

Tb₂Mo₄O₁₅**Haruo Naruke* and Toshihiro Yamase**

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Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{Mo}-\text{O}) = 0.004 \text{ \AA}$

R factor = 0.023

wR factor = 0.060

Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, tetramolybdenum(VI) diterbate(III), was prepared by pyrolysis of $\text{Tb}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}\cdot 6\text{H}_2\text{O}$ at 1023 K for 2 h in air. The structure consists of trigonal bipyramidal MoO_5 , tetrahedral MoO_4 , and monocapped trigonal prismatic TbO_7 units. The two MoO_5 and two MoO_4 units are corner-shared, to form a Mo_4O_{15} group.

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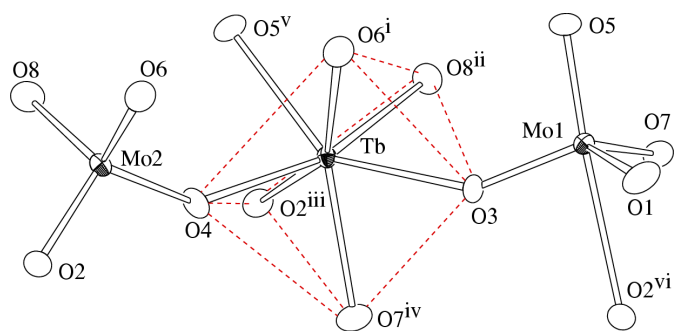
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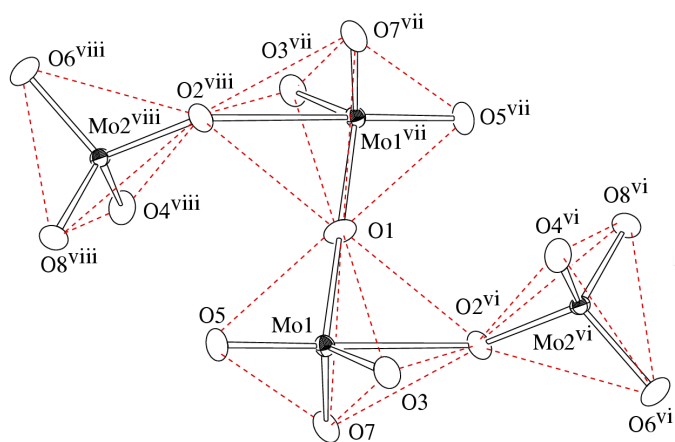
Comment

Much attention has been paid to the physical properties of rare earth (RE) molybdates: for example, the ferroelectric and ferroelastic properties of $\text{Gd}_2(\text{MoO}_4)_3$ (Borchardt & Bierstedt, 1966), fast oxide-ion conduction in $\text{La}_2\text{Mo}_2\text{O}_9$ (Lacorre *et al.*, 2000), trivalent scandium conduction in $\text{Sc}_2(\text{MoO}_4)_3$ (Imanaka *et al.*, 2000), and unusual negative thermal expansion for $\text{RE}_2(\text{MoO}_4)_3$ (Evans *et al.*, 1997). RE molybdates are usually prepared by firing stoichiometric mixtures of RE_2O_3 and MoO_3 . However, because of the strong vaporization behavior of MoO_3 (>1043 K), it is not easy to maintain their initial stoichiometry. For this reason, although many $n\text{RE}_2\text{O}_3\cdot m\text{MoO}_3$ phases are found in equilibrium studies, only a few compounds have been crystallized and their structures determined. Recently, we obtained single crystals of novel europium molybdates, $\text{Eu}_4\text{Mo}_7\text{O}_{27}$ ($n:m = 2:7$) and $\text{Eu}_6\text{Mo}_{10}\text{O}_{39}$ (3:10), in a melt of $\text{Eu}_2\text{O}_3\cdot 6\text{MoO}_3$, by 1073 K pyrolysis of an Mo-rich precursor $\text{Eu}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}\cdot 6\text{H}_2\text{O}$ (= $\text{Eu}_2\text{O}_3\cdot 8\text{MoO}_3\cdot 18\text{H}_2\text{O}$) (Naruke & Yamase, 2001). We applied this preparation method to synthesize $n\text{Tb}_2\text{O}_3\cdot m\text{MoO}_3$ phases, and obtained single crystals of $\text{Tb}_2\text{Mo}_4\text{O}_{15}$.

