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Dehydration synthesis and crystal structure of terbium oxychloride, TbOCl

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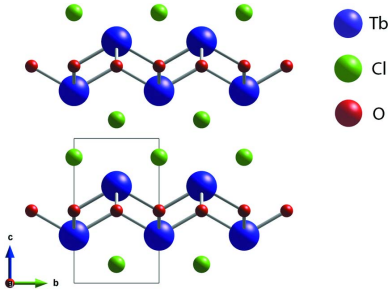
Terbium oxychloride, TbOCl, was synthesized *via* the simple heat-treatment of $TbCl_3{\cdot}6H_2O$ and its structure was determined by refinement against X-ray powder diffraction data. TbOCl crystallizes with the matlockite (PbFCl) structure in the tetragonal space group *P*4/*nmm* and is composed of alternating (001) layers of $(TbO)_n$ and n Cl^-. The unit-cell parameters, unit-cell volume, and density were compared to the literature data of other isostructural rare-earth oxychlorides in the same space group and showed good agreement when compared to the calculated trendlines.

1. Chemical context

Rare-earth oxychlorides, *RE*OCl, are promising materials for various applications including use as catalysts, sensors, and phosphors (Podkolzin *et al.*, 2007; Au *et al.*, 1997; Peringer *et al.*, 2009; Marsal *et al.*, 2005,; Kim *et al.*, 2019; Berdowski *et al.*, 1984; Imanaka *et al.*, 2001*a*,*b*; Okamoto *et al.*, 2002; Kim *et al.*, 2014). LaOCl is a stable catalyst for converting methane to methyl chloride (Podkolzin *et al.*, 2007) and can be used as a sensor material to detect CO_2 and Cl_2 gases (Marsal *et al.*, 2005; Imanaka *et al.*, 2001*b*). The EuOCl catalyst showed high efficiency in converting ethylene to vinyl chloride (Scharfe *et al.*, 2016). The luminescent properties of *RE*O*X* (*RE* = La, Eu; *X* = F, Cl, Br, I) can be controlled to emit a wide range of visible light from blue to red by changing the crystal symmetries and compositions (Kim *et al.*, 2014, 2019). As part of our studies in this area, we now describe the dehydration synthesis and structure of the title compound.

2. Structural commentary

The structural parameters of *RE*OCl (*RE* = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho) in the literature and current study are summarized in Table 1. All these *RE*OCl compounds crystallize in the matlockite (PbFCl; Bannister, 1934) structure within the tetragonal *P*4/*nmm* space group. The crystal structure of TbOCl contains alternating (001) layers of $(TbO)_n$ and n Cl^- (Fig. 1*a*). The Tb cation is coordinated by five chloride ions and four oxygen atoms, forming a mono-capped TbO_4Cl_5 square antiprism (Fig. 1*b* and 1*c*). The *RE*—Cl and *RE*—O bond lengths in the *RE*OCl compounds are provided in Table 1. With larger *RE* cations in the structures, the *RE*—Cl and *RE*—O bond lengths increase (Fig. 2).



The shortest Cl···Cl separation in TbOCl is 3.271 (4) Å, which compares with the van der Waals diameter of a Cl^- ion of about 3.62 Å. The Cl···Cl distances of other *RE*OCl compounds are also short, ranging from 3.24 to 3.46 Å on

