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Potassium aquaterbium(III) oxalate sulfate

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Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.023; wR factor = 0.051; data-to-parameter ratio = 8.5.

Single crystals of $\text{KTb}(\text{C}_2\text{O}_4)(\text{SO}_4)(\text{H}_2\text{O})$, potassium aquaterbium(III) oxalate sulfate, were obtained under hydrothermal conditions. In the crystal structure, the Tb(III) atom is coordinated by four O atoms from two oxalate anions, three O atoms from three sulfate anions and one O atom from a water molecule within a TbO_8 distorted square antiprismatic coordination. The potassium and terbium(III) atoms are bridged by the oxalate and sulfate groups, forming a three-dimensional structure. The coordination mode of the oxalate has not yet been reported. $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding between the water molecules and the oxygen atoms of oxalate and sulfate anions is also observed.

Related literature

For oxalates and their coordination modes, see: Audebrand *et al.* (2003); Dean *et al.* (2004); Lu *et al.* (2004).

Experimental

Crystal data

 $\text{KTb}(\text{C}_2\text{O}_4)(\text{SO}_4)(\text{H}_2\text{O})$ $M_r = 400.14$ Monoclinic, $P2_1/c$ $a = 6.5274$ (13) Å $b = 8.5072$ (17) Å $c = 14.591$ (4) Å $\beta = 112.65$ (3)° $V = 747.7$ (3) Å³ $Z = 4$ Mo $K\alpha$ radiation $\mu = 10.32$ mm⁻¹ $T = 113$ K $0.06 \times 0.04 \times 0.02$ mm

Data collection

Bruker SMART 1000 CCD diffractometer

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

 $T_{\min} = 0.576$, $T_{\max} = 0.820$

4812 measured reflections

1317 independent reflections

1079 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.057$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.023$ $wR(F^2) = 0.051$ $S = 1.05$

1317 reflections

127 parameters

24 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.92$ e Å⁻³ $\Delta\rho_{\text{min}} = -0.78$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O9}-\text{H9A}\cdots\text{O2}^{\text{i}}$	0.96 (6)	1.88 (4)	2.731 (4)	145 (5)
$\text{O9}-\text{H9B}\cdots\text{O3}^{\text{ii}}$	0.96 (6)	1.86 (3)	2.787 (5)	160 (9)
$\text{O9}-\text{H9B}\cdots\text{O7}^{\text{i}}$	0.97 (6)	2.83 (9)	3.149 (5)	100 (6)

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x, -y + 1, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BR2105).

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supplementary materials

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Potassium aquaterbium(III) oxalate sulfate

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Comment

Recently, rationally design of novel inorganic compounds based on alkali metal ions and rare earth ions are currently of great interest because of their potential applications in photoluminescent fields. For purpose of enriching the chemistry field of this compound family, we have successfully synthesized the title compound.

In the title compound, the coordination environments of the rare earth Tb^{III} cations consist of eight O atoms which are associated with one water molecule, two sulfate groups and two oxalates. Tb^{III} cations are at the shared apex of two dicapped rectangular pyramids (Fig.1). The K⁺ cations are surrounded by nine O atoms, including one water O atom, six O atoms from oxalates and two O atoms from sulfate groups.

Oxalates are of considerable interest because many of them are natural minerals and in addition, the oxalate anion can adopt different coordination modes to bind metals to form infinite chains, sheets and networks, leading to the rich structural chemistry (Lu *et al.*, 2004; Dean *et al.*, 2004; Audebrand *et al.*, 2003). In the title compound, the oxalate ligand has a unique coordination mode ($\kappa^3\text{-}\kappa^2\text{-}\mu_4$)-($\kappa^3\text{-}\kappa^2\text{-}\mu_4$)- $\mu_6\text{-ox}^{2-}$. Fig.2 shows coordination mode of the oxalate and sulfate ligands in the title compound.

Two adjacent Tb^{III} ions were connected through the oxalates to form one-dimensional chain structure (see Fig.3), and then were connected through the sulfate anions and water molecules to form the three-dimensional framework (see Fig.4).

Experimental

A mixture of FeSO₄·7H₂O (0.1 mmol), Tb(NO₃)₃·5H₂O (0.1 mmol) and oxalic acid (0.2 mmol) in H₂O (10 mL) was adjust to pH=6.8 with KOH aqueous solution, sealed in a 25 mL Teflon-lined bomb at 430 K for 4 days and then slowly cooled to room temperature at a rate of 5° K per hour. Colorless block crystals were obtained by filtration. The structure was determined by single-crystal diffraction.