$\text{Tb}_2\text{Mo}_4\text{O}_{15}$ is isomorphous with $\text{Ho}_2\text{Mo}_4\text{O}_{15}$ (Efremov *et al.*, 1988). Fig. 1a shows the coordination environment of the Tb, Mo1, and Mo2 atoms. The Tb atom is coordinated by seven O atoms with a mean Tb—O distance of 2.330 Å, which is slightly longer than the Ho—O distance (mean 2.305 Å) in $\text{Ho}_2\text{Mo}_4\text{O}_{15}$ (Efremov *et al.*, 1988), as a result of the difference in the ionic radii of Tb^{3+} and Ho^{3+} (Shannon, 1976). The TbO_7 polyhedron is approximated to a monocapped trigonal prism, comprising two trigonal planes of $[\text{O}2^{\text{iii}}, \text{O}4, \text{O}7^{\text{iv}}]$ and $[\text{O}3, \text{O}6^{\text{i}}, \text{O}8^{\text{ii}}]$, and a capping $\text{O}5^{\text{v}}$ atom. As shown in Fig. 1(b), the resulting $\text{Mo}1\text{O}_5$ and $\text{Mo}2\text{O}_4$ polyhedra share a corner at the O2 atom. Furthermore, $\text{Mo}1\text{O}_5$ and the symmetry-related $\text{Mo}1^{\text{vii}}\text{O}_5$ are corner-shared by the O1 atom which lies on a center of symmetry. As a result, the molybdate polyhedra form a tetrameric Mo_4O_{15} cluster (Fig. 1b). In the $\text{Mo}1\text{O}_5$ polyhedron, the Mo1—O2^{vi} bond length is much longer than the others (Table 1). A similar distorted MoO_5 trigonal bipyramid has also been observed in $\text{Eu}_4\text{Mo}_7\text{O}_{27}$ (Naruke & Yamase, 2001). It is interesting to note that $\text{Ce}_2\text{Mo}_4\text{O}_{15}$ (Fallon & Gatehouse, 1982) and $\text{La}_2\text{Mo}_4\text{O}_{15}$ (Dubois *et al.*, 2001) possess different molybdate groups ($\{\text{Mo}_4\text{O}_{14}\}_\infty$ and Mo_6O_{22} groups,



(a)



(b)

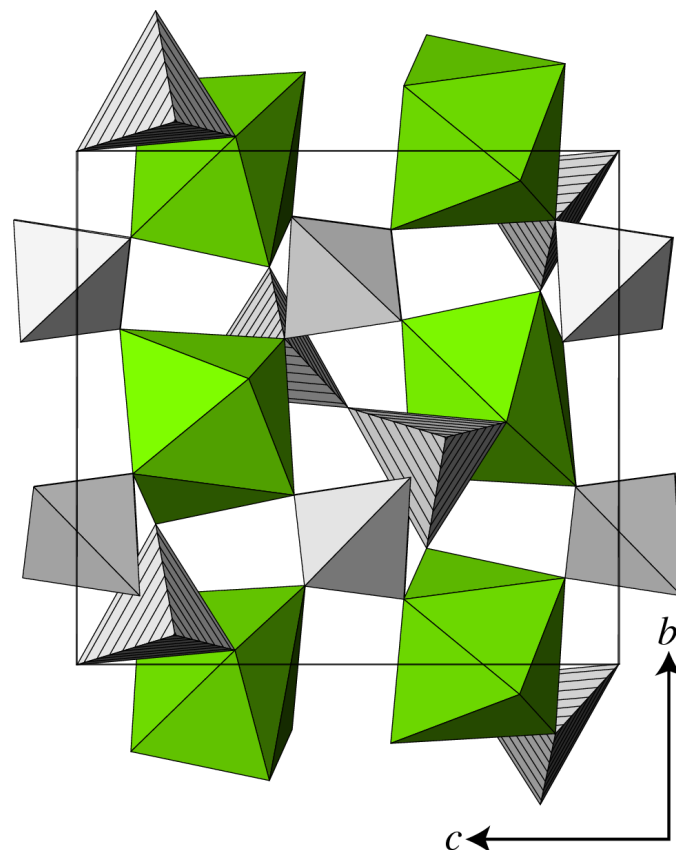
Figure 1

ORTEP (Johnson, 1976) views of the coordination environments of (a) Tb, Mo1 and Mo2, and (b) the Mo_4O_{15} group in $\text{Tb}_2\text{Mo}_4\text{O}_{15}$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $2-x, -y, 1-z$; (ii) $2-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (iv) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (v) $2-x, y-\frac{1}{2}, \frac{3}{2}-z$; (vi) $1-x, -y, 1-z$; (vii) $1-x, 1-y, 1-z$; (viii) $x, 1+y, z$.]

respectively) and coordination numbers of the RE (8 and 9, respectively). The TbO_7 , Mo1O_5 and Mo_2O_4 polyhedra are connected by edge- and corner-sharing in the crystal lattice (Fig. 2).

