

Hydroflux synthesis and crystal structure of Tl_3IO Ralf Albrecht,^a Heinrich Menning,^a Thomas Doert^a and Michael Ruck^{a,b,*}^aTechnische Universität Dresden, Chair of Inorganic Chemistry II, Bergstrasse 66, 01069 Dresden, Germany, and ^bMax-Planck Institute for Chemical Physics of Solids, Nöthnitzer Strasse 40, 01187 Dresden, Germany. *Correspondence e-mail: michael.ruck@tu-dresden.de

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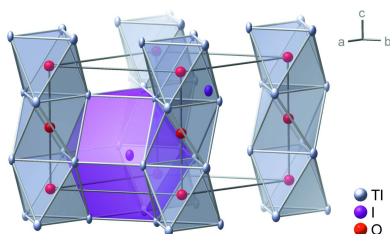
Keywords: crystal structure; hydroflux synthesis; thallium; oxide iodide; single-crystal XRD.**CCDC reference:** 2030857**Supporting information:** this article has supporting information at journals.iucr.org/e

Single-crystals of thallium(I) iodide oxide Tl_3IO were obtained as by-product in a hydroflux synthesis at 473 K for 10 h. A potassium hydroxide hydroflux with a water-base molar ratio of 1.6 and the starting materials TlNO_3 , RhI_3 and $\text{Ba}(\text{NO}_3)_2$ was used, resulting in a few black needle-shaped crystals. X-ray diffraction on a single-crystal revealed the hexagonal space group $P6_3/mmc$ (No. 194) with lattice parameters $a = 7.1512(3)$ Å and $c = 6.3639(3)$ Å. Tl_3IO crystallizes as hexagonal anti-perovskite (anti- BaNiO_3 type) and is thus structurally related to the alkali-metal halide/auride oxides $M_3\text{XO}$ ($M = \text{K}, \text{Rb}, \text{Cs}$; $X = \text{Cl}, \text{Br}, \text{I}, \text{Au}$). The oxygen atoms center thallium octahedra. The $[\text{OTl}_6]$ octahedra share *trans* faces, forming a linear chain along $[001]$. Twelve thallium atoms surround each iodine atom in an $[\text{ITl}_{12}]$ anti-cuboctahedron. Thallium and iodine atoms together form a hexagonal close-sphere packing, in which every fourth octahedral void is occupied by oxygen.

1. Chemical context

The class of alkali-metal halide/auride oxides comprises several compounds with the general formula $M_3\text{XO}$ ($M = \text{K}, \text{Rb}, \text{Cs}$; $X = \text{Cl}, \text{Br}, \text{I}, \text{Au}$) (Sitta *et al.*, 1991*a,b*; Feldmann & Jansen, 1995*a,b,c*; Sabrowsky *et al.*, 1996), Li_3BrO (Wortmann *et al.*, 1989), $\text{Na}_3\text{X}'\text{O}$ ($X' = \text{Cl}, \text{Br}$) (Sabrowsky *et al.*, 1988; Hippler *et al.*, 1990). These ternary oxides crystallize typically as anti-perovskites, *i.e.* in the cubic anti- CaTiO_3 type. The cesium derivatives Cs_3BrO , Cs_3IO and Cs_3AuO adopt hexagonal anti-perovskite structures (anti- BaNiO_3 type), whereas the Cs_3ClO crystallizes as anti- NH_4CdCl_3 type and thus does not form a perovskite structure. The crystal structure of Rb_3IO has both face and corner-sharing $[\text{ORB}_6]$ octahedra (anti- BaFeO_{3-x} type). The adopted structure type depends on the size of the alkali-metal and halide/auride ions and their ratio. The stability range of the different perovskite phases can be estimated by using Goldschmidt's tolerance factor, where larger M and X ions tend to destabilize the cubic anti-perovskite structure resulting in the hexagonal polymorph (Babel, 1969; Feldmann & Jansen, 1995*b*).