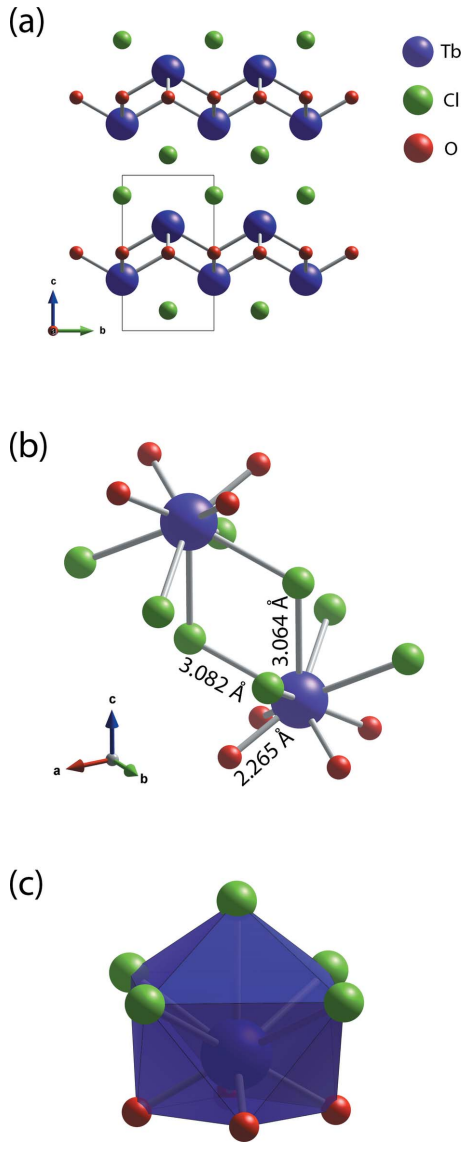


Figure 1
(*a*) Crystal structure of TbOCl, (*b*) the coordination environment of Tb, and (*c*) polyhedron representation of the Tb environment.

going from Ho^{3+} to La^{3+}. With non-bonded vectors shorter than the van der Waals separation, strong interactions between atoms are expected in the structure (Maslen *et al.*, 1996). Templeton & Dauben (1953) mention the presence of weaker anion–anion repulsion between Cl atoms in *RE*OCl structures. The structural parameters of TbOCl were compared with the trendlines calculated using the values from Table 1 (Fig. 3). The unit-cell parameters and volumes increase linearly with the larger *RE* cations (Shannon, 1976) whereas the densities decrease non-linearly, fitting well to a 2nd order polynomial trend.

3. Synthesis and crystallization

The title compound was synthesized by a simple heat treatment of $TbCl_3{\cdot}6H_2O$ (Alfa Aesar, 99.99%). About 0.5 g of $TbCl_3{\cdot}6H_2O$ was placed in an alumina crucible, heated to 400°C at 5°C min^{-1}, held for 8 h, and then cooled to room temperature at 5°C min^{-1}. This synthesis method was used in our previous study (Riley *et al.*, 2018). The resulting product was a light-brown powder, which was ground in a mortar and pestle for X-ray powder diffraction analysis.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The unit-cell parameters were obtained using *TOPAS* (version 4.2; Bruker, 2009) by refining the GdOCl pattern (ICSD 77820) with geometrical and chemical resemblance as a starting model. The Rietveld refinement was performed using *JANA2006* (Petříček *et al.*, 2014) with the obtained unit-cell parameters as initial values.