Experimental

The precursor $\text{Tb}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}\cdot 6\text{H}_2\text{O}$ was prepared by modification of the synthesis procedure of $\text{Eu}_2(\text{H}_2\text{O})_{12}\text{Mo}_8\text{O}_{27}\cdot 6\text{H}_2\text{O}$ (Yamase & Naruke, 1991). An aqueous solution (10 ml) containing MoO_3 (1.93 g) and KOH (1.5 g) was diluted to 1000 ml, and acidified to pH = 4.5 with HClO_4 . $\text{Tb}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ (3.8 g) was dissolved in water (20 ml) and added slowly to the molybdate solution with stirring. The

**Figure 2**

Packing diagram of $\text{Tb}_2\text{Mo}_4\text{O}_{15}$ viewed parallel to the a axis. The green polyhedra denote the TbO_7 , the hatched grey polyhedra the Mo1O_5 , and the plain grey tetrahedra the Mo_2O_4 units.

final pH was adjusted to 3.0 with HClO_4 , and the solution was kept at room temperature. The pale yellow polycrystalline product, obtained after a week, was collected by filtration, washed with water, and dried in air. Powder (0.1 g) was placed on an alumina container and fired at 1023 K for 2 h in air. Single crystals of $\text{Tb}_2\text{Mo}_4\text{O}_{15}$ were formed in a glassy substance. Reuse of the same container was effective in the crystallization of $\text{Tb}_2\text{Mo}_4\text{O}_{15}$. Details of the firing conditions are described in the earlier paper (Naruke & Yamase, 2001).

Crystal data

$\text{Mo}_4\text{O}_{15}\text{Tb}_2$
 $M_r = 941.60$
 Monoclinic, $P2_1/c$
 $a = 6.8666$ (4) Å
 $b = 9.6596$ (3) Å
 $c = 10.5866$ (5) Å
 $\beta = 105.827$ (2)°
 $V = 675.57$ (6) Å³
 $Z = 2$

$D_x = 4.629$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3943 reflections
 $\theta = 3.7\text{--}27.5^\circ$
 $\mu = 13.97$ mm⁻¹
 $T = 296.2$ K
 Block, colorless
 $0.10 \times 0.10 \times 0.05$ mm

Data collection

Rigaku R-AXIS-RAPID Imaging
 Plate diffractometer
 ω scans
 Absorption correction: numerical
 (Higashi, 1999a,b)
 $T_{\min} = 0.284$, $T_{\max} = 0.512$
 6254 measured reflections

1545 independent reflections
 1454 reflections with $F^2 > 2\sigma(F^2)$
 $R_{\text{int}} = 0.045$
 $\theta_{\max} = 27.5^\circ$
 $h = 0 \rightarrow 8$
 $k = 0 \rightarrow 12$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 0.90$
 1543 reflections
 98 parameters
 $w = 1/[\sigma^2(F_o^2) + \{0.05[\max(F_o^2, 0) + 2F_c^2/3]^2\}]$

$(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.82 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.97 \text{ e } \text{\AA}^{-3}$
 Extinction correction: Zachariasen
 (1967) type 2 Gaussian isotropic
 Extinction coefficient: 0.052 (1)

Table 1
 Selected interatomic distances (Å).

Tb—O4	2.276 (3)	Mo1—O7	1.749 (3)
Tb—O6 ⁱ	2.303 (3)	Mo1—O1	1.8695 (3)
Tb—O8 ⁱⁱ	2.304 (3)	Mo1—O2 ^{vi}	2.544 (3)
Tb—O3	2.331 (3)	Mo2—O6	1.747 (3)
Tb—O2 ⁱⁱⁱ	2.335 (3)	Mo2—O8	1.752 (4)
Tb—O7 ^{iv}	2.374 (4)	Mo2—O4	1.760 (3)
Tb—O5 ^v	2.389 (3)	Mo2—O2	1.782 (3)
Mo1—O3	1.728 (4)	Mo2—O5 ⁱ	3.211 (4)
Mo1—O5	1.736 (3)		

Symmetry codes: (i) $2 - x, -y, 1 - z$; (ii) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (iv) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (v) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (vi) $1 - x, -y, 1 - z$.

Difference Fourier peaks with $\Delta\rho_{\max} = 1.82$ and $\Delta\rho_{\min} = -1.97 \text{ e } \text{\AA}^{-3}$ are observed at positions 0.744 and 0.038 Å from the Tb atom, respectively.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

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