For the synthesis of the title compound, the hydroflux method was used, which can be classified as intermediate between hydrothermal and flux synthesis (Chance *et al.*, 2013). An approximately equimolar mixture of alkali-metal hydroxide (typically NaOH or KOH) and water is used as reaction medium (Albrecht *et al.*, 2020*a*). Good solubility of oxides and hydroxides, highly crystalline reaction products suitable for single-crystal X-ray diffraction analysis, comparably low reaction temperatures and a pressureless setup are essential advantages of the hydroflux method. In this communication,



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Table 1

 Atomic coordinates and equivalent isotropic displacement parameters (in 10^{-4} \AA^2) in Tl_3IO at 100 (1) K.

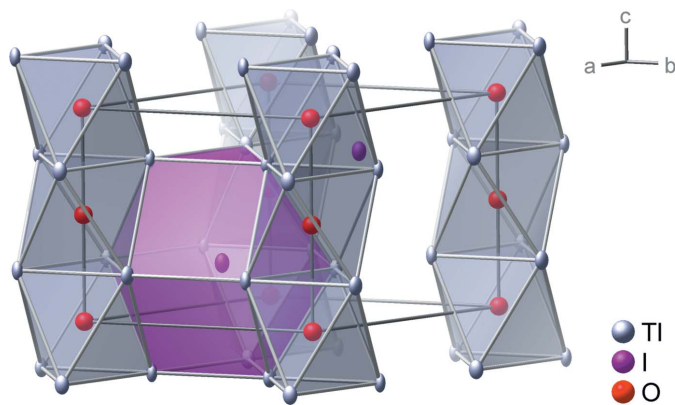
Atom	Wyckoff symbol	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
Tl	6 <i>h</i>	0.1608 (1)	0.3216 (1)	1/4	47 (1)
I	2 <i>d</i>	2/3	1/3	1/4	53 (1)
O	2 <i>a</i>	0	0	0	68 (7)

we report on the synthesis and crystal structure analysis of the thallium(I) iodide oxide Tl_3IO .

2. Structural commentary

Single-crystal X-ray diffraction on a black needle revealed the composition Tl_3IO and a hexagonal structure in the space group $P6_3/mmc$ (no. 194) with lattice parameters $a = 7.1512$ (3) \AA and $c = 6.3639$ (3) \AA at 100 (1) K. Tl_3IO crystallizes as hexagonal anti-perovskite (anti- BaNiO_3 type; Fig. 1, Tables 1 and 2). The asymmetric unit consists of three atoms, thallium (site symmetry $mm2$, Wyckoff position 6*h*), iodine ($\bar{6}m2$, 2*d*) and oxygen ($\bar{3}m.$, 2*a*). The oxygen atoms center thallium octahedra. The $[\text{OTl}_6]$ octahedra share *trans* faces, forming a linear chain along $[001]$. Twelve thallium atoms surround each iodine atom in a $[\text{ITl}_{12}]$ anti-cuboctahedron (triangular orthobicupola). Thallium and iodine atoms together form a hexagonal close-sphere packing, in which every fourth octahedral void is occupied by oxygen. Thus, also the thallium atom centers an anti-cuboctahedron, which has the composition $[\text{Tl}(\text{I}_4\text{Tl}_8)]$.

The $[\text{OTl}_6]$ octahedron is slightly elongated along the chain direction. The O–Tl bond length of 2.549 (1) \AA is about 1% longer than in Tl_2O , at 2.517 (1) \AA (Sabrowsky, 1971). The Tl–O–Tl angles along the chain parallel to *c* are 94.8 (1) $^\circ$. The shortest Tl \cdots Tl distances in Tl_3IO are with 3.449 (1) \AA , very similar to those in thallium metal, which has Tl \cdots Tl distances of 3.405 (1) and 3.455 (1) \AA in its hexagonal sphere packing (Barrett, 1958). Accordingly, the $[\text{ITl}_{12}]$ anticuboctahedra are also stretched along $[001]$, with Tl–I distances of


Figure 1

Crystal structure of Tl_3IO in $P6_3/mmc$, highlighting the one-dimensional chains consisting of $[\text{OTl}_6]$ octahedra. Ellipsoids enclose 99% of the probability density of the atoms.