Refinement

Water H atoms were located in a difference Fourier maps and refined to restraint with O—H distance of 0.97 Å and U_{iso}(H) = 1.2U_{eq}(O). In order improve the *R* and *wR* factors, weak diffraction reflections in high 2 theta angles were omitted. Because of difficulties in obtaining convergence in the refinement the anisotropy of the atomic displacement parameters of some O and C atoms were restrained.

Figures

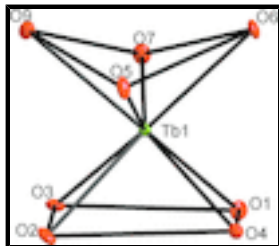


Fig. 1. A view of the environment of (a) the Tb atom, The symmetry codes are in Table 1. Displacement ellipsoids are drawn at the 50% probability level.

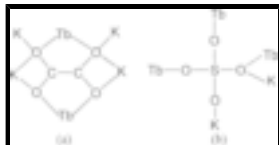


Fig. 2. A view of coordination modes of (a) the Oxalate and (b) the sulfate anion.

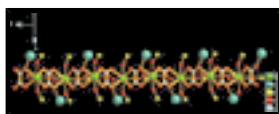


Fig. 3. The one-dimensional chain structure of the $\text{KTb}(\text{SO}_4)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})$ along c axis (hydrogen atoms omitted).

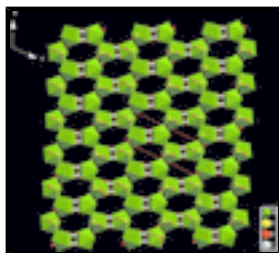


Fig. 4. The structural arrangement of $\text{KTb}(\text{SO}_4)(\text{C}_2\text{O}_4)(\text{H}_2\text{O})$ along b axis (hydrogen and potassium atoms omitted). The green polyhedras are TbO_8 .

Potassium aquaterbium(III) oxalate sulfate

Crystal data

$\text{KTb}(\text{C}_2\text{O}_4)(\text{SO}_4)(\text{H}_2\text{O})$

$M_r = 400.14$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.5274$ (13) Å

$b = 8.5072$ (17) Å

$c = 14.591$ (4) Å

$\beta = 112.65$ (3)°

$V = 747.7$ (3) Å³

$Z = 4$

$F_{000} = 744$

$D_x = 3.554$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1317 reflections

$\theta = 2.8$ – 27.2°

$\mu = 10.32$ mm⁻¹

$T = 113$ K

Block, colorless

$0.06 \times 0.04 \times 0.02$ mm

Data collection

Bruker SMART 1000 CCD
diffractometer

Radiation source: rotating anode

Monochromator: confocal

1317 independent reflections

1079 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$T = 113$ K $\theta_{\max} = 25.0^\circ$
 ω scans $\theta_{\min} = 2.8^\circ$
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003) $h = -7 \rightarrow 7$
 $T_{\min} = 0.576$, $T_{\max} = 0.820$ $k = -9 \rightarrow 10$
 4812 measured reflections $l = -17 \rightarrow 17$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.023$ H-atom parameters constrained
 $wR(F^2) = 0.051$ $w = 1/[\sigma^2(F_o^2) + (0.0171P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.05$ $(\Delta/\sigma)_{\max} = 0.001$
 1317 reflections $\Delta\rho_{\max} = 0.92 \text{ e } \text{\AA}^{-3}$
 127 parameters $\Delta\rho_{\min} = -0.78 \text{ e } \text{\AA}^{-3}$
 24 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

Special details

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Tb1	0.33208 (4)	0.24112 (3)	0.086605 (17)	0.00425 (11)
K1	0.9670 (2)	-0.15405 (14)	0.19899 (9)	0.0144 (3)
S1	0.7406 (2)	0.16467 (15)	-0.02448 (9)	0.0057 (3)
O1	0.2682 (6)	0.1255 (4)	0.2251 (3)	0.0079 (8)
O2	0.6044 (6)	0.4446 (4)	0.1557 (2)	0.0074 (8)
O3	0.2189 (6)	0.4466 (4)	0.1717 (2)	0.0079 (8)
O4	0.6523 (6)	0.1083 (4)	0.1984 (3)	0.0065 (8)
O5	0.5568 (7)	0.2364 (4)	-0.0040 (3)	0.0077 (8)
O6	0.7540 (6)	-0.0053 (4)	-0.0015 (3)	0.0080 (8)
O7	0.9493 (7)	0.2388 (4)	0.0409 (3)	0.0096 (9)
O8	0.7035 (7)	0.1876 (5)	-0.1285 (3)	0.0119 (9)

