Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
W	0.1099 (1)	x	0	0.003 (1)
Ni	0.6381 (1)	x	0	0.005 (1)
P	0.3302 (1)	0.8228 (1)	0.0031 (1)	0.004 (1)
K	0.0001 (1)	0.7103 (1)	0.0475 (1)	0.026 (1)
O(1)	0.2190 (2)	0.2398 (3)	0.1278 (2)	0.008 (1)
O(2)	0.2839 (2)	−0.0138 (2)	0.0279 (2)	0.007 (1)
O(3)	0.7614 (3)	0.2448 (3)	0.1075 (2)	0.009 (1)
O(4)	0.8153 (2)	0.4934 (2)	0.0174 (2)	0.008 (1)
O(5)	−0.0059 (2)	0.0447 (2)	0.1179 (2)	0.009 (1)

Table 2. *Selected geometric parameters* (Å, °)

W—O(5^{i})	1.752 (2)	P—O(4^{i})	1.513 (2)
W—O(5)	1.752 (2)	P—O(3^{i})	1.524 (2)
W—O(2^{i})	1.978 (2)	P—O(1^{v})	1.548 (2)
W—O(2)	1.978 (2)	P—O(2^{vi})	1.578 (2)
W—O(1)	2.068 (2)	K—O(3^{v})	2.621 (3)
W—O(1^{i})	2.068 (2)	K—O(4^{vii})	2.630 (2)
Ni—O(3^{ii})	2.029 (2)	K—O(1^{v})	2.708 (2)
Ni—O(3^{iii})	2.029 (2)	K—O(3^{i})	2.825 (3)
Ni—O(5^{iv})	2.046 (2)	K—O(4^{viii})	3.000 (2)
Ni—O(5^{v})	2.046 (2)	K—O(3^{viii})	3.107 (3)
Ni—O(4^{i})	2.104 (2)	K—O(5^{vi})	3.156 (2)
Ni—O(4)	2.104 (2)	K—O(5^{ix})	3.169 (2)
O(5^{i})—W—O(5)	95.9 (1)	O(3^{iii})—Ni—O(4)	88.9 (1)
O(2^{i}) -W—O(2)	161.1 (1)	O(5^{v})—Ni—O(4)	97.6 (1)
O(1)—W—O(1^{i})	83.1 (1)	O(3^{i})—P—O(4^{i})	112.2 (1)
O(5)—W—O(2)	100.6 (1)	O(3^{i})—P—O(2^{vi})	110.0 (1)
O(2)—W—O(1)	80.9 (1)	O(4^{i})—P—O(2^{vi})	109.4 (1)
W—O(5)—Ni^{x}	135.4 (1)	O(3^{i})—P—O(1^{v})	107.8 (1)
O(5^{iv})—Ni—O(5^{v})	88.9 (1)	O(4^{i})—P—O(1^{v})	112.6 (1)
O(3^{ii})—Ni—O(3^{iii})	97.2 (1)	O(2^{vi})—P—O(1^{v})	104.5 (1)
O(4^{i})—Ni—O(4)	168.5 (1)		

Symmetry codes: (i) $y, x, -z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (iii) $\frac{1}{2}+y, \frac{3}{2}-x, z-\frac{1}{4}$; (iv) $\frac{1}{2}+y, \frac{1}{2}-x, z-\frac{1}{4}$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4}-z$; (vi) $x, 1+y, z$; (vii) $x-1, y, z$; (viii) $y-\frac{1}{2}, \frac{3}{2}-x, z-\frac{1}{4}$; (ix) $y, 1+x, -z$; (x) $\frac{1}{2}-y, x-\frac{1}{2}, \frac{1}{4}+z$.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SH1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$CsNbOB_2O_5$: the Basic Structure Type of the Borates $AMOB_2O_5$ (A = K, Rb, Cs, Tl; M = Nb, Ta)

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Abstract

A new anhydrous borate, $CsNbOB_2O_5$ (caesium niobatodiborate), has been found in the ternary system Cs_2O–Nb_2O_5–B_2O_3. The compound belongs to the already known $AMOB_2O_5$ family (originally reported as AMB_2O_6) with A = K, Rb, Cs, Tl; M = Nb, Ta. These published members exhibit superstructures, the length of the superperiod depending on the chemical composition A and M. The structure of $CsNbOB_2O_5$ reported here has the smallest possible unit cell and represents the basic structural type for the family.

