The *matlockite*-type praseodymium(III) oxide bromide PrOBr

Pia Talmon-Gros, Christian M. Schurz and Thomas Schleid

*Acta Cryst.* (2011). *E*67, i74

This open-access article is distributed under the terms of the Creative Commons Attribution Licence [http://creativecommons.org/licenses/by/2.0/uk/legalcode](http://creativecommons.org/licenses/by/2.0/uk/legalcode), which permits unrestricted use, distribution, and reproduction in any medium, provided the original authors and source are cited.

Acta *Crystallographica Section E: Structure Reports Online* is the IUCr's highly popular open-access structural journal. It provides a simple and easily accessible publication mechanism for the growing number of inorganic, metal-organic and organic crystal structure determinations. The electronic submission, validation, refereeing and publication facilities of the journal ensure very rapid and high-quality publication, whilst key indicators and validation reports provide measures of structural reliability. The journal publishes over 4000 structures per year. The average publication time is less than one month.

Crystallography Journals Online is available from [journals.iucr.org](http://journals.iucr.org)
The matlockite-type praseodymium(III) oxide bromide PrOBr

Pia Talmon-Gros, Christian M. Schurz and Thomas Schleid*

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany
Correspondence e-mail: schleid@iac.uni-stuttgart.de

Received 19 October 2011; accepted 14 November 2011

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(Pr–Br) = 0.001 Å; R factor = 0.026; wR factor = 0.059; data-to-parameter ratio = 11.3.

The crystal structure of the praseodymium(III) oxide bromide, PrOBr, can be best described with layers of agglomerated square antiprisms [PrO4Br4]9−. These slabs are stacked along the c axis and linked via two different secondary contacts between Pr3+ and Br−. The Pr3+ cations occupy the Wyckoff site 2c with 4mm symmetry and carry four O2− anions as well as four primary Br− anions, yielding a coordination number of 8. While the Br− anions exhibit the same site symmetry as the Pr3+ cations, the oxide anions are located at the Wyckoff position 2a with site symmetry 4m2 and have four Pr3+ cations as neighbours, defining a tetrahedron.

Table 1

Selected bond lengths (Å).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr−O</td>
<td>2.3496 (3)</td>
</tr>
<tr>
<td>Pr−Br</td>
<td>3.2457 (8)</td>
</tr>
</tbody>
</table>

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: numerical (X-SHAPE; Stoe & Cie, 1999) Tmin = 0.049, Tmax = 0.535

Refinement

R[F2 > 2σ(F2)] = 0.026
wR(F2) = 0.059
S = 1.20
113 reflections
10 parameters
Δρmax = 1.14 e Å−3
Δρmin = −2.52 e Å−3

Related literature

For prototypic PbFCl (mineral name: matlockite), see: Nieuenkamp & Bijvoet (1932) and for an early powder study, see: Mayer et al. (1965). For other PrOX structures, see: Baenziger et al. (1950) for X = F, Zachariasen (1949) for X = Cl, and Potapova et al. (1977) for X = I. For data used for a comparison of the unit-cell dimensions, see: Shannon (1976) for ionic radii and Biltz (1934) for volume increments. For a proper classification of primary and secondary contacts, see: MAPLE (Hoppe, 1975) and for the bond-valence method, see: Brown (2002). For a comparison of intended synthesis attempts, see: Mattausch & Simon (1996); Lulei (1998).

Experimental

Crystal data

PrOBr
Mw = 236.82
Tetragonal, P4/nmm
a = 4.0671 (3) Å
c = 7.4669 (5) Å
V = 123.51 (2) Å³
Z = 2
Mo Kα radiation
μ = 35.52 mm−1
T = 293 K

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: numerical (X-SHAPE; Stoe & Cie, 1999) Tmin = 0.049, Tmax = 0.535

Refinement

R[F2 > 2σ(F2)] = 0.026
wR(F2) = 0.059
S = 1.20
113 reflections
10 parameters
Δρmax = 1.14 e Å−3
Δρmin = −2.52 e Å−3

Table 1

Selected bond lengths (Å).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr−O</td>
<td>2.3496 (3)</td>
</tr>
<tr>
<td>Pr−Br</td>
<td>3.2457 (8)</td>
</tr>
</tbody>
</table>

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2117).

References

supplementary materials
The matlockite-type praseodymium(III) oxide bromide PrOBr

