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Dysprosium Tantalum Oxide, $\text{DyTa}_7\text{O}_{19}$

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Abstract

Crystals of $\text{DyTa}_7\text{O}_{19}$ were obtained by a chemical transport reaction using NH_4Cl as the transport agent. The structure was refined in space group $P\bar{6}c2$ and is built up from double layers of Ta2 polyhedra, which may be described as edge-shared pentagonal bipyramids, alternating with layers of $[\text{Ta}_3\text{Dy}_3\text{O}_{30}]$ rings.

Comment

Rare earth niobates and tantalates have been studied extensively because of their potentially interesting physical properties. Members of the systems $\text{LnTa}_7\text{O}_{19}$ (Ln = rare earth) have been reported (Bodiot, 1968; Gatehouse, 1979; Putilin, Krylov, Men'shenina & Evdokimov, 1985; Langenbach-Kutttert, Strurm & Gruehn, 1986; Pushcharovskii, Yamnova, Leonyuk & Bogdanova, 1987; Schaffrath & Gruehn, 1990). Johnson & Gatehouse (1980) redetermined the space group of $\text{CeTa}_7\text{O}_{19}$ by convergent-beam diffraction to be $P\bar{6}c2$ and not $P6_3/mcm$ as previously reported from X-ray diffraction. We report here the determination of the single-crystal structure of $\text{DyTa}_7\text{O}_{19}$, which was finally refined in space group $P\bar{6}c2$.

The polyhedron of Ta2 can be described as a distorted pentagonal bipyramid with a long Ta—O distance of 2.45 (1) Å. Fig. 1 shows a layer of edge-shared pentagonal Ta_2O_7 bipyramids along [001]. The layers of pentagonal bipyramids are corner-shared with another layer through the O1 atoms in the c direction to form double layers (see Fig. 3). The average Ta—O distance in the double layers is 2.06 Å.

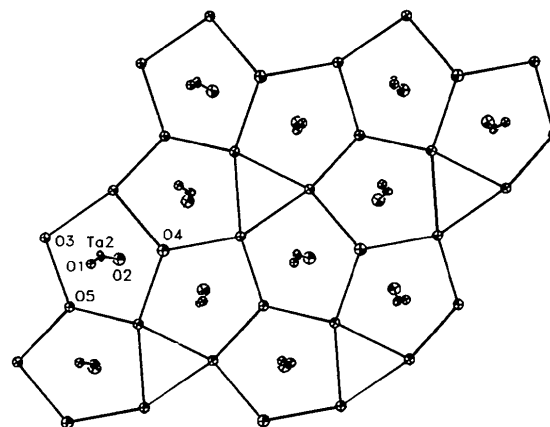


Fig. 1. A layer of Ta2 pentagonal bipyramids projected along [001] (bonds Ta2—O3, Ta2—O4 and Ta2—O5 omitted).

The Ta1 atoms are octahedrally coordinated by six O2 atoms. The Dy polyhedron is a distorted bicapped trigonal antiprism. The Ta_1O_6 octahedra are edge-shared with DyO_8 bicapped trigonal antiprisms through O2 atoms to form six-membered $[\text{Ta}_3\text{Dy}_3\text{O}_{30}]$ rings. These six-membered rings intersect each other in the ab plane to form layers of $[\text{Ta}_3\text{Dy}_3\text{O}_{30}]$ (Fig. 2).

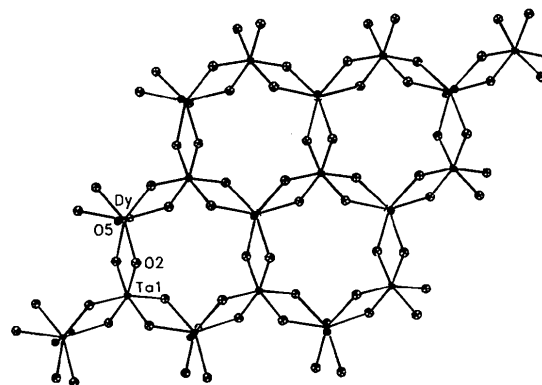


Fig. 2. A layer of six-membered $[\text{Ta}_3\text{Dy}_3\text{O}_{19}]$ rings projected along [001].

Fig. 3 shows the crystal structure of DyTa₇O₁₉ along [100]. The structure is built up from the double layers of Ta₂ octahedra alternating with the layers of [Ta₃Dy₃O₃₀] through sharing the O2 and O5 atoms in the *c* direction.

