)
O <sup>ii</sup> —Lu—Br <sup>iv</sup>	141.696 (9)	O <sup>ii</sup> —Lu—Lu <sup>viii</sup>	37.533 (10)
O <sup>iii</sup> —Lu—Br <sup>iv</sup>	75.29 (3)	O <sup>iii</sup> —Lu—Lu <sup>viii</sup>	37.533 (10)
O—Lu—Br <sup>iv</sup>	75.29 (3)	O—Lu—Lu <sup>viii</sup>	98.23 (4)
O <sup>i</sup> —Lu—Br	75.29 (3)	Br <sup>iv</sup> —Lu—Lu <sup>viii</sup>	109.55 (3)
O <sup>ii</sup> —Lu—Br	75.29 (3)	Br—Lu—Lu <sup>viii</sup>	109.55 (3)
O <sup>iii</sup> —Lu—Br	141.696 (9)	Br <sup>v</sup> —Lu—Lu <sup>viii</sup>	71.33 (5)
O—Lu—Br	141.696 (9)	Br <sup>vi</sup> —Lu—Lu <sup>viii</sup>	171.72 (5)
Br <sup>iv</sup> —Lu—Br	116.95 (8)	Lu <sup>vii</sup> —Lu—Lu <sup>viii</sup>	65.81 (3)
O <sup>i</sup> —Lu—Br <sup>v</sup>	141.696 (9)	Lu <sup>i</sup> —Lu—Lu <sup>viii</sup>	100.39 (5)
O <sup>ii</sup> —Lu—Br <sup>v</sup>	75.29 (3)	O <sup>i</sup> —Lu—Lu <sup>iii</sup>	98.23 (4)
O <sup>iii</sup> —Lu—Br <sup>v</sup>	75.29 (3)	O <sup>ii</sup> —Lu—Lu <sup>iii</sup>	98.23 (4)
O—Lu—Br <sup>v</sup>	141.696 (9)	O <sup>iii</sup> —Lu—Lu <sup>iii</sup>	37.533 (10)
Br <sup>iv</sup> —Lu—Br <sup>v</sup>	74.13 (4)	O—Lu—Lu <sup>iii</sup>	37.533 (10)
Br—Lu—Br <sup>v</sup>	74.13 (4)	Br <sup>iv</sup> —Lu—Lu <sup>iii</sup>	71.33 (5)
O <sup>i</sup> —Lu—Br <sup>vi</sup>	75.29 (3)	Br—Lu—Lu <sup>iii</sup>	171.72 (5)
O <sup>ii</sup> —Lu—Br <sup>vi</sup>	141.696 (9)	Br <sup>v</sup> —Lu—Lu <sup>iii</sup>	109.55 (3)

O <sup>iii</sup> —Lu—Br <sup>vi</sup>	141.696 (9)	Br <sup>vi</sup> —Lu—Lu <sup>iii</sup>	109.55 (3)
O—Lu—Br <sup>vi</sup>	75.29 (3)	Lu <sup>vii</sup> —Lu—Lu <sup>iii</sup>	100.39 (5)
Br <sup>iv</sup> —Lu—Br <sup>vi</sup>	74.13 (4)	Lu <sup>i</sup> —Lu—Lu <sup>iii</sup>	65.81 (3)
Br—Lu—Br <sup>vi</sup>	74.13 (4)	Lu <sup>viii</sup> —Lu—Lu <sup>iii</sup>	65.81 (3)
Br <sup>v</sup> —Lu—Br <sup>vi</sup>	116.95 (8)	Lu <sup>ix</sup> —Br—Lu <sup>ii</sup>	74.13 (4)
O <sup>i</sup> —Lu—Lu <sup>vii</sup>	37.533 (10)	Lu <sup>ix</sup> —Br—Lu <sup>x</sup>	74.13 (4)
O <sup>ii</sup> —Lu—Lu <sup>vii</sup>	37.533 (10)	Lu <sup>ii</sup> —Br—Lu <sup>x</sup>	116.95 (8)
O <sup>iii</sup> —Lu—Lu <sup>vii</sup>	98.23 (4)	Lu <sup>ix</sup> —Br—Lu	116.95 (8)
O—Lu—Lu <sup>vii</sup>	98.23 (4)	Lu <sup>ii</sup> —Br—Lu	74.13 (4)
Br <sup>iv</sup> —Lu—Lu <sup>vii</sup>	171.72 (5)	Lu <sup>x</sup> —Br—Lu	74.13 (4)
Br—Lu—Lu <sup>vii</sup>	71.33 (5)	Lu <sup>i</sup> —O—Lu <sup>vi</sup>	104.93 (2)
Br <sup>v</sup> —Lu—Lu <sup>vii</sup>	109.55 (3)	Lu <sup>i</sup> —O—Lu <sup>iii</sup>	118.99 (4)
Br <sup>vi</sup> —Lu—Lu <sup>vii</sup>	109.55 (3)	Lu <sup>vi</sup> —O—Lu <sup>iii</sup>	104.93 (2)
O <sup>i</sup> —Lu—Lu <sup>i</sup>	37.533 (10)	Lu <sup>i</sup> —O—Lu	104.93 (2)
O <sup>ii</sup> —Lu—Lu <sup>i</sup>	98.23 (4)	Lu <sup>vi</sup> —O—Lu	118.99 (4)
O <sup>iii</sup> —Lu—Lu <sup>i</sup>	98.23 (4)	Lu <sup>iii</sup> —O—Lu	104.93 (2)