Comment

The present work is a part of a systematic search for non-centrosymmetric compounds, especially borates, to obtain new materials for application in nonlinear optics. The first members of the borates $AMOB_2O_5$ (A = Rb, Tl and M = Nb, Ta) were described by Gasperin (1974) and Baucher & Gasperin (1975). They found them to be non-centrosymmetric with very similar crystal structures [space group Pn for $RbNbOB_2O_5$ (Baucher, Gasperin & Cervelle, 1976), $Pn2_1a$ for $TlNbOB_2O_5$ (setting $a\bar{c}b$) and $Pn2_1m$ (setting bca) for the other compounds]. The lattice constants are given as $a = 2 \times 3.91$, $b = 9.48$, $c = 7.40$ Å for $TlNbOB_2O_5$, $a = 5 \times 3.86$, $b = 9.50$, $c = 7.44$ Å for $TlTaOB_2O_5$, $a = 5 \times 3.94$, $b = 9.49$, $c = 7.42$ Å for $RbNbOB_2O_5$, and $a = 5 \times 3.88$, $b = 9.52$, $c = 7.44$ Å for $RbTaOB_2O_5$. The multiplying factors of the a lattice constants result from the superstructures of the members of the family. These data are in good agreement with our results. Further members of this crystal family, $KNbOB_2O_5$, $KTaOB_2O_5$ and $CsNbOB_2O_5$, were synthesized for the first time in our laboratory and show similar superstructures with cell dimensions of $a = 7.318\,(1)$, $b = 8 \times 3.904\,(1)$, $c = 9.219\,(1)$ Å for $KNbOB_2O_5$, $a = 7.333\,(1)$, $b = 8 \times 3.843\,(1)$, $c = 9.313\,(1)$ Å for $KTaOB_2O_5$, and a

= 7.552 (1), $b = 8 \times 3.908(1)$, $c = 9.779(1)$ Å for $CsTaOB_2O_5$ (all standard setting), as proved by X-ray powder diffraction diagrams and Buerger precession photographs (Becker, Bohatý & Fröhlich, 1991; Becker, 1992).

During our investigations of the ternary system $Cs_2O–Nb_2O_5–B_2O_3$, we found the title compound: $CsNbOB_2O_5$. It can be grown easily from caesium borate flux, forming colourless, tabular, short prismatic or equant crystals which are terminated by prism $\{110\}$ and basal pinacoids (001) and $(00\bar{1})$. The crystals attain dimensions of up to 1 × 1 × 1 mm. Powder diffraction diagrams of $CsNbOB_2O_5$ are very similar to those of the other members of the group. The crystals are homogenous; electron microbeam analysis does not show any variation of their stoichiometry. Buerger precession photographs of $CsNbOB_2O_5$ show no evidence of any superstructure; they show the same patterns of the main reflections as the other members of the family but no superstructure reflections were observed.

The crystal structure of $CsNbOB_2O_5$ exhibits a very close relationship to the well known structure of $TlNbOB_2O_5$ (Gasperin, 1974). It consists of $[NbO_6]$ octahedra linked by the apical O(4) atoms, thus forming chains parallel to the crystallographic *b* axis (standard setting). These chains are linked by pairs of $[BO_3]$ triangles whose planes are perpendicular to the chain axes. The Cs atoms are positioned in the cavities formed by the chains of octahedra (Fig. 1).

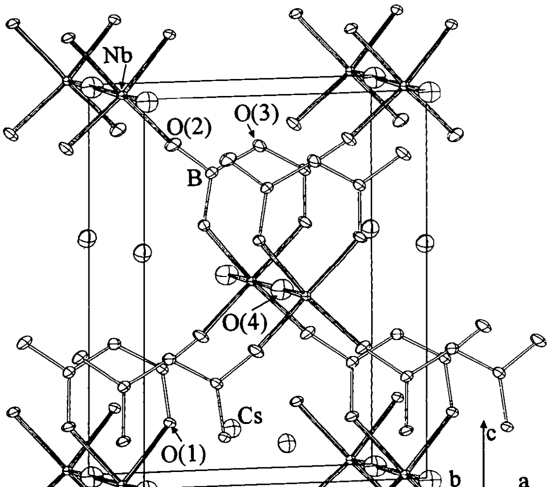

Fig. 1. *ORTEP* (Johnson, 1965) plot of the unit cell of $CsNbOB_2O_5$ showing 50% probability displacement ellipsoids.