Table 2

 Anisotropic displacement parameters (in 10^{-4} \AA^2) in Tl_3IO at 100 (1) K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{12}	U_{13}
Tl	38 (1)	24 (1)	73 (1)	0	0	12 (1)
I	42 (1)	42 (1)	77 (2)	0	0	21 (1)
O	68 (10)	68 (10)	68 (19)	0	0	34 (5)

3.576 (1) \AA and 3.833 (1) \AA . Although thallium(I) has a larger ionic radius (1.70 \AA for c.n. = 12; Shannon, 1976) than potassium (1.64 \AA for c.n. = 12), the M –O, $M \cdots M$ and the average M –I distances in Tl_3IO are smaller than in K_3IO by 3.5%, 7.5% and 1%, respectively (Feldmann & Jansen, 1995*b*).

3. Synthesis and crystallization

Thallium(I) iodide oxide, Tl_3IO , was synthesized in a potassium hydroxide hydroflux. The reaction was carried out in a PTFE-lined 50 mL Berghof type DAB-2 stainless steel autoclave starting from TlNO_3 (0.38 mmol; abcr, 99.5%), RhI_3 (0.06 mmol; abcr, 99%), and $\text{Ba}(\text{NO}_3)_2$ (0.19 mmol; VEB Laborchemie Apolda, 99%). Water and potassium hydroxide (86%, Fisher Scientific) in the molar ratio of 1.6:1.0 were added to these compounds. The sealed autoclave was heated at a heating rate of 2 K min^{-1} to 473 K and after 10 h cooled to room temperature at a rate of 0.1 K min^{-1} . The reaction product after washing with water mainly consisted of thallium(I) iodide, thallium(III) oxide, barium carbonate and a brown powder of an unidentified rhodium-containing compound. A few black single crystals of Tl_3IO with a needle-like morphology were found, which are sensitive to water and other protic solvents. In contact with water, the Tl_3IO crystals immediately turn yellow, probably due to the formation of thallium(I) hydroxide and thallium(I) iodide, which are both yellow. Energy-dispersive X-ray spectroscopy on Tl_3IO single-crystals revealed a disproportionately high oxygen content, indicating surface decomposition.

Several experiments failed to exchange rhodium(III) iodide with other iodine sources like potassium iodide, copper(I) iodide or silver(I) iodide. Likewise, experiments without barium nitrate were not successful. However, when both starting materials were used, Tl_3IO was obtained reproducibly, also at reaction temperatures of 423 K or 523 K. Similarly, the hydrothermal synthesis of $\text{Na}_3[\text{Tl}(\text{OH})_6]$ starting from thallium(I) sulfate required heavy metal salts like bismuth nitrate (Giesselbach, 2002). The oxidation of thallium(I) to thallium(III) in this reaction was achieved by oxygen in alkaline solutions (Rich, 2007).

The alkali-metal oxide halides $M_3\text{XO}$ are reported to be very sensitive to traces of moisture or carbon dioxide due to their highly basic nature (Feldmann & Jansen, 1995*b*). Remarkably, Tl_3IO crystallizes in the presence of water from the hydroflux. In other experiments, we synthesized a water sensitive oxohydroxoferrate (Albrecht *et al.*, 2019) or an oxidation sensitive manganate(V) from hydroflux (Albrecht *et al.*, 2020*b*). Obviously, the activity of water is dramatically reduced in these aqueous salt melts.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3.

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Table 3

Experimental details.