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O9	0.1774 (6)	0.4070 (4)	-0.0544 (3)	0.0072 (8)
H9A	0.285 (8)	0.475 (6)	-0.063 (5)	0.04 (2)*
H9B	0.047 (6)	0.448 (9)	-0.107 (5)	0.13 (4)*
C1	0.4137 (9)	0.0364 (6)	0.2801 (4)	0.0043 (11)
C2	0.3644 (9)	0.5312 (6)	0.2329 (4)	0.0052 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Tb1	0.00438 (17)	0.00457 (17)	0.00411 (16)	0.00031 (11)	0.00197 (12)	0.00024 (10)
K1	0.0141 (8)	0.0162 (7)	0.0164 (7)	-0.0038 (6)	0.0099 (6)	-0.0061 (5)
S1	0.0054 (8)	0.0063 (7)	0.0061 (7)	-0.0002 (6)	0.0029 (6)	-0.0010 (5)
O1	0.006 (2)	0.009 (2)	0.010 (2)	0.0033 (17)	0.0045 (18)	0.0001 (15)
O2	0.010 (2)	0.0070 (19)	0.008 (2)	-0.0028 (17)	0.0067 (18)	-0.0041 (16)
O3	0.008 (2)	0.009 (2)	0.006 (2)	-0.0019 (17)	0.0013 (18)	-0.0020 (15)
O4	0.0068 (12)	0.0062 (11)	0.0066 (11)	-0.0001 (9)	0.0028 (9)	-0.0002 (8)
O5	0.011 (2)	0.0047 (19)	0.013 (2)	0.0011 (16)	0.0096 (18)	-0.0002 (14)
O6	0.011 (2)	0.0035 (19)	0.010 (2)	-0.0010 (17)	0.0048 (17)	-0.0014 (14)
O7	0.008 (2)	0.009 (2)	0.012 (2)	0.0002 (17)	0.0041 (18)	0.0008 (16)
O8	0.016 (3)	0.014 (2)	0.008 (2)	-0.0015 (19)	0.0071 (19)	0.0010 (16)
O9	0.0063 (12)	0.0077 (12)	0.0083 (11)	-0.0003 (9)	0.0036 (9)	0.0017 (8)
C1	0.0048 (14)	0.0036 (14)	0.0043 (13)	0.0005 (9)	0.0015 (10)	-0.0011 (9)
C2	0.0052 (14)	0.0046 (14)	0.0057 (14)	0.0003 (9)	0.0019 (10)	0.0010 (9)

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

Tb1—O6 ⁱ	2.311 (4)	S1—O5	1.476 (3)
Tb1—O5	2.323 (3)	S1—O6	1.480 (4)
Tb1—O7 ⁱⁱ	2.325 (4)	O1—C1	1.238 (6)
Tb1—O9	2.375 (4)	O1—K1 ^{vii}	2.900 (3)
Tb1—O4	2.382 (4)	O1—K1 ⁱⁱ	3.016 (4)
Tb1—O2	2.406 (4)	O2—C1 ^{vii}	1.261 (5)
Tb1—O3	2.419 (3)	O2—K1 ^{viii}	2.909 (4)
Tb1—O1	2.423 (3)	O3—C2	1.250 (6)
K1—O8 ⁱⁱⁱ	2.733 (4)	O3—K1 ^{vii}	2.744 (3)
K1—O3 ^{iv}	2.744 (3)	O4—C2 ^{iv}	1.238 (6)
K1—O1 ^{iv}	2.900 (3)	O4—K1 ^{viii}	3.105 (4)
K1—O9 ⁱ	2.903 (4)	O6—Tb1 ⁱ	2.311 (4)
K1—O2 ^v	2.909 (4)	O7—Tb1 ^{vi}	2.325 (4)
K1—O6	2.992 (4)	O8—K1 ⁱⁱⁱ	2.733 (4)
K1—O1 ^{vi}	3.016 (4)	O9—K1 ⁱ	2.903 (4)
K1—O4	3.032 (4)	O9—H9A	0.96 (6)
K1—O4 ^v	3.105 (4)	O9—H9B	0.97 (6)
K1—C2 ^{iv}	3.132 (5)	C1—O2 ^{iv}	1.261 (5)
K1—C1 ^{vi}	3.141 (6)	C1—C2 ^{iv}	1.532 (7)