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

Fig. 1

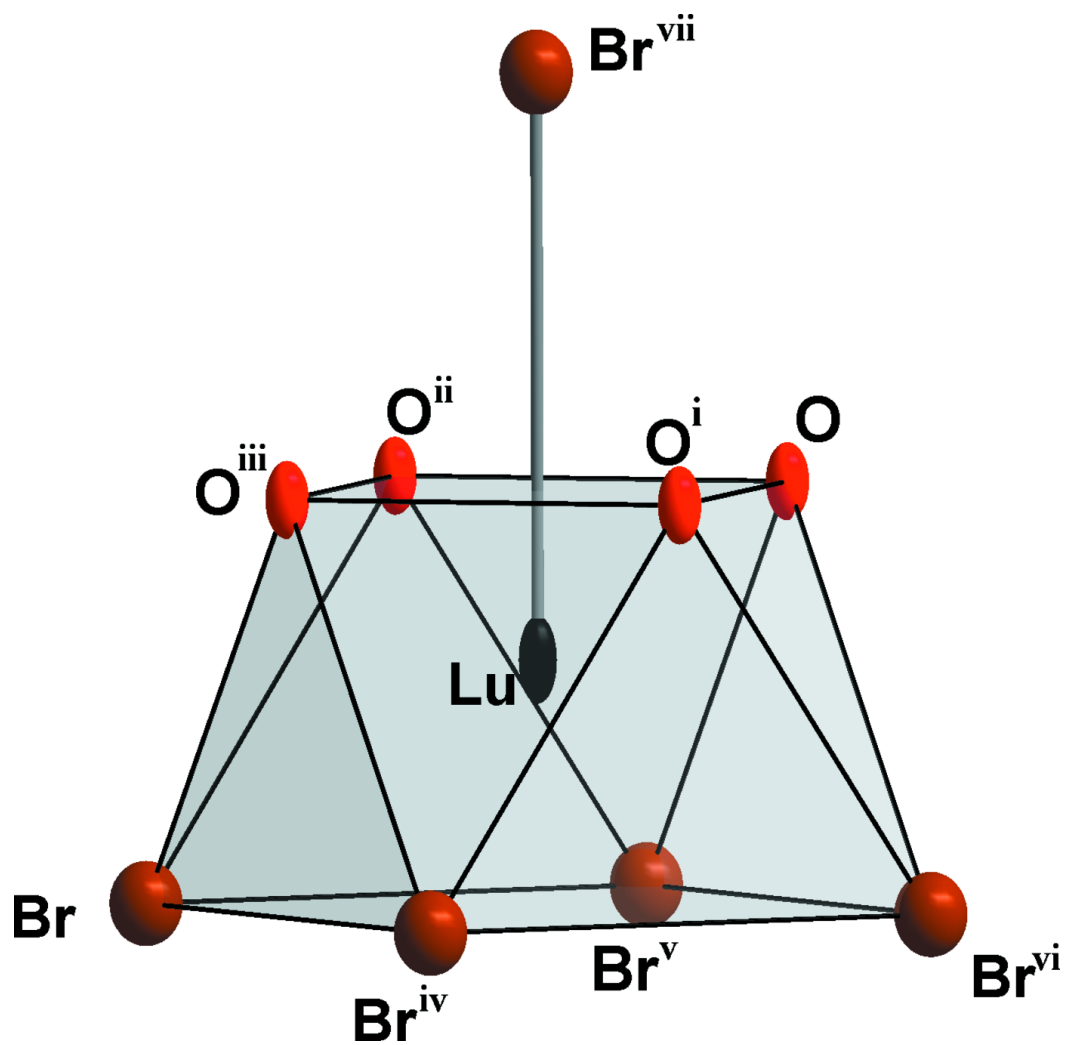




Fig. 2

