Redetermination of the crystal structure of BaTeO$_3$(H$_2$O), including the localization of the hydrogen atoms

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The redetermination of the crystal structure of barium oxidotellurate(IV) monohydrate allowed the localization of the hydrogen atoms that were not determined in the previous study [Nielsen, Hazell & Rasmussen (1971). *Acta Chem. Scand.* **25**, 3037–3042], thus making an unambiguous assignment of the hydrogen-bonding scheme possible. The crystal structure shows a layered arrangement parallel to (001), consisting of edge-sharing [BaO$_6$(H$_2$O)] polyhedra and flanked by isolated [TeO$_3$] trigonal pyramids on the top and bottom. O—H···O hydrogen bonds of medium strength link adjacent layers along [001].

3D view
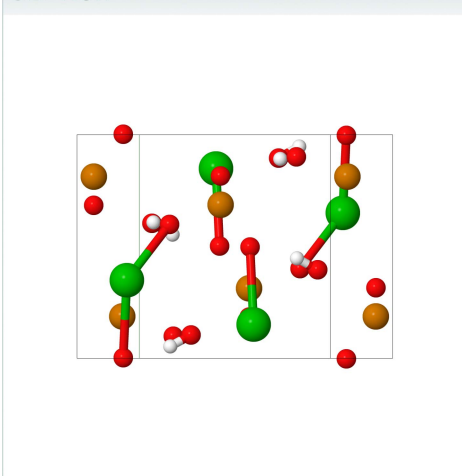
Structure description

In a recent project it was shown that sulfate or selenate anions can be incorporated into oxidotellurates(IV) of calcium, cadmium or strontium (Weil & Shirkhanlou, 2017). In order to expand this series to larger divalent metals, similar experiments with barium were started. Instead of the desired barium compounds with mixed oxidochalcogenate anions, high-quality crystals of BaTeO$_3$(H$_2$O) were frequently obtained under the given hydrothermal conditions. The crystal structure of BaTeO$_3$(H$_2$O) was determined nearly fifty years ago (Nielsen *et al.*, 1971), however without localization of the hydrogen atoms. For an unambiguous assignment of the hydrogen-bonding scheme, a redetermination of this structure with modern CCD-based diffraction data seemed appropriate. In fact, alongside more precise data in terms of bond lengths and angles (Table 1), the current redetermination clearly revealed the positions of the hydrogen atoms of the water molecule (O4). Numerical data for the hydrogen-bonding interactions are collated in Table 2.

Table 1
Comparison of selected bond lengths (Å) from the current and the previous (Nielsen *et al.*, 1971) refinement of BaTeO$_3$(H$_2$O).

	current refinement	previous refinement[a]
Ba—O2[i]	2.6755 (17)	2.667 (8)
Ba—O1[ii]	2.6905 (16)	2.675 (8)
Ba—O3[iii]	2.7064 (15)	2.688 (7)
Ba—O1[iv]	2.7867 (16)	2.780 (6)
Ba—O4[iv]	2.792 (2)	2.786 (6)
Ba—O1[v]	2.7980 (15)	2.781 (6)
Ba—O3[iv]	2.8461 (17)	2.823 (6)
Te—O2	1.8571 (16)	1.847 (7)
Te—O3	1.8632 (16)	1.859 (6)
Te—O1	1.8644 (15)	1.858 (6)
O2—Te1—O3	102.18 (8)	102.7 (3)
O2—Te1—O1	99.12 (8)	98.8 (3)
O3—Te1—O1	96.48 (7)	96.5 (3)

Notes (a) a = 8.58 (2), b = 7.53 (2), c = 7.70 (2) Å; β = 106.03 (20)°, T = 298 K; R = 0.039. Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z$; (iv) $-x, -y + 1, -z$; (v) $x + \frac{1}{2}, -y + \frac{3}{2}, z$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H1⋯O3[i]	0.85 (1)	1.86 (1)	2.679 (3)	164 (4)
O4—H2⋯O2[ii]	0.85 (1)	1.93 (1)	2.761 (3)	167 (4)

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

The crystal structure comprises Ba^{2+} cations with a coordination number of seven by oxygen atoms, and isolated trigonal–pyramidal TeO$_3^{2-}$ anions. The coordination sphere of the alkaline earth cation is irregular with a Ba—O bond-length distribution from 2.6755 (17) to 2.8461 (17) Å. The Te—O bond lengths and O—Te—O angles are typical for Te^{IV} bonded to three oxygen atoms (Christy *et al.*, 2016). In the crystal structure, [BaO$_6$(H$_2$O)] polyhedra share edges and are linked into layers extending parallel to (001). The [TeO$_3$]
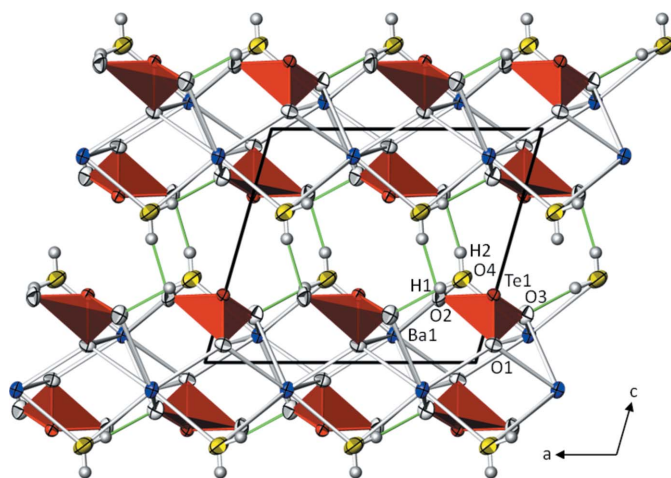