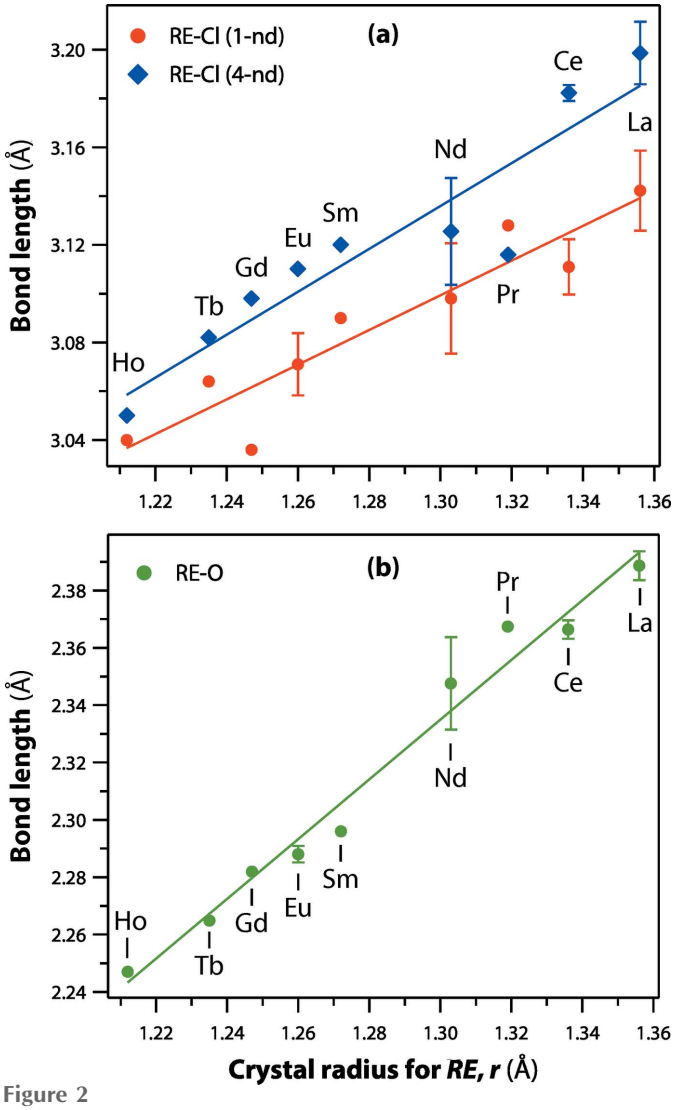


Figure 2
The *RE*—Cl and *RE*—O bond lengths in the *RE*OCl compounds listed in Table 1 as a function of *RE* crystal radius (coordination = 9) according to Shannon (1976). Where multiple values were available, averages and standard deviations are included for the datapoints. For (*a*), 1-nd and 4-nd denote 1 and 4 neighbor distances, respectively

Table 1
Structural parameters of *RE*OCl compounds.

All compounds crystallize in the *P*4/*nmm* space group. For the *RE*—Cl bond lengths, the first value refers to one neighboring Cl atom, and the second number refers to four neighboring Cl atoms. Densities are calculated from crystallographic data.

RE	*a* (Å)	*c* (Å)	*V* (Å^3)	Density (g cm^{-3})	*RE*—O (Å)	*RE*—Cl (Å)	Cl···Cl (Å)	Cl···O (Å)	O···O (Å)	ICSD/PDF
Ho	3.893	6.602	100.1	7.182	2.247	3.04, 3.05	3.24	3.12	2.753	76171 (Templeton & Dauben, 1953)
Dy	3.91	6.62	101.2	7.023						00–047-1725 (Kirik *et al.*, 1996)
Tb	3.9269	6.648	102.5	6.815						00–048-1648 (Kirik *et al.*, 1996)
Tb	3.9279	6.6556	102.7	6.804	2.2649	3.064, 3.082	3.271	3.151	2.7774	Current study
Gd	3.9495	6.6708	104.1	6.661	2.2839	3.036, 3.098	3.267	3.176	2.7927	59232 (Meyer & Schleid, 1986)
Gd	3.9698	6.7008	105.6	6.564	2.28	3.212, 3.071	3.428	3.089	2.8071	77820 (Hölsä *et al.*, 1996)
Eu	3.9646	6.695	105.2	6.42	2.286	3.08, 3.11	3.3	3.17	2.8034	28529 (Bärnighausen *et al.*, 1965)
Eu	3.9668	6.6955	105.4	6.412	2.2901	3.062, 3.1103	3.289	3.183	2.80492	54682 (Schnick, 2004)
Sm	3.982	6.721	106.6	6.289	2.296	3.09, 3.12	3.31	3.19	2.8157	26581 (Templeton & Dauben, 1953)
Nd	4.04	6.77	110.5	5.882	2.359	3.114, 3.11	3.428	3.165	2.86	31665 (Zachariasen, 1949)
Nd	4.0249	6.7837	109.9	5.914	2.3362	3.082, 3.141	3.343	3.221	2.84603	59231 (Meyer & Schleid, 1986)
Pr	4.053	6.799	111.7	5.723	2.3674	3.128, 3.116	3.441	3.178	2.866	31664 (Zachariasen, 1949)
Ce	4.0866	6.8538	114.5	5.558	2.3687	3.1190, 3.1846	3.3942	3.2572	2.8897	412069 (Schnick, 2004)
Ce	4.0785	6.8346	113.7	5.596	2.36413	3.103, 3.180	3.38	3.254	2.88393	72154 (Wołcyrz & Kepinski, 1992)
La	4.109	6.865	115.9	5.454	2.39	3.14, 3.18	3.45	3.24	2.9055	24611 (Sillen & Nylander, 1941)
La	4.117	6.881	116.6	5.42	2.3866	3.126, 3.2046	3.416	3.2751	2.9112	40297 (Brixner & Moore, 1983)
La	4.1351	6.904	118.1	5.355	2.395	3.165, 3.209	3.457	3.268	2.92397	77815 (Hölsä *et al.*, 1996)
La	4.1162	6.8746	116.5	5.428	2.3832	3.138, 3.201	3.425	3.265	2.9106	84330 (Hölsä *et al.*, 1997)
La	4.12	6.882	116.8	5.412						00–008-0477 (Swanson *et al.*, 1957)