P. Talmon-Gros, C. M. Schurz and T. Schleid

Comment

With the exception of PrOF (Baenziger et al. 1950) all praseodymium(III) oxide halides of the general composition PrOX (X = Cl – I; Zachariasen 1949, Potapova et al. 1977) crystallize with the matlockite-type structure (Nieuwenkamp & Bijvoet, 1932). The tetragonal crystal structure of the here presented praseodymium(III) oxide bromide PrOBr can be best described with layers of agglomerated square antiprisms [PrO4Br4]9− (d(Pr3+–O2−) = 234.96 (4) pm, d(Pr3+–Br−) = 324.57 (8) pm, d(Pr3+–Br−) = 360.8 (1) and 385.9 (1) pm; Figure 1). These slabs are stacked along the c-axis and linked via two different secondary contacts between Pr3+ and Br− (Figure 2). According to the ionic radii (rCl− = 180 pm, rBr− = 195 pm, rI− = 220 pm; Shannon, 1976) of the halide anions the expansion of the unit-cell dimensions occurs in quite an usual range, but the c-axes become significantly longer than the a-axes (a-axes: from 405.3 pm to 408.6 pm; c-axes: from 679.9 pm to 916.2 pm) along the Cl−–Br−–I− track. The lattice parameters of single crystalline PrOBr (a = 406.71 pm, c = 746.69 pm) fit almost perfectly with that from a previous powder diffraction study (a = 407.1 pm, c = 748.7 pm; Mayer et al. 1965). Differences in the molar volumes of the PbFCI-type praseodymium(III) oxide halides (Vm(PrOCI) = 33.6 cm3/mol, Vm(PrOBr) = 37.2 cm3/mol, Vm(PrOI) = 46.1 cm3/mol) correspond well with the differences of the molar volumes of the respective halide anions (Vm(Cl−) = 16.3 cm3/mol, Vm(Br−) = 19.2 cm3/mol, Vm(I−) = 24.5 cm3/mol; Biltz 1934). However, the Pr3+ cations occupy the Wyckoff site 2c (symmetry: 4mm) and bond four O2− anions as well as four one one Br− anions ending up with a total coordination number of 8+l+l (Figure 1). While the Br− anions exhibit the same site symmetry as the Pr3+ cations, the oxide anions are located at Wyckoff position 2a with the site symmetry 4m2. Bond-Valence and MAPLE calculations support the interpretation of one important (d(Pr3+–Br−) = 360.8 (1) pm) and one less important secondary contact (d(Pr3+–Br−) = 385.9 (1) pm): The valency and ECoN for the first bond amounts to values of about 0.08 (with R0 = 267 pm, b = 37 pm; Brown, 2002) and 0.12 (Hoppe, 1975), but almost nil for the second one, since this next nearest contact to bromide has only very low influence on the effective coordination sphere of the Pr3+ cations (ECoN = 0.03).

Experimental

Pale green, transparent, plate-shaped single crystals of PrOBr were obtained as by-product from a mixture of 0.06 g Pr, 0.38 g PrBr3 and 0.01 g NaN3, along with 0.30 g NaBr added as a flux. The mixture was kept at 800 °C for 7 days in an evacuated, sealed fused-silica vessel designed to produce the praseodymium(III) nitride bromide Pr3NBr6 in analogy with La3NBr6 (Lulei, 1998) and Ce3NBr6 (Mattausch & Simon, 1996).

Refinement

The highest peak and the deepest hole in the final difference Fourier map are 95 pm and 84 pm apart from Pr.
supplementary materials

Figures

Fig. 1. View at the square antiprism [PrO₄Br₄]⁰⁻ with two different Br⁻ caps in matlockite-type PrOBr. Displacement ellipsoids are drawn at 90% probability level. Symmetry codes: (i) -x+1, -y, -z; (ii) x-1, y, z; (iii) -x+1, -y+1, -z; (iv) -x+1, -y+1, -z+1; (v) -x, -y, -z+1; (vi) -x, -y+1, -z+1; (vii) -x+1, -y, -z+1; (viii) x, y, z-1.

Fig. 2. Polyhedral representation of the matlockite-type PrOBr structure (dotted lines indicate the first of the two kinds of secondary contacts between Pr³⁺ and Br⁻).

Praseodymium(III) oxide bromide

Crystal data

PrBrO

\[ M_r = 236.82 \]

Tetragonal, P4/nmm

Hall symbol: -P 4a 2a

\[ a = 4.0671 (3) \text{ Å} \]

\[ c = 7.4669 (5) \text{ Å} \]

\[ V = 123.51 (2) \text{ Å}^3 \]

\[ Z = 2 \]

\[ F(000) = 204 \]

\[ D_x = 6.368 \text{ Mg m}^{-3} \]

Mo Kα radiation, \( \lambda = 0.71069 \text{ Å} \)

Cell parameters from 3957 reflections

\[ \theta = 0.4-27.9° \]

\[ \mu = 35.52 \text{ mm}^{-1} \]

\[ T = 293 \text{ K} \]

Plate, pale green

\[ 0.11 \times 0.07 \times 0.02 \text{ mm} \]

Data collection

Bruker–Nonius KappaCCD
diffractometer

113 independent reflections

Radiation source: fine-focus sealed tube

111 reflections with \( I > 2\sigma(I) \)

\[ \omega \text{ and } \phi \text{ scans} \]

\[ R_{int} = 0.082 \]

\[ \theta_{max} = 27.9°, \theta_{min} = 5.5° \]

Absorption correction: numerical

\( h = -5 \rightarrow 5 \)

\( k = -5 \rightarrow 5 \)

\( l = 0.049, T_{max} = 0.535 \)

sup-2
1621 measured reflections

\( l = -9 \rightarrow 9 \)

**Refinement**

Refinement on \( F^2 \)