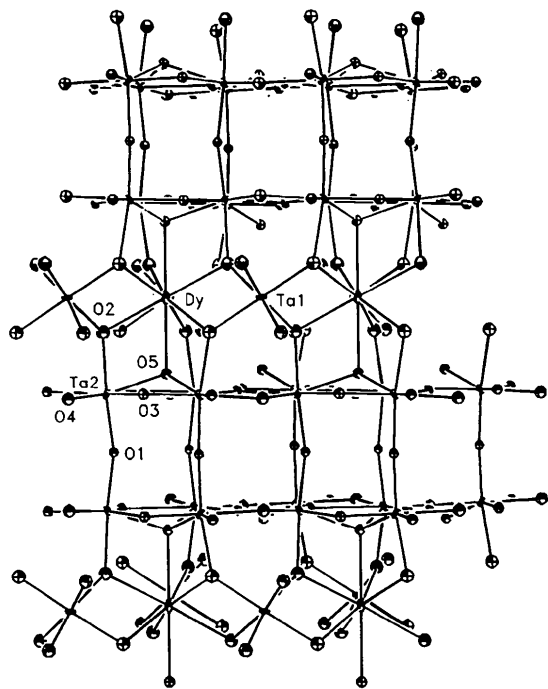


Fig. 3. Crystal structure of DyTa₇O₁₉ projected along [100].

Experimental

The appropriate quantities of powdered DyOCl, Ta₂O₅ and Ta (2:1:1 mol ratio) were mixed, pressed into a pellet and heated in a sealed and evacuated quartz tube at 1223 K for 9 d. The product mixture and *ca* 30 mg NH₄Cl were sealed in an evacuated silica tube. The tube was progressively heated to 1223 K for 7 d, then cooled to 1073 K at a rate of 6.25 K h⁻¹ and finally cooled to room temperature. The yellow crystals, which are stable in air, were chosen from the product mixture. Electron-probe micro-analysis of a single crystal for X-ray diffraction analysis showed that it contained the elements Dy and Ta, and no Cl.

Crystal data

DyTa₇O₁₉
M_r = 1733.12
 Hexagonal
*P*6*c*2
a = 6.199 (3) Å
c = 19.859 (6) Å
V = 660.9 (8) Å³
Z = 2
D_x = 8.71 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 25 reflections
 θ = 10–25°
 μ = 62.78 mm⁻¹
T = 293 K
 Prismatic
 0.30 × 0.10 × 0.10 mm
 Yellow

Data collection

Rigaku AFC-5R diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
 T_{\min} = 0.113, T_{\max} = 0.995
 933 measured reflections
 923 independent reflections
 463 observed reflections
 $[I > 3.0\sigma(I)]$

R_{int} = 0.139
 θ_{max} = 40.0°
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 5$
 $l = 0 \rightarrow 34$
 3 standard reflections monitored every 150 reflections
 intensity decay: 0.2%

Refinement

Refinement on *F*
 R = 0.0471
 wR = 0.0548
 S = 1.23
 463 reflections
 29 parameters
 $w = 1/[\sigma^2(F) + (0.020F)^2 + 1.0] - F$

$(\Delta/\sigma)_{\text{max}}$ = 0.0323
 $\Delta\rho_{\text{max}}$ = 4.47 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -5.90 e Å⁻³
 Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

U_{iso} for O atoms, $U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$ for Ta and Dy atoms.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}/U_{\text{eq}}$
Ta1	2/3	1/3	0	0.0073 (3)
Ta2	0.3586 (2)	0.3631 (2)	0.15558 (4)	0.0079 (1)
Dy	1/3	2/3	0	0.0097 (5)
O1	0.375 (4)	0.408 (4)	1/4	0.007 (4)
O2	0.423 (4)	0.385 (4)	0.054 (1)	0.016 (4)
O3	0.018 (4)	0.253 (3)	0.1530 (8)	0.010 (3)
O4	2/3	1/3	0.161 (2)	0.014 (7)
O5	1/3	2/3	0.123 (2)	0.010 (6)

Table 2. Selected geometric parameters (Å, °)