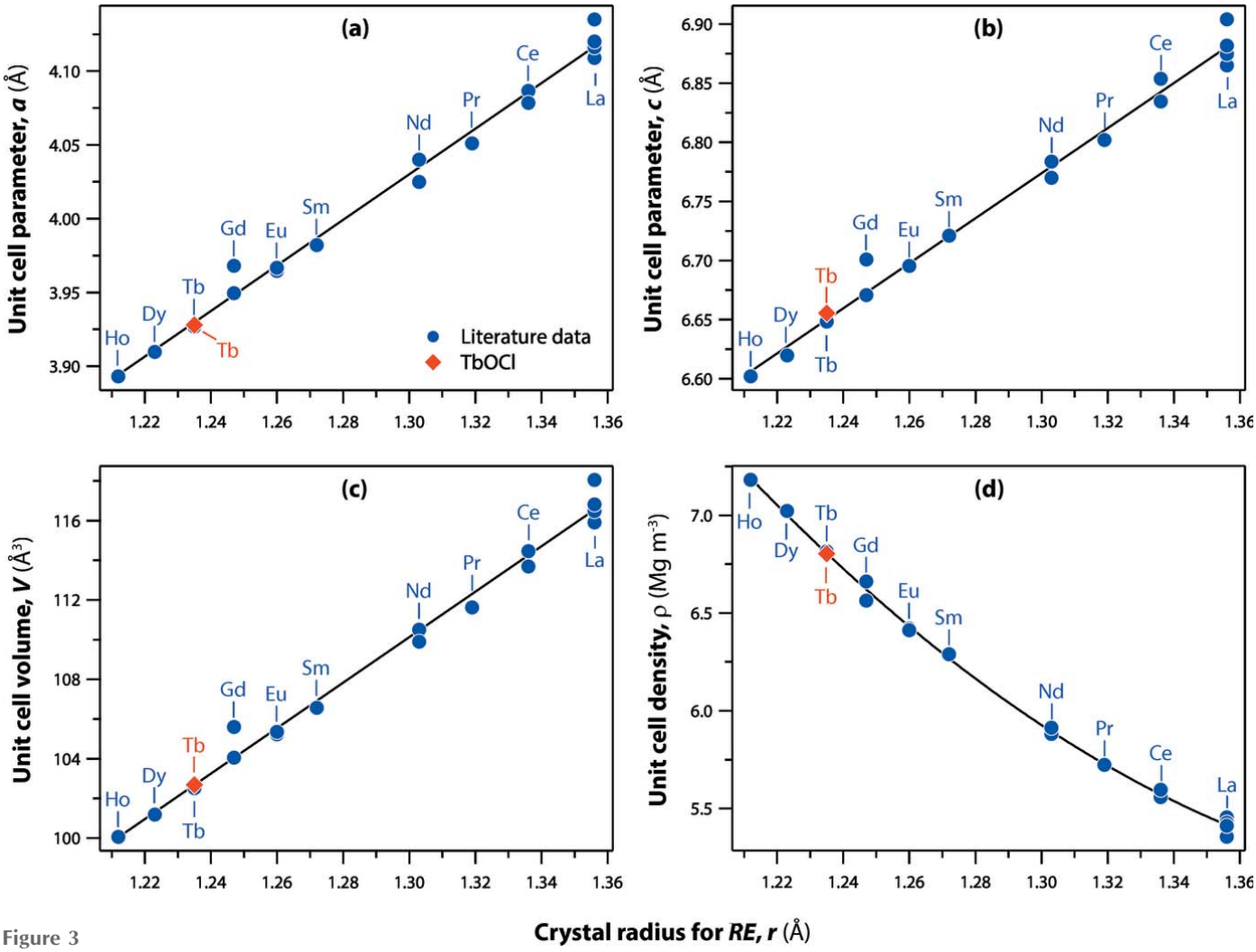


Figure 3
(*a*, *b*) Unit-cell parameters (*a* and *c*, respectively), (*c*) unit-cell volumes, and calculated unit-cell densities as a function of the crystal radius of the *RE* (coordination = 9) according to Shannon (1976) compared to literature values provided in Table 1.

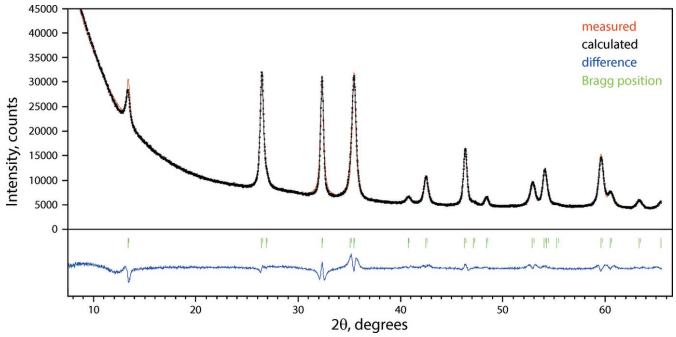


Figure 4
Measured, calculated, and difference XRD patterns of TbOCl.

A pseudo-Voigt function with other peak-shape parameters were used to fit peaks, and the background was modeled with a Chebychev polynomial. The plot of the Rietveld refinement result is shown in Fig. 4. The final refinement converged at R_{wp} = 3.22%.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	TbOCl
M_r	210.4
Crystal system, space group	Tetragonal, *P*4/*nmm*
Temperature (K)	293
a, *c* (Å)	3.9279 (2), 6.6556 (5)
V (Å^3)	102.68 (1)
Z	2
Radiation type	Cu *Kα*, λ = 1.54188 Å
Specimen shape, size (mm)	Cylinder, 25 × 25
Data collection	
Diffractometer	Bruker D8 Advance
Specimen mounting	Packed powder pellet
Data collection mode	Reflection
Scan method	Step
2*θ* values (°)	$2\theta_{min}$ = 5, $2\theta_{max}$ = 68.977, $2\theta_{step}$ = 0.019
Refinement	
R factors and goodness of fit	R_p = 0.020, R_{wp} = 0.032, R_{exp} = 0.009, *R*(*F*) = 0.033, χ^2 = 13.690
No. of parameters	17

Computer programs: *XRD Commander* (Kienle & Jacob, 2003), *TOPAS* (Bruker, 2009), *SUPERFLIP* (Palatinus & Chapuis, 2007), *JANA2006* (Petříček *et al.*, 2014), *VESTA* (Momma & Izumi, 2011) and *publCIF* (Westrip, 2010).