Least-squares matrix: full

\[ R[F^2 > 2\sigma(F^2)] = 0.026 \]

\[ wR(F^2) = 0.059 \]

\[ S = 1.20 \]

113 reflections

10 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

\[ w = 1/[\sigma^2(F_o^2) + (0.0378P)^2] \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\( \Delta\omega_{\text{max}} < 0.001 \)

\( \Delta\rho_{\text{max}} = 1.14 \text{ e} \AA^{-3} \)

\( \Delta\rho_{\text{min}} = -2.52 \text{ e} \AA^{-3} \)

Extinction correction: *SHELXL97* (Sheldrick, 2008),

\[ F_c^* = kF_c[1+0.001xFe^2\lambda^2\sin(2\theta)]^{1/4} \]

Extinction coefficient: 0.032 (5)

**Special details**

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 \( F^2 > 2\sigma(F^2) \) 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 (\( \AA^2 \))**

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{iso}/U_{eq} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.15763 (8)</td>
<td>0.0106 (4)</td>
</tr>
<tr>
<td>O</td>
<td>0.7500</td>
<td>0.2500</td>
<td>0.0000</td>
<td>0.0129 (13)</td>
</tr>
<tr>
<td>Br</td>
<td>0.2500</td>
<td>0.2500</td>
<td>0.64087 (17)</td>
<td>0.0153 (4)</td>
</tr>
</tbody>
</table>

**Atomic displacement parameters (\( \AA^2 \))**

<table>
<thead>
<tr>
<th></th>
<th>( U^{11} )</th>
<th>( U^{22} )</th>
<th>( U^{33} )</th>
<th>( U^{12} )</th>
<th>( U^{13} )</th>
<th>( U^{23} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr</td>
<td>0.0084 (4)</td>
<td>0.0084 (4)</td>
<td>0.0148 (6)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>O</td>
<td>0.0114 (17)</td>
<td>0.0114 (17)</td>
<td>0.016 (3)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Br</td>
<td>0.0149 (5)</td>
<td>0.0149 (5)</td>
<td>0.0160 (7)</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**Geometric parameters (\( \AA, \degree \))**

| Pr—O | 2.3496 (3) | Pr—Pr | 3.7165 (8) |
| Pr—O | 2.3496 (3) | Pr—Pr | 3.7165 (8) |
| Pr—O | 2.3496 (3) | Pr—Pr | 3.7165 (8) |
supplementary materials

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr—O</td>
<td>2.3496 (3)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>3.2457 (8)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>3.2457 (8)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;vi&lt;/sup&gt;</td>
<td>3.2457 (8)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;vii&lt;/sup&gt;</td>
<td>3.2457 (8)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;viii&lt;/sup&gt;</td>
<td>3.6083 (14)</td>
</tr>
<tr>
<td>Pr—Br&lt;sup&gt;ix&lt;/sup&gt;</td>
<td>3.8586 (14)</td>
</tr>
<tr>
<td>Pr—Pr&lt;sup&gt;ix&lt;/sup&gt;</td>
<td>3.7165 (8)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—O&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>75.466 (11)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Pr&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>119.87 (3)</td>
</tr>
<tr>
<td>O&lt;sup&gt;ii&lt;/sup&gt;—Pr—O&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>75.466 (11)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Pr&lt;sup&gt;ii&lt;/sup&gt;</td>
<td>75.466 (11)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Br&lt;sup&gt;vi&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;vi&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
<tr>
<td>O&lt;sup&gt;1&lt;/sup&gt;—Pr—Br&lt;sup&gt;v&lt;/sup&gt;</td>
<td>140.758 (5)</td>
</tr>
</tbody>
</table>

sup-4
Br\(_{\text{v}}\)---Pr---Pr\(_{\text{vi}}\)  &  168.31 (4)  &  Pr\(_{\text{v}}\)---O---Pr\(_{\text{iii}}\)  &  104.534 (11) \\
Br\(_{\text{v}}\)---Pr---Pr\(_{\text{vi}}\)  &  66.920 (19)  &  Pr\(_{\text{vi}}\)---Br---Pr\(_{\text{v}}\)  &  124.77 (5) \\
Br\(_{\text{vii}}\)---Pr---Pr\(_{\text{vi}}\)  &  107.075 (12)  &  Pr\(_{\text{vi}}\)---Br---Pr\(_{\text{vii}}\)  &  77.59 (2) \\
O\(_{\text{i}}\)---Pr---Pr\(_{\text{i}}\)  &  37.733 (6)  &  Pr\(_{\text{v}}\)---Br---Pr\(_{\text{vi}}\)  &  77.59 (2) \\
O\(_{\text{ii}}\)---Pr---Pr\(_{\text{i}}\)  &  98.99 (2)  &  Pr\(_{\text{v}}\)---Br---Pr\(_{\text{v}}\)  &  77.59 (2) \\
O\(_{\text{iii}}\)---Pr---Pr\(_{\text{i}}\)  &  98.99 (2)  &  Pr\(_{\text{v}}\)---Br---Pr\(_{\text{vi}}\)  &  124.77 (5) \\

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