K1—S1 ⁱⁱⁱ	3.7251 (18)	C2—O4 ^{vii}	1.238 (6)
S1—O8	1.455 (4)	C2—C1 ^{vii}	1.532 (7)
S1—O7	1.470 (4)		
O6 ⁱ —Tb1—O5	75.84 (12)	O1 ^{vi} —K1—O4	80.09 (10)
O6 ⁱ —Tb1—O7 ⁱⁱ	80.00 (13)	O8 ⁱⁱⁱ —K1—O4 ^v	60.90 (11)
O5—Tb1—O7 ⁱⁱ	132.93 (13)	O3 ^{iv} —K1—O4 ^v	110.83 (11)
O6 ⁱ —Tb1—O9	96.65 (12)	O1 ^{iv} —K1—O4 ^v	80.67 (10)
O5—Tb1—O9	70.62 (12)	O9 ⁱ —K1—O4 ^v	80.98 (10)
O7 ⁱⁱ —Tb1—O9	72.86 (12)	O2 ^v —K1—O4 ^v	57.98 (10)
O5—Tb1—O4	78.58 (12)	O6—K1—O4 ^v	136.94 (9)
O7 ⁱⁱ —Tb1—O4	138.98 (12)	O1 ^{vi} —K1—O4 ^v	95.21 (11)
O9—Tb1—O4	147.42 (11)	O4—K1—O4 ^v	153.72 (5)
O6 ⁱ —Tb1—O2	146.78 (11)	O8—S1—O7	111.1 (2)
O5—Tb1—O2	74.00 (11)	O8—S1—O5	109.5 (2)
O7 ⁱⁱ —Tb1—O2	131.70 (12)	O7—S1—O5	108.3 (2)
O9—Tb1—O2	86.26 (13)	O8—S1—O6	109.8 (2)
O4—Tb1—O2	75.09 (13)	O7—S1—O6	108.2 (2)
O6 ⁱ —Tb1—O3	147.54 (12)	O5—S1—O6	109.9 (2)
O5—Tb1—O3	133.59 (11)	C1—O1—Tb1	117.0 (3)
O7 ⁱⁱ —Tb1—O3	69.30 (12)	C1—O1—K1 ^{vii}	122.4 (3)
O4—Tb1—O3	110.60 (12)	Tb1—O1—K1 ^{vii}	110.02 (12)
O2—Tb1—O3	65.64 (12)	C1—O1—K1 ⁱⁱ	84.2 (3)
O6 ⁱ —Tb1—O1	90.64 (12)	Tb1—O1—K1 ⁱⁱ	121.87 (14)
O5—Tb1—O1	144.76 (13)	K1 ^{vii} —O1—K1 ⁱⁱ	98.21 (10)
O9—Tb1—O1	144.20 (12)	C1 ^{vii} —O2—Tb1	119.4 (3)
O4—Tb1—O1	67.90 (12)	C1 ^{vii} —O2—K1 ^{viii}	88.6 (3)
O2—Tb1—O1	106.20 (11)	Tb1—O2—K1 ^{viii}	116.49 (13)
O3—Tb1—O1	71.38 (11)	C2—O3—Tb1	119.0 (3)
O8 ⁱⁱⁱ —K1—O3 ^{iv}	155.77 (13)	C2—O3—K1 ^{vii}	96.0 (3)
O8 ⁱⁱⁱ —K1—O1 ^{iv}	133.26 (11)	Tb1—O3—K1 ^{vii}	115.52 (14)
O3 ^{iv} —K1—O1 ^{iv}	59.99 (10)	C2 ^{iv} —O4—Tb1	118.6 (3)
O8 ⁱⁱⁱ —K1—O9 ⁱ	74.43 (11)	C2 ^{iv} —O4—K1	83.0 (3)
O3 ^{iv} —K1—O9 ⁱ	128.67 (11)	Tb1—O4—K1	139.97 (14)
O1 ^{iv} —K1—O9 ⁱ	74.15 (10)	C2 ^{iv} —O4—K1 ^{viii}	105.0 (3)
O8 ⁱⁱⁱ —K1—O2 ^v	68.22 (11)	Tb1—O4—K1 ^{viii}	110.44 (12)
O3 ^{iv} —K1—O2 ^v	87.98 (11)	K1—O4—K1 ^{viii}	93.58 (10)
O1 ^{iv} —K1—O2 ^v	114.22 (11)	S1—O5—Tb1	149.7 (2)
O9 ⁱ —K1—O2 ^v	134.04 (11)	S1—O6—Tb1 ⁱ	138.2 (2)
O8 ⁱⁱⁱ —K1—O6	79.21 (11)	S1—O6—K1	126.8 (2)
O3 ^{iv} —K1—O6	112.22 (11)	Tb1 ⁱ —O6—K1	94.79 (12)
O1 ^{iv} —K1—O6	122.12 (12)	S1—O7—Tb1 ^{vi}	144.5 (2)