References

Au, C. T., He, H., Lai, S. Y. & Ng, C. F. (1997). *Appl. Catal. Gen.* **159**, 133–145.
Bannister, F. A. (1934). *Miner. Mag. j. Miner. Soc.* **23**, 587–597.
Bärnighausen, H., Brauer, G. & Schultz, N. (1965). *Z. Anorg. Allg. Chem.* **338**, 250–265.
Berdowski, P. A. M., van Herk, J., Jansen, L. & Blasse, G. (1984). *Phys. Status Solidi B*, **125**, 387–391.
Brixner, L. H. & Moore, E. P. (1983). *Acta Cryst.* C**39**, 1316.
Bruker (2009). *TOPAS*. Bruker AXS, Karlsruhe, Germany.
Hölsä, J., Lastusaari, M. & Valkonen, J. (1997). *J. Alloys Compd*, **262**, 299–304.
Hölsä, J., Säilynoja, E., Koski, K., Rahiala, H. & Valkonen, J. (1996). *Powder Diffr.* **11**, 129–133.
Imanaka, N., Okamoto, K. & Adachi, G. (2001*a*). *Chem. Lett.* **30**, 130–131.
Imanaka, N., Okamoto, K. & Adachi, G. (2001*b*). *Electrochem. Commun.* **3**, 49–51.
Kienle, M. & Jacob, M. (2003). *XRD Commander*. Bruker AXS GmbH, Karlsruhe, Germany.
Kim, D., Jeong, J. R., Jang, Y., Bae, J.-S., Chung, I., Liang, R., Seo, D.-K., Kim, S.-J. & Park, J.-C. (2019). *Phys. Chem. Chem. Phys.* **21**, 1737–1749.
Kim, D., Park, S., Kim, S., Kang, S.-G. & Park, J.-C. (2014). *Inorg. Chem.* **53**, 11966–11973.
Kirik, S., Yakimov, I., Blochin, A. & Soloyov, L. (1996). ICDD Grant-in-Aid, Institute of Chemistry, Krasnoyarsk, Russia.
Marsal, A., Centeno, M. A., Odriozola, J. A., Cornet, A. & Morante, J. R. (2005). *Sens. Actuators B Chem.* **108**, 484–489.
Maslen, E. N., Streltsov, V. A., Streltsova, N. R. & Ishizawa, N. (1996). *Acta Cryst.* B**52**, 576–579.
Meyer, G. & Schleid, T. (1986). *Z. Anorg. Allg. Chem.* **533**, 181–185.
Momma, K. & Izumi, F. (2011). *J. Appl. Cryst.* **44**, 1272–1276.
Okamoto, K., Imanaka, N. & Adachi, G. (2002). *Solid State Ionics*, **154–155**, 577–580.
Palatinus, L. & Chapuis, G. (2007). *J. Appl. Cryst.* **40**, 786–790.
Peringer, E., Salzinger, M., Hutt, M., Lemonidou, A. A. & Lercher, J. A. (2009). *Top. Catal.* **52**, 1220–1231.
Petříček, V., Dusek, M. & Palatinus, L. (2014). *Z. Kristallogr.* **229**, 345–352.
Podkolzin, S. G., Stangland, E. E., Jones, M. E., Peringer, E. & Lercher, J. A. (2007). *J. Am. Chem. Soc.* **129**, 2569–2576.
Riley, B. J., Pierce, D. A., Crum, J. V., Williams, B. D., Snyder, M. M. V. & Peterson, J. A. (2018). *Prog. Nucl. Energy*, **104**, 102–108.
Scharfe, M., Lira-Parada, P. A., Amrute, A. P., Mitchell, S. & Pérez-Ramírez, J. (2016). *J. Catal.* **344**, 524–534.
Schnick, W. (2004). Private Communication.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sillen, L. G. & Nylander, A. L. (1941). *Svensk Kemisk Tidskrift*, **53**, 367–372.
Swanson, H. E., Gilfrich, N. T. & Cook, M. I. (1957). *Circ. Bur. Stand.* pp. 539.
Templeton, D. H. & Dauben, C. H. (1953). *J. Am. Chem. Soc.* **75**, 6069–6070.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wołcyrz, M. & Kepinski, L. (1992). *J. Solid State Chem.* **99**, 409–413.
Zachariasen, W. H. (1949). *Acta Cryst.* **2**, 388–390.

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Computing details

Data collection: *XRD Commander* (Kienle & Jacob, 2003); cell refinement: *TOPAS* (Bruker, 2009); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007); program(s) used to refine structure: JANA2006 (Petříček *et al.*, 2014); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Terbium oxychloride

Crystal data

TbOCl
M_r = 210.4
Tetragonal, *P*4/*nmm*
a = 3.9279 (2) Å
c = 6.6556 (5) Å
V = 102.68 (1) Å^3
Z = 2
D_x = 6.804 Mg m^{-3}
Cu *Kα* radiation, *λ* = 1.54188 Å
T = 293 K
light brown
cylinder, 25 × 25 mm

Data collection

Bruker D8 Advance diffractometer
Radiation source: sealed X-ray tube
Specimen mounting: packed powder pellet
Data collection mode: reflection
Scan method: step
$2\theta_{min}$ = 5°, $2\theta_{max}$ = 68.977°, $2\theta_{step}$ = 0.019°

