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BaNaBO₃

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Abstract

Barium sodium orthoborate, BaNaBO₃, was prepared and its structure established by single-crystal X-ray methods. It crystallizes in the monoclinic system, space group *C2/m*. The structure is constructed from BO₃, NaO₆ and BaO₉ groups which are linked by shared edges, vertices and faces. The NaO₆ octahedra share triangular faces to form chains extending along the *c* axis.

Comment

During an investigation of phase equilibria in the BaO–Na₂O₃ system, we discovered three new phases: BaNaBO₃, BaNaB₅O₉ and BaNaB₉O₁₅ (Tu & Keszler 1995). We describe here the structure of BaNaBO₃. A drawing of the unit cell is given in Fig. 1. The structure contains a triangular BO₃ group, a BaO₉ polyhedron and two crystallographically distinct distorted NaO₆ octahedra. A distinguishing feature of the structure is the presence of one-dimensional chains of face-sharing NaO₆ octahedra extending along the *c* axis (Fig. 2). The stacking of these octahedra is consistent with a distorted *ABAB* packing of the O atoms. The octahedra

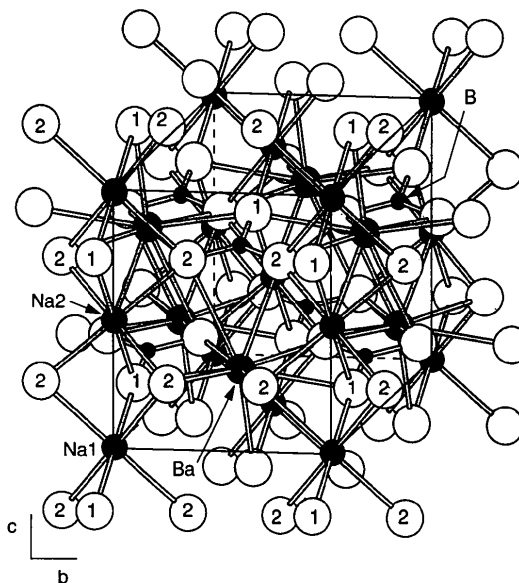


Fig. 1. Labelled drawing of the unit cell of BaNaBO₃. The largest circles represent O atoms.

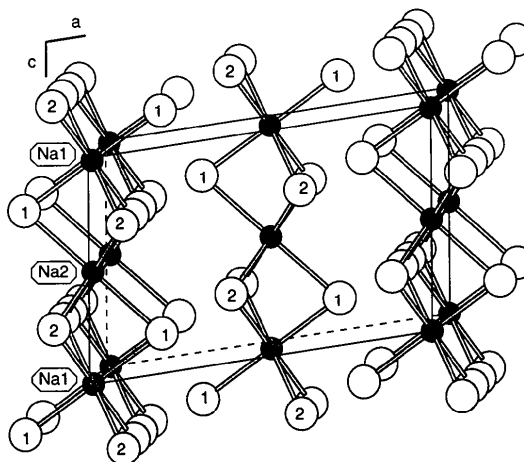


Fig. 2. View of chains of face-sharing NaO₆ octahedra. The largest circles represent O atoms.

share edges with the BaO₉ groups and vertices with the BO₃ planes. The BO₃ triangles are isolated by the Ba- and Na-centered polyhedra, and the BaO₉ polyhedra are linked to one another by shared faces and vertices. The overall structure is similar to those of γ -Na₂CO₃ (Aalst, Hollander, Peterse & Wolff, 1976) and K₂CO₃ (Gatehouse & Lloyd, 1973; Dubbeldam & Wolff, 1969) which also contain chains of face-sharing octahedra, NaO₆ or KO₆, linked by nine-coordinate Na or K atoms and triangular CO₃ groups.

Selected interatomic distances and angles are listed in Table 2. The Ba—O distances range from 2.759 (5) to 3.014 (5) with a mean of 2.85 (10) Å. The short Na1—O1 distance [2.367 (6) Å] indicates tetragonal compression of the Na1O₆ octahedron, while the Na2—O1 distance of 2.552 (7) Å indicates tetragonal elongation of the Na2O₆ octahedron. The O1—Na—O2 angles reflect the elongation of the octahedra along the chain axis. The B—O distances vary from 1.372 (7) to 1.401 (1) Å with an average of 1.382 (17) Å, which is consistent with the sum of the ionic radii (Shannon, 1976).

Experimental

A powder sample was prepared by grinding stoichiometric amounts of Ba(NO₃)₂ (Johnson Matthey, ACS grade), Na₂CO₃·H₂O (JTB, ACS grade) and B₂O₃ (ALFA, 99.98%) and then heating at 893 K for 1 h, followed by additional grinding and heating at 993 K for 6 h. Analysis of an X-ray powder pattern indicated the product to be single phase. Single crystals were grown in a platinum crucible from a stoichiometric melt that was cooled from 1053 to 803 K at 6 K h⁻¹ and then to room temperature at 60 K h⁻¹.