Figure 1
The crystal structure of BaTeO$_3$(H$_2$O) in a projection along [0$\bar{1}$0]. Displacement ellipsoids are drawn at the 74% probability level. [TeO$_3$] trigonal pyramids are red, hydrogen atoms are of arbitrary size and O—H⋯O hydrogen-bonding interactions are shown as green lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	BaTeO$_3$(H$_2$O)
M_r	330.96
Crystal system, space group	Monoclinic, $P2_1/a$
Temperature (K)	296
a, b, c (Å)	8.6061 (2), 7.5820 (1), 7.7252 (2)
β (°)	105.8800 (11)
V (Å^3)	484.84 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	13.98
Crystal size (mm)	0.18 × 0.09 × 0.01
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.541, 0.748
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	24774, 3003, 2535
R_{int}	0.048
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.904
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.020, 0.042, 1.01
No. of reflections	3003
No. of parameters	63
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.36, −1.03

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXL* (Sheldrick, 2015), *ATOMS* (Dowty, 2006) and *publCIF* (Westrip, 2010).

trigonal pyramids flank these layers on both sides with the free-electron pair pointing into the interlayer space (Fig. 1). Adjacent layers are held together along [001] by O—H⋯O hydrogen bonds involving one of the water hydrogen atoms (H2). The other hydrogen atom (H1) is engaged in an intralayer hydrogen bond. Judging by the O⋯O contact distances (Table 2), both hydrogen bonds are of medium strength.

Synthesis and crystallization

Ba(OH)$_2$·8H$_2$O, H$_2$SeO$_4$ (96%$_{wt}$), TeO$_2$ and KOH were mixed in a stoichiometric ratio of 2:1:1:2 (overall load *ca* 0.3 g) and were placed in a Teflon container with an 8 ml capacity that was filled to about two-thirds of its volume with water. The container was sealed with a Teflon lid, transferred to a steel autoclave and heated at 483 K for one week. A few colourless transparent crystals with a plate-like form of BaTeO$_3$(H$_2$O) were separated from microcrystalline material that consisted of BaSeO$_4$ as the main phase and unknown phase(s) as minor products, as revealed by powder X-ray diffraction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The same non-standard setting $P2_1/a$ of space group No. 14 (standard setting $P2_1/c$) and atom-labelling scheme as given in the original structure study

(Nielsen *et al.*, 1971) were used. The published atomic coordinates were taken as starting parameters for the refinement. The two H atoms bonded to O4 were clearly discernible from a difference Fourier map. The corresponding O—H distances were treated with restraints $d(O-H) = 0.85\,(1)$ Å, and an independent U_{iso} parameter was refined for each H atom.

References

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full crystallographic data

Redetermination of the crystal structure of BaTeO₃(H₂O), including the localization of the hydrogen atoms

Matthias Weil

Barium oxidotellurate(IV) monohydrate

Crystal data

$BaTeO_3(H_2O)$	$F(000) = 568$
$M_r = 330.96$	$D_x = 4.534$ Mg m^{-3}
Monoclinic, $P2_1/a$	Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å
$a = 8.6061$ (2) Å	Cell parameters from 8647 reflections
$b = 7.5820$ (1) Å	$\theta = 2.7–39.9°$
$c = 7.7252$ (2) Å	$\mu = 13.98$ mm^{-1}
$\beta = 105.8800$ (11)°	$T = 296$ K
$V = 484.84$ (2) Å^3	Plate, colourless
$Z = 4$	$0.18 \times 0.09 \times 0.01$ mm

Data collection

Bruker APEXII CCD diffractometer	3003 independent reflections
	2535 reflections with $I > 2\sigma(I)$
$\omega–$ and $\varphi–$scans	$R_{int} = 0.048$
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)	$\theta_{max} = 40.0°$, $\theta_{min} = 2.7°$
	$h = -15 \rightarrow 15$
$T_{min} = 0.541$, $T_{max} = 0.748$	$k = -13 \rightarrow 13$
24774 measured reflections	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.020$	and constrained refinement
$wR(F^2) = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.013P)^2 + 0.3124P]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
3003 reflections	$(\Delta/\sigma)_{max} = 0.001$
63 parameters	$\Delta\rho_{max} = 1.36$ e Å^{-3}
3 restraints	$\Delta\rho_{min} = -1.03$ e Å^{-3}