Ta1—O2	2.01 (2)	Ta2—O4	2.011 (3)
Ta1—O2'	2.01 (2)	Ta2—O5	2.07 (1)
Ta1—O2''	2.01 (2)	Dy—O2	2.34 (3)
Ta1—O2'''	2.01 (3)	Dy—O2 ¹	2.34 (2)
Ta1—O2 ²	2.01 (2)	Dy—O2 ²	2.34 (2)
Ta1—O2 ³	2.01 (2)	Dy—O2 ³	2.34 (3)
Ta2—O1	1.891 (3)	Dy—O2 ⁴	2.34 (2)
Ta2—O2	2.04 (2)	Dy—O2 ⁵	2.34 (2)
Ta2—O3	1.87 (2)	Dy—O5	2.45 (4)
Ta2—O3 ¹	2.45 (1)	Dy—O5 ¹	2.45 (4)
Ta2—O3 ²	2.09 (2)		
O2—Ta1—O2'	94 (1)	O3 ¹ —Ta2—O5	63.3 (6)
O2—Ta1—O2''	93.7 (9)	O3 ² —Ta2—O4	74.2 (7)
O2—Ta1—O2'''	75.8 (9)	O3 ³ —Ta2—O5	150.5 (9)
O2—Ta1—O2 ¹	164.0 (8)	O4—Ta2—O5	127.5 (4)
O2—Ta1—O2 ²	98.9 (9)	O2—Dy—O2 ¹	100.4 (8)
O2 ¹ —Ta1—O2 ²	93.7 (8)	O2—Dy—O2 ²	100.4 (8)
O2 ² —Ta1—O2 ³	164.0 (8)	O2—Dy—O2 ³	63.5 (8)
O2 ³ —Ta1—O2 ⁴	99 (1)	O2—Dy—O2 ⁴	99.8 (8)
O2 ⁴ —Ta1—O2 ⁵	75.8 (9)	O2—Dy—O2 ⁵	156.2 (7)
O2 ⁵ —Ta1—O2 ¹	98.9 (9)	O2—Dy—O5	62.5 (5)
O2 ¹ —Ta1—O2 ²	75.8 (8)	O2—Dy—O5 ¹	117.5 (5)
O2 ² —Ta1—O2 ³	164 (1)	O2 ¹ —Dy—O2 ²	100.4 (7)
O2 ³ —Ta1—O2 ⁴	93.7 (9)	O2 ² —Dy—O2 ³	99.8 (7)
O2 ⁴ —Ta1—O2 ⁵	93.7 (9)	O2 ³ —Dy—O2 ⁴	156 (1)

O2 ^{iv} —Ta1—O2 ^x	93.7 (8)	O2 ^{vi} —Dy—O2 ^x	63.5 (7)
O1—Ta2—O2	166.5 (8)	O2 ^{vii} —Dy—O5	62.5 (5)
O1—Ta2—O3	93 (1)	O2 ^{viii} —Dy—O5 ⁱⁱⁱ	117.5 (5)
O1—Ta2—O3 ^{vi}	85.3 (7)	O2 ^{ix} —Dy—O2 ^x	156.2 (7)
O1—Ta2—O3 ^{vii}	98.8 (9)	O2 ^x —Dy—O2 ^{ix}	63.5 (7)
O1—Ta2—O4	89 (1)	O2 ^{xi} —Dy—O2 ^x	99.8 (8)
O1—Ta2—O5	101 (1)	O2 ^{xii} —Dy—O5	62.5 (5)
O2—Ta2—O3	98.4 (8)	O2 ^{xiii} —Dy—O5 ⁱⁱⁱ	117.5 (5)
O2—Ta2—O3 ^{vi}	81.4 (6)	O2 ^{xiv} —Dy—O2 ^{ix}	100.4 (8)
O2—Ta2—O3 ^{vii}	90.1 (8)	O2 ^{xv} —Dy—O2 ^x	100.4 (8)
O2—Ta2—O4	84 (1)	O2 ^{xvi} —Dy—O5	117.5 (5)
O2—Ta2—O5	75 (1)	O2 ^{xvii} —Dy—O5 ⁱⁱⁱ	62.5 (5)
O3—Ta2—O3 ^{vi}	136.7 (9)	O2 ^{xviii} —Dy—O2 ^x	100.4 (7)
O3—Ta2—O3 ^{vii}	82.8 (9)	O2 ^{xix} —Dy—O5	117.5 (5)
O3—Ta2—O4	156.9 (6)	O2 ^{xx} —Dy—O5 ⁱⁱⁱ	62.5 (5)
O3—Ta2—O5	74.9 (6)	O2 ^{xxi} —Dy—O5	117.5 (5)
O3 ^{vi} —Ta2—O3 ^{vii}	140.2 (9)	O2 ^{xxii} —Dy—O5 ⁱⁱⁱ	62.5 (5)
O3 ^{vii} —Ta2—O4	66.4 (6)	O5—Dy—O5 ⁱⁱⁱ	180

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

The structure was solved in space group $P\bar{6}c2$ by direct methods using *MITHRIL* (Gilmore, 1983). The coordinates of the remaining atoms were found in succeeding difference Fourier syntheses. The structure was refined by full-matrix least-squares methods using *MolEN* (Fair, 1990). Attempts were made to refine the structure in space group $P6_3/mcm$ which converged at $R = 0.049$ and $wR = 0.056$. However, taking aspects of structural chemistry and the references into account, the space group $P\bar{6}c2$ was preferably selected. (The results of the refinement in space group $P6_3/mcm$ are available from the authors).

Data collection: *CONTROL* (Molecular Structure Corporation, 1988). Cell refinement: *CONTROL*. Data reduction: Lorentz-polarization using *MolEN* (Fair, 1990). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: OH1087). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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