The octahedral coordination of the Nb atoms is only very slightly distorted, the central Nb atom being shifted by 0.2 Å towards one of the apical O atoms. The O(4) atoms are linked only with Nb and do not belong to the borate group. The Nb—O distances range from 1.8 to 2.2 Å. The coordination geometry of the B atom is that of a planar undistorted triangle (B—O distances 1.35–1.39 Å, O—O distances 2.3–2.4 Å). Each $[BO_3]$ triangle is linked to another $[BO_3]$ group by a common O atom, O(3), thus forming $[B_2O_5]$ units. The O-atom arrangement around the Cs atoms is irregular, showing very different Cs—O distances. If the coordination sphere of Cs is defined by taking the shortest distance to the next cation (here B) of 3.58 Å as a limit, the resulting coordination number for Cs is 8. The Cs—O distances vary between 3.10–3.30 Å (Table 2).

While in $TlNbOB_2O_5$, and probably also in the other members of the family, a zigzag tilt of the $[NbO_6]$ octahedra causes the observed superstructures (Gasperin, 1974), the crystal structure of $CsNbOB_2O_5$ does not show any tilt of the $[NbO_6]$ octahedra towards the *b* axis of the structure (Fig. 2). Therefore, $CsNbOB_2O_5$ can be regarded as the parent basic structure type of the $AMOB_2O_5$ family.

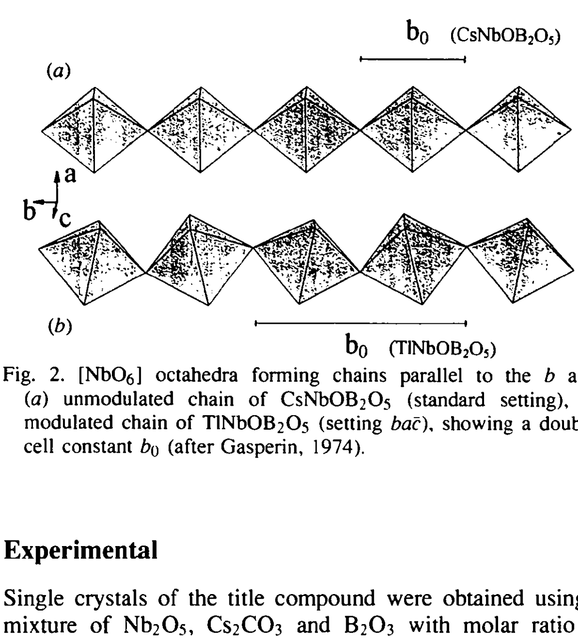

Fig. 2. $[NbO_6]$ octahedra forming chains parallel to the *b* axis: (*a*) unmodulated chain of $CsNbOB_2O_5$ (standard setting), (*b*) modulated chain of $TlNbOB_2O_5$ (setting *ba$\bar{c}$*), showing a doubled cell constant b_0 (after Gasperin, 1974).

Experimental

Single crystals of the title compound were obtained using a mixture of Nb_2O_5, Cs_2CO_3 and B_2O_3 with molar ratio of 1:2.5:6.5. The powder was ground, loaded into a platinum crucible and melted in a tube furnace at 1273 K. This temperature was held for 20 h. Then the melt was cooled to 1073 K at 4 K h^{-1}, then cooled to room temperature at 10 K h^{-1}. The resulting product is a mixture of three components: caesium borate and a glass, both of which are water soluble, and colourless crystals of $CsNbOB_2O_5$ (up to 1 × 1 × 1 mm). These can be extracted by hot water.