Crystal data

BaNaBO₃
M_r = 219.13
 Monoclinic
*C*2/*m*
a = 9.561 (2) Å
b = 5.557 (2) Å
c = 6.179 (2) Å
 β = 98.85 (2)°
V = 324.4 (3) Å³
Z = 4
D_x = 4.487 Mg m⁻³

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 20 reflections
 θ = 13.8–18.0°
 μ = 12.17 mm⁻¹
T = 296 K
 Plate
 0.07 (3) × 0.06 (4) × 0.04 (2) mm
 Colorless

Data collection

Rigaku AFC-6R diffractometer
 ω -2 θ scans
 Absorption correction: refined from ΔF (DIFABS; Walker & Stuart, 1983)
 T_{\min} = 0.41, T_{\max} = 0.61
 564 measured reflections
 522 independent reflections

461 observed reflections
 $[F_o^2 \geq 3\sigma(F_o^2)]$
 R_{int} = 0.086
 θ_{max} = 30.0°
 h = -13 → 13
 k = 0 → 7
 l = 0 → 8
 3 standard reflections monitored every 200 reflections
 intensity decay: 1.9%

Refinement

Refinement on *F*
 R = 0.033
 wR = 0.040
 S = 1.39
 461 reflections
 36 parameters
 $w = 1/\sigma^2(F_o)$
 $(\Delta/\sigma)_{\text{max}}$ = 0.03
 $\Delta\rho_{\text{max}}$ = 0.58 e Å⁻³
 $\Delta\rho_{\text{min}}$ = -0.55 e Å⁻³

Extinction correction: TEXSAN (Molecular Structure Corporation, 1989)
 Extinction coefficient: 0.37 (1) × 10⁻⁶
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Ba	-0.3334 (7)	0	0.7436 (1)	0.0111 (3)
Na1	0	0	0	0.018 (3)
Na2	0	0	1/2	0.018 (3)
O1	-0.2023 (7)	0	1.178 (1)	0.013 (3)
O2	-0.3977 (5)	0.213 (1)	0.291 (1)	0.019 (3)
B1	-0.332 (1)	0	0.257 (2)	0.008 (4)

Table 2. Selected geometric parameters (Å, °)

Ba—O1	2.783 (7)	Na1—O1 ^{ix}	2.367 (6)
Ba—O1 ⁱ	2.832 (2)	Na1—O1 ^x	2.367 (6)
Ba—O1 ⁱⁱ	2.832 (2)	Na1—O2 ^{xi}	2.486 (1)
Ba—O2	3.014 (5)	Na1—O2 ^{xiii}	2.486 (1)
Ba—O2 ⁱⁱⁱ	3.014 (5)	Na1—O2 ^{xiii}	2.486 (1)
Ba—O2 ^{iv}	2.759 (5)	Na1—O2 ^{viii}	2.486 (1)
Ba—O2 ^v	2.759 (5)	Na2—O1 ^{ix}	2.552 (7)
Ba—O2 ^{vi}	2.809 (5)	Na2—O1 ^{xiv}	2.552 (7)
Ba—O2 ^{vii}	2.809 (5)	Na2—O1 ^{xi}	2.358 (5)
Na2—O2 ^v	2.358 (5)	Na2—O1 ^v	2.358 (5)
Na2—O2 ^{viii}	2.358 (5)	B1—O1 ^{ix}	1.401 (7)
B1—O1	1.372 (7)	B1—O2 ⁱⁱⁱ	1.372 (7)
O1 ^{ix} —Na1—O1 ^x	180	O1 ^{ix} —B1—O2	120.2 (4)
O1 ^{ix} —Na1—O2 ^{xi}	85.6 (2)	O2—B1—O2 ⁱⁱⁱ	119.5 (8)
O1 ^{ix} —Na1—O2 ^{xiii}	94.4 (2)	O1—Ba—O2	153.2 (1)
O2 ^{xi} —Na1—O2 ^{viii}	79.7 (3)	O2—Ba—O2 ⁱⁱⁱ	46.3 (1)
O2 ^{xi} —Na1—O2 ^{xiii}	100.3 (3)	O2—Ba—O2 ^{iv}	101.9 (1)
O2 ^{xiii} —Na1—O2 ^{viii}	180	O2 ^{xi} —Na2—O2 ^{viii}	85.0 (3)
O2 ^{xi} —Na2—O2 ^{iv}	180	O1 ^{ix} —B1—O2 ⁱⁱⁱ	120.2 (4)
O2 ^{iv} —Na2—O2 ^{viii}	95.0 (3)		

Symmetry codes: (i) $-\frac{1}{2} - x, -\frac{1}{2} - y, 2 - z$; (ii) $-\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$; (iii) $x, -y, z$; (iv) $-\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (v) $-\frac{1}{2} - x, \frac{1}{2} + y, 1 - z$; (vi) $-1 - x, -y, 1 - z$; (vii) $-1 - x, y, 1 - z$; (viii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (ix) $x, y, z - 1$; (x) $-x, -y, 1 - z$; (xi) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (xii) $-\frac{1}{2} - x, y - \frac{1}{2}, -z$; (xiii) $-\frac{1}{2} - x, \frac{1}{2} - y, -z$; (xiv) $-x, -y, 2 - z$.