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
Ba	0.33203 (2)	0.84905 (2)	0.11771 (2)	0.01402 (3)
Te	0.00420 (2)	0.18710 (2)	0.28883 (2)	0.01247 (3)
O1	−0.0478 (2)	0.31565 (19)	0.0749 (2)	0.0166 (3)
O2	0.2033 (2)	0.0987 (2)	0.2807 (2)	0.0234 (3)
O3	−0.1331 (2)	−0.0024 (2)	0.2030 (2)	0.0198 (3)
O4	0.1377 (3)	0.6040 (3)	0.3567 (3)	0.0361 (5)
H1	0.210 (3)	0.553 (5)	0.319 (5)	0.047 (11)*
H2	0.172 (4)	0.608 (5)	0.4705 (14)	0.048 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	0.01206 (5)	0.01126 (5)	0.01810 (6)	−0.00019 (3)	0.00307 (4)	0.00052 (4)
Te	0.01224 (6)	0.01311 (5)	0.01221 (5)	0.00006 (4)	0.00361 (4)	−0.00102 (4)
O1	0.0191 (7)	0.0155 (6)	0.0155 (7)	−0.0003 (5)	0.0055 (6)	0.0029 (5)
O2	0.0145 (7)	0.0298 (8)	0.0266 (9)	0.0050 (6)	0.0065 (6)	−0.0042 (7)
O3	0.0192 (7)	0.0147 (6)	0.0248 (8)	−0.0040 (5)	0.0050 (6)	0.0002 (6)
O4	0.0224 (9)	0.0602 (14)	0.0215 (9)	0.0147 (9)	−0.0012 (7)	−0.0131 (10)

Geometric parameters (Å, °)

Ba—O2^i	2.6755 (17)	Ba—O3^{iv}	2.8461 (17)
Ba—O1^{ii}	2.6905 (16)	Te—O2	1.8571 (16)
Ba—O3^{iii}	2.7064 (15)	Te—O3	1.8632 (16)
Ba—O1^{iv}	2.7867 (16)	Te—O1	1.8644 (15)
Ba—O4^v	2.792 (2)	O4—H1	0.846 (10)
Ba—O1^v	2.7980 (15)	O4—H2	0.849 (10)
O2^i—Ba—O1^{ii}	139.83 (5)	O4^v—Ba—O3^{iv}	139.19 (5)
O2^i—Ba—O3^{iii}	127.23 (5)	O1^v—Ba—O3^{iv}	71.32 (5)
O1^{ii}—Ba—O3^{iii}	89.77 (5)	O2—Te—O3	102.18 (8)
O2^i—Ba—O1^{iv}	98.76 (5)	O2—Te—O1	99.12 (8)
O1^{ii}—Ba—O1^{iv}	107.47 (5)	O3—Te—O1	96.48 (7)
O3^{iii}—Ba—O1^{iv}	73.59 (5)	Te—O1—Ba^{vi}	120.32 (7)
O2^i—Ba—O4^v	92.01 (7)	Te—O1—Ba^{iv}	101.64 (6)
O1^{ii}—Ba—O4^v	73.13 (6)	Ba^{vi}—O1—Ba^{iv}	112.62 (6)
O3^{iii}—Ba—O4^v	86.63 (6)	Te—O1—Ba^{vii}	112.15 (7)
O1^{iv}—Ba—O4^v	160.17 (6)	Ba^{vi}—O1—Ba^{vii}	108.25 (5)
O2^i—Ba—O1^v	68.09 (5)	Ba^{iv}—O1—Ba^{vii}	99.87 (5)
O1^{ii}—Ba—O1^v	71.75 (5)	Te—O2—Ba^{viii}	140.90 (9)
O3^{iii}—Ba—O1^v	153.03 (5)	Te—O3—Ba^{ix}	148.51 (8)
O1^{iv}—Ba—O1^v	130.01 (4)	Te—O3—Ba^{iv}	99.59 (6)
O4^v—Ba—O1^v	69.54 (6)	Ba^{ix}—O3—Ba^{iv}	100.63 (5)
O2^i—Ba—O3^{iv}	83.85 (5)	Ba^{vii}—O4—H1	119 (2)
O1^{ii}—Ba—O3^{iv}	84.18 (5)	Ba^{vii}—O4—H2	133 (3)

O3^{iii}—Ba—O3^{iv}	127.51 (4)	H1—O4—H2	107 (3)
O1^{iv}—Ba—O3^{iv}	59.15 (4)		

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

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H1⋯O3^{iii}	0.85 (1)	1.86 (1)	2.679 (3)	164 (4)
O4—H2⋯O2^{x}	0.85 (1)	1.93 (1)	2.761 (3)	167 (4)

Symmetry codes: (iii) $x+1/2, -y+1/2, z$; (x) $-x+1/2, y+1/2, -z+1$.