Refinement

R_p = 0.020
R_{wp} = 0.032
R_{exp} = 0.009
R(*F*) = 0.033
3292 data points
Profile function: Pseudo-Voigt
17 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{max}$ = 0.030
Background function: 8 Chebyshev polynoms
Preferred orientation correction: March & Dollase

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Tb1	0.5	0	0.3305 (2)	0.002
Cl1	0	0.5	0.1298 (9)	0.002
O1	1	0	0.5	0.002

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.002	0.002	0.002	0	0	0
Cl1	0.002	0.002	0.002	0	0	0
O1	0.002	0.002	0.002	0	0	0

Geometric parameters (Å, º)

Tb1—Tb1^{i}	3.5784 (13)	Tb1—O1^{v}	2.2649 (7)
Tb1—Tb1^{ii}	3.5784 (13)	Tb1—O1	2.2649 (7)
Tb1—Tb1^{iii}	3.5784 (13)	Tb1—O1^{vi}	2.2649 (7)
Tb1—Tb1^{iv}	3.5784 (13)	Tb1—O1^{vii}	2.2649 (7)
Tb1^{i}—Tb1—Tb1^{ii}	66.57 (2)	Tb1^{iii}—Tb1—O1^{vii}	99.31 (4)
Tb1^{i}—Tb1—Tb1^{iii}	66.57 (2)	Tb1^{iv}—Tb1—O1^{v}	99.31 (4)
Tb1^{i}—Tb1—Tb1^{iv}	101.82 (4)	Tb1^{iv}—Tb1—O1	37.817 (14)
Tb1^{i}—Tb1—O1^{v}	37.817 (14)	Tb1^{iv}—Tb1—O1^{vi}	99.31 (4)
Tb1^{i}—Tb1—O1	99.31 (4)	Tb1^{iv}—Tb1—O1^{vii}	37.817 (14)
Tb1^{i}—Tb1—O1^{vi}	37.817 (14)	O1^{v}—Tb1—O1	120.25 (6)
Tb1^{i}—Tb1—O1^{vii}	99.31 (4)	O1^{v}—Tb1—O1^{vi}	75.63 (3)
Tb1^{ii}—Tb1—Tb1^{iii}	101.82 (4)	O1^{v}—Tb1—O1^{vii}	75.63 (3)
Tb1^{ii}—Tb1—Tb1^{iv}	66.57 (2)	O1—Tb1—O1^{vi}	75.63 (3)
Tb1^{ii}—Tb1—O1^{v}	37.817 (14)	O1—Tb1—O1^{vii}	75.63 (3)
Tb1^{ii}—Tb1—O1	99.31 (4)	O1^{vi}—Tb1—O1^{vii}	120.25 (6)
Tb1^{ii}—Tb1—O1^{vi}	99.31 (4)	Tb1—O1—Tb1^{viii}	120.25 (4)
Tb1^{ii}—Tb1—O1^{vii}	37.817 (14)	Tb1—O1—Tb1^{iii}	104.37 (2)
Tb1^{iii}—Tb1—Tb1^{iv}	66.57 (2)	Tb1—O1—Tb1^{iv}	104.37 (2)
Tb1^{iii}—Tb1—O1^{v}	99.31 (4)	Tb1^{viii}—O1—Tb1^{iii}	104.37 (2)
Tb1^{iii}—Tb1—O1	37.817 (14)	Tb1^{viii}—O1—Tb1^{iv}	104.37 (2)
Tb1^{iii}—Tb1—O1^{vi}	37.817 (14)	Tb1^{iii}—O1—Tb1^{iv}	120.25 (4)

Symmetry codes: (i) $-x+1/2, y-1/2, -z+1$; (ii) $-x+1/2, y+1/2, -z+1$; (iii) $-x+3/2, y-1/2, -z+1$; (iv) $-x+3/2, y+1/2, -z+1$; (v) $x-1, y, z$; (vi) $-y+1/2, x-3/2, z$; (vii) $-y+1/2, x-1/2, z$; (viii) $x+1, y, z$.