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O9 ⁱ —K1—O6	72.82 (10)	S1—O8—K1 ⁱⁱⁱ	122.7 (2)
O2 ^v —K1—O6	123.02 (10)	Tb1—O9—K1 ⁱ	95.73 (12)
O8 ⁱⁱⁱ —K1—O1 ^{vi}	63.92 (11)	Tb1—O9—H9A	113 (4)
O3 ^{iv} —K1—O1 ^{vi}	96.12 (11)	K1 ⁱ —O9—H9A	113 (4)
O1 ^{iv} —K1—O1 ^{vi}	151.31 (6)	Tb1—O9—H9B	149 (4)
O9 ⁱ —K1—O1 ^{vi}	133.59 (10)	K1 ⁱ —O9—H9B	75 (6)
O2 ^v —K1—O1 ^{vi}	44.18 (10)	H9A—O9—H9B	97.7 (13)
O6—K1—O1 ^{vi}	79.92 (11)	O1—C1—O2 ^{iv}	126.4 (5)
O8 ⁱⁱⁱ —K1—O4	134.96 (11)	O1—C1—C2 ^{iv}	117.6 (4)
O3 ^{iv} —K1—O4	45.03 (10)	O2 ^{iv} —C1—C2 ^{iv}	116.0 (5)
O1 ^{iv} —K1—O4	91.10 (10)	O4 ^{vii} —C2—O3	127.1 (5)
O9 ⁱ —K1—O4	120.90 (11)	O4 ^{vii} —C2—C1 ^{vii}	117.8 (5)
O2 ^v —K1—O4	104.49 (11)	O3—C2—C1 ^{vii}	115.0 (4)
O6—K1—O4	68.10 (9)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9A \cdots O2 ^{ix}	0.96 (6)	1.88 (4)	2.731 (4)	145 (5)
O9—H9B \cdots O3 ^x	0.96 (6)	1.86 (3)	2.787 (5)	160 (9)
O9—H9B \cdots O7 ^{ix}	0.97 (6)	2.83 (9)	3.149 (5)	100 (6)

Symmetry codes: (ix) $-x+1, -y+1, -z$; (x) $-x, -y+1, -z$.