Crystal data

$CsNbOB_2O_5$
$M_r = 343.44$
Orthorhombic
$Pmn2_1$
$a = 7.532(1)$ Å
$b = 3.992(1)$ Å
$c = 9.728(1)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.25–25.76°$
$\mu = 8.149$ mm^{-1}
$T = 293(2)$ K

$V = 292.5$ Å^3
$Z = 2$
$D_x = 3.899$ Mg m^{-3}
Cube
0.12 × 0.12 × 0.12 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.949$, $T_{\max} = 0.999$
1355 measured reflections
1293 independent reflections
1279 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0093$
$\theta_{\max} = 34.20°$
$h = -11 \rightarrow 0$
$k = -6 \rightarrow 0$
$l = -15 \rightarrow 15$
3 intensity and 2 orientation control reflections; orientation control every 200 reflections intensity control every 120 min intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0241$
$wR(F^2) = 0.0661$
$S = 1.023$
1293 reflections
53 parameters
$w = 1/[\sigma^2(F_o^2) + (0.060P)^2$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.764$ e Å^{-3}
$\Delta\rho_{\min} = -3.28$ e Å^{-3}
Extinction correction: $F_c^* = |F_c|k[1 + (0.001\chi \times F_c^2\lambda^3/\sin 2\theta)]^{-1/4}$
Extinction coefficient: $\chi = 0.111\,(5)$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)
Absolute configuration: $\chi = 0.00\,(2)$ (Flack, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Nb	0	0.3846 (1)	0.9958 (1)	0.006 (1)
Cs	1/2	0.9717 (1)	0.1047 (1)	0.020 (1)
O(1)	0.1787 (3)	0.4455 (8)	0.1480 (2)	0.015 (1)
O(2)	0.1893 (4)	0.4386 (9)	0.8612 (3)	0.020 (1)
O(3)	1/2	0.4646 (13)	0.8496 (4)	0.019 (1)
O(4)	1/2	0.0602 (11)	0.4956 (6)	0.026 (1)
B	0.3363 (4)	0.4877 (9)	0.7839 (4)	0.013 (1)

Table 2. *Selected geometric parameters* (Å, °)

[NbO$_6$] octahedron			
Nb—O(2)	1.948 (3)	O(4$^{\rm i}$)—Nb—O(4$^{\rm v}$)	179.9 (3)
Nb—O(2$^{\rm ii}$)	1.948 (3)	O(2)—Nb—O(1$^{\rm iii}$)	89.5 (1)
Nb—O(1$^{\rm iii}$)	2.016 (3)	O(2$^{\rm ii}$)—Nb—O(1$^{\rm iv}$)	89.5 (1)
Nb—O(1$^{\rm iv}$)	2.016 (2)	O(2$^{\rm ii}$)—Nb—O(4$^{\rm v}$)	83.6 (1)
Nb—O(4$^{\rm i}$)	1.775 (5)	O(2)—Nb—O(4$^{\rm v}$)	83.6 (1)
Nb—O(4$^{\rm v}$)	2.217 (5)	O(2$^{\rm ii}$)—Nb—O(2)	94.1 (2)
[BO$_3$] triangle			
B—O(1$^{\rm v}$)	1.353 (4)	O(2)—B—O(1$^{\rm v}$)	120.2 (3)
B—O(2)	1.353 (4)	O(1$^{\rm v}$)—B—O(3)	122.4 (3)
B—O(3)	1.392 (4)	B—O(3)—B$^{\rm viii}$	124.7 (4)
Cs coordination			
Cs—O(1$^{\rm vi}$)	3.101 (3)	Cs—O(3$^{\rm xi}$)	3.167 (4)
Cs—O(1$^{\rm vii}$)	3.101 (3)	Cs—O(3$^{\rm xii}$)	3.202 (5)
Cs—O(1)	3.232 (3)		
Cs—O(1$^{\rm viii}$)	3.232 (3)		
Cs—O(2$^{\rm ix}$)	3.308 (3)	Cs—B$^{\rm ix}$	3.580 (4)
Cs—O(2$^{\rm x}$)	3.308 (3)	Cs—B$^{\rm x}$	3.580 (4)

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

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *MolEN* (Fair, 1990). Structure solution: *SHELXS*86 (Sheldrick, 1990). Structure refinement: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SH1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$SrTa_4O_{11}$: a Rietveld Refinement Using Neutron Powder Diffraction Data

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Abstract

Rietveld refinement using neutron powder diffraction data for the low-temperature form of strontium tantalum oxide, $SrTa_4O_{11}$, resulted in $R_{wp} = 3.10\%$. The structure is of the $CaTa_4O_{11}$ type and consists of layers of Ta(2)O_7

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