Crystal data	
Chemical formula	Tl ₃ IO
<i>M_r</i>	756.01
Crystal system, space group	Hexagonal, <i>P6₃/mmc</i>
Temperature (K)	100
<i>a</i> , <i>c</i> (Å)	7.1512 (3), 6.3639 (3)
<i>V</i> (Å ³)	281.85 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	90.87
Crystal size (mm)	0.09 × 0.05 × 0.03
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2016)
<i>T_{min}</i> , <i>T_{max}</i>	0.113, 0.749
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	15853, 480, 442
<i>R_{int}</i>	0.049
(sin θ/λ) _{max} (Å ⁻¹)	0.995
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.018, 0.041, 1.29
No. of reflections	480
No. of parameters	10
Δρ _{max} , Δρ _{min} (e Å ⁻³)	2.80, -2.01

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

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Hydroflux synthesis and crystal structure of Tl_3IO

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINTE* (Bruker, 2016); data reduction: *SAINTE* (Bruker, 2016); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

Thallium(I) iodide oxide

Crystal data

Tl_3IO	$D_x = 8.908 \text{ Mg m}^{-3}$
$M_r = 756.01$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hexagonal, $P6_3/mmc$	Cell parameters from 8223 reflections
$a = 7.1512 (3) \text{ \AA}$	$\theta = 3.2\text{--}46.5^\circ$
$c = 6.3639 (3) \text{ \AA}$	$\mu = 90.87 \text{ mm}^{-1}$
$V = 281.85 (3) \text{ \AA}^3$	$T = 100 \text{ K}$
$Z = 2$	Needle, black
$F(000) = 608$	$0.09 \times 0.05 \times 0.03 \text{ mm}$

Data collection

Bruker APEXII CCD diffractometer	480 independent reflections
φ and ω scans	442 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2016)	$R_{\text{int}} = 0.049$
$T_{\text{min}} = 0.113$, $T_{\text{max}} = 0.749$	$\theta_{\text{max}} = 45.0^\circ$, $\theta_{\text{min}} = 3.3^\circ$
15853 measured reflections	$h = -14 \rightarrow 14$
	$k = -11 \rightarrow 14$
	$l = -11 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0193P)^2]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.018$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$wR(F^2) = 0.041$	$\Delta\rho_{\text{max}} = 2.80 \text{ e \AA}^{-3}$
$S = 1.29$	$\Delta\rho_{\text{min}} = -2.01 \text{ e \AA}^{-3}$
480 reflections	Extinction correction: SHELXL-2016/6
10 parameters	(Sheldrick 2015b),
0 restraints	$F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.0035 (2)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Tl	0.16078 (2)	0.32156 (2)	0.250000	0.00465 (5)
I	0.666667	0.333333	0.250000	0.00534 (7)
O	0.000000	0.000000	0.000000	0.0068 (7)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tl	0.00378 (6)	0.00238 (6)	0.00733 (9)	0.00119 (3)	0.000	0.000
I	0.00418 (9)	0.00418 (9)	0.00765 (18)	0.00209 (5)	0.000	0.000
O	0.0068 (10)	0.0068 (10)	0.0068 (19)	0.0034 (5)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Tl—Tl ⁱ	3.4494 (3)	Tl—Tl ^{vi}	3.7538 (1)
Tl—Tl ⁱⁱ	3.7538 (1)	Tl—Tl ^{vii}	3.7018 (3)
Tl—Tl ⁱⁱⁱ	3.7538 (1)	Tl—Tl ^{viii}	3.7018 (3)
Tl—Tl ^{iv}	3.4494 (3)	Tl—O	2.5490 (1)
Tl—Tl ^v	3.7538 (1)	Tl—O ^{ix}	2.5490 (1)
Tl ⁱ —Tl—Tl ^{iv}	60.0	O—Tl—Tl ^{viii}	132.580 (2)
Tl ^{iv} —Tl—Tl ⁱⁱⁱ	62.648 (2)	O ^{ix} —Tl—Tl ^{viii}	132.580 (2)
Tl ^{vii} —Tl—Tl ^{vi}	90.0	O ^{ix} —Tl—Tl ^{iv}	47.420 (2)
Tl ⁱ —Tl—Tl ^{viii}	180.0	O ^{ix} —Tl—Tl ⁱ	47.420 (2)
Tl ^v —Tl—Tl ⁱⁱⁱ	115.917 (5)	O—Tl—Tl ⁱⁱⁱ	42.580 (2)
Tl ^{iv} —Tl—Tl ^{viii}	120.0	O—Tl—Tl ^{iv}	47.420 (2)
Tl ⁱⁱ —Tl—Tl ^v	149.235 (3)	O ^{ix} —Tl—Tl ^{vii}	132.580 (2)
Tl ⁱ —Tl—Tl ^{vii}	120.0	O—Tl—Tl ^{vii}	132.580 (2)
Tl ⁱⁱⁱ —Tl—Tl ^{vi}	149.235 (3)	O—Tl—Tl ⁱ	47.420 (2)
Tl ^{iv} —Tl—Tl ^{vii}	180.0	O—Tl—Tl ^v	108.774 (4)
Tl ^{iv} —Tl—Tl ^{vi}	90.0	O—Tl—Tl ⁱⁱ	42.580 (2)
Tl ^{viii} —Tl—Tl ^{vii}	60.0	O—Tl—Tl ^{vi}	108.774 (4)
Tl ^v —Tl—Tl ^{vi}	54.704 (4)	O ^{ix} —Tl—Tl ^{vi}	42.580 (2)
Tl ⁱ —Tl—Tl ⁱⁱ	62.648 (2)	O ^{ix} —Tl—Tl ⁱⁱⁱ	108.774 (4)
Tl ⁱ —Tl—Tl ⁱⁱⁱ	90.0	O—Tl—O ^{ix}	77.242 (5)
Tl ^{iv} —Tl—Tl ⁱⁱ	90.0	Tl ^x —O—Tl ⁱ	94.839 (4)
Tl ^{viii} —Tl—Tl ⁱⁱⁱ	90.0	Tl ^x —O—Tl ⁱⁱⁱ	85.161 (4)
Tl ^{viii} —Tl—Tl ⁱⁱ	117.352 (2)	Tl—O—Tl ^x	180.0
Tl ⁱⁱ —Tl—Tl ⁱⁱⁱ	54.704 (4)	Tl ^{iv} —O—Tl ⁱ	85.161 (4)
Tl ^{vii} —Tl—Tl ⁱⁱ	90.0	Tl—O—Tl ⁱⁱ	94.840 (4)