Fig. 1

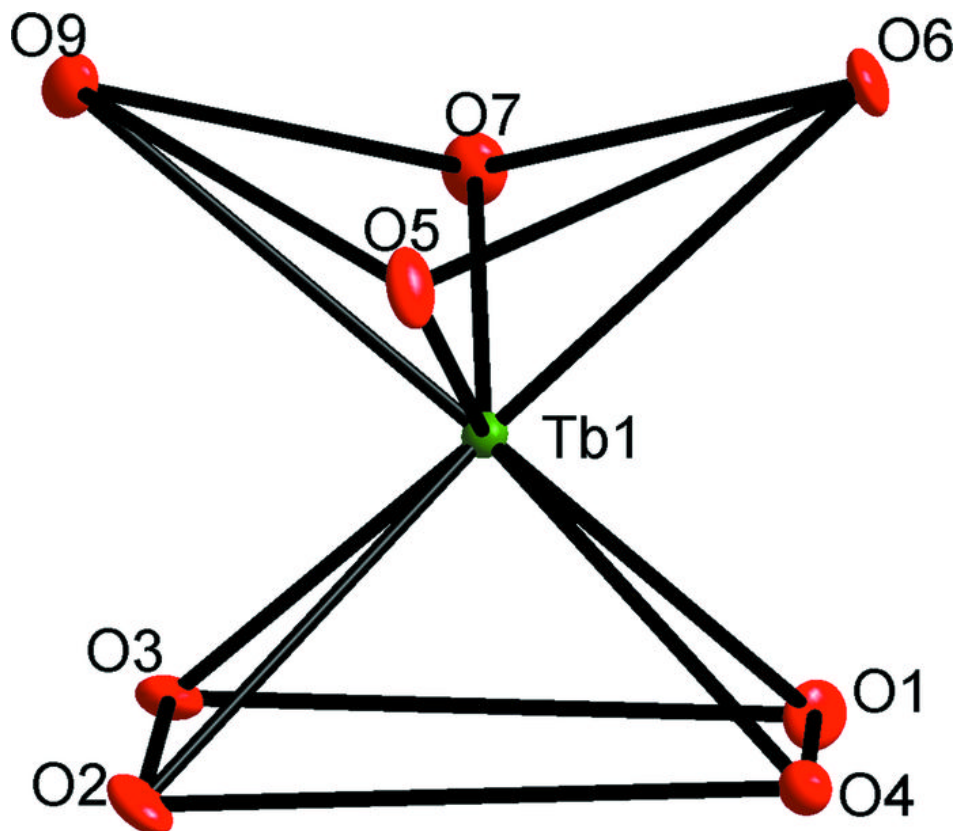


Fig. 2

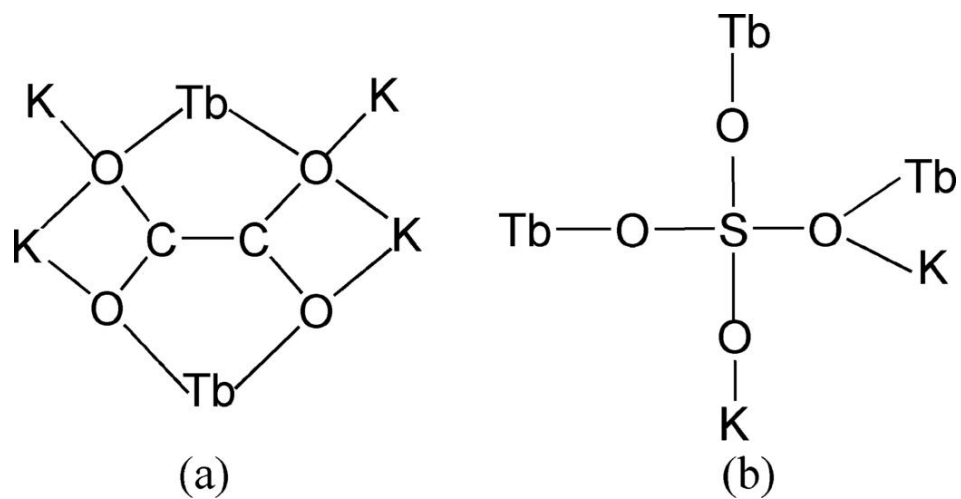


Fig. 3

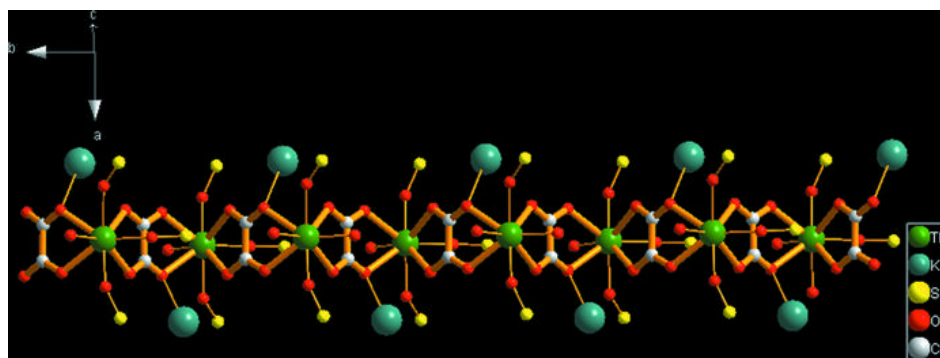


Fig. 4