The crystal was mounted on a glass fiber for data collection. Crystallographic calculations were performed using the TEXSAN package (Molecular Structure Corporation, 1989).

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1082). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Samarium Tantalum Oxysulfide, Sm₂Ta₃S₂O₈

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Abstract

The title compound is isostructural with La₂Ta₃S₂O₈. The Sm atoms are in tricapped trigonal prismatic sites enclosed by two S and seven O atoms. The Ta atoms are octahedrally coordinated, one to six O atoms and the other to two *trans*-O and four S atoms. The structure comprises alternate layers of Sm tricapped trigonal prisms and Ta octahedra. The Ta(1)···Ta(1) distances in the octahedral layers are 3.314 (4), 3.775 (1) and 4.236 (4) Å.

Comment

The present work constitutes part of our study of the structure and physical properties of the lanthanide-transition metal oxysulfide compounds. A family

of RCrS₂O (*R* = La to Sm) quaternary oxysulfides is known (Dugue, Vovan & Villers, 1990*a,b*) and Dugue, Vovan & Laruelle (1985) reported the structure of La₅V₃S₆O₇, which contains both V⁵⁺ and V³⁺ sites. The series of compounds Ln₂Ta₃Se₂O₈ (Ln = La, Ce, Pr, Nd) were synthesized by Brennan, Aleandri & Ibers (1991) and the isostructural compounds La₂Ta₃S₂O₈ and La₂Nb₃S₂O₈, which contain mixed-valency Ta atoms, were subsequently characterized (Brennan & Ibers, 1992). We present here the crystal structure of Sm₂Ta₃S₂O₈.

Each Sm atom is coordinated to two S and seven O atoms in arrangement whereby the two S and one of the O atoms can be described as being face-capped trigonal prismatic. The Sm—S distances are 2.95 (1) and 2.99 (1) Å and the Sm—O distances are in the range 2.39 (1)–2.53 (2) Å. The Sm tricapped trigonal prisms are face shared through the O(1), O(2) and O(4) atoms, forming chains in the *c*-axis direction. The Sm···Sm distance is 3.775 (1) Å. The prisms are corner shared through the S atoms in the *a* direction, forming layers of Sm tricapped trigonal prisms.

Fig. 1 shows the layer of Ta octahedra. Ta(1) is octahedrally coordinated to four S and two O atoms. The Ta(1)—O distance is 1.98 (3) Å and the Ta(1)—S distances are 2.386 (8) and 2.728 (7) Å; these distances are 1.978 (9), 2.462 (3) and 2.692 (3) Å, respectively, in La₂Ta₃S₂O₈. The Ta(1) octahedra form chains in the *c*-axis direction *via* edge-shared S atoms, with three Ta(1)···Ta(1) distances of 3.314 (4), 3.775 (1) and 4.236 (4) Å. Ta(2) is octahedrally coordinated to six O atoms with Ta—O distances ranging from 1.85 (2) to 2.33 (2) Å [1.820 (2)–2.299 (8) Å in La₂Ta₃S₂O₈]. The Ta(2)O₆ octahedra are edge shared in the *a* direction through O(1) atoms, and corner shared through O(3) atoms in the *c* direction, forming double chains of octahedral Ta(2) dimers. The edge-shared Ta(2)···Ta(2) distance is 3.286 (2) Å, compared with 3.292 (2) Å in

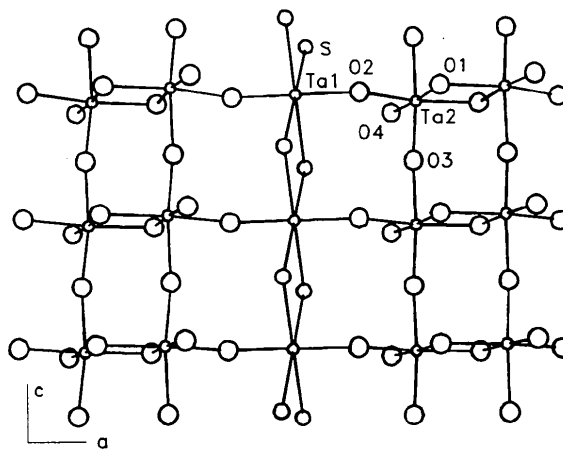


Fig. 1. A layer of Ta octahedra viewed along the *b*-axis direction.