Tl ⁱ —Tl—Tl ^{vi}	62.648 (2)	Tl ^{iv} —O—Tl ⁱⁱⁱ	94.839 (4)
Tl ⁱ —Tl—Tl ^v	90.0	Tl ^x —O—Tl ⁱⁱ	85.160 (4)
Tl ^{viii} —Tl—Tl ^{vi}	117.352 (2)	Tl ⁱⁱⁱ —O—Tl ⁱ	94.839 (4)
Tl ^{iv} —Tl—Tl ^v	62.648 (2)	Tl—O—Tl ^{iv}	85.160 (4)
Tl ⁱⁱ —Tl—Tl ^{vi}	115.917 (5)	Tl—O—Tl ⁱⁱⁱ	94.840 (4)
Tl ^{viii} —Tl—Tl ^v	90.0	Tl ^x —O—Tl ^{iv}	94.840 (4)
Tl ^{vii} —Tl—Tl ^v	117.352 (2)	Tl ⁱⁱ —O—Tl ⁱⁱⁱ	85.161 (4)
Tl ^{vii} —Tl—Tl ⁱⁱⁱ	117.352 (2)	Tl ⁱⁱ —O—Tl ^{iv}	180.0
O ^{ix} —Tl—Tl ⁱⁱ	108.774 (4)	Tl ⁱ —O—Tl ⁱⁱⁱ	180.0
O ^{ix} —Tl—Tl ^v	42.580 (2)	Tl—O—Tl ⁱ	85.160 (4)

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