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$Ba_{68}Pd_{32}O_x$, with $x \simeq 13.5$

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The title compound, barium palladium oxide, $Ba_{68}Pd_{32}O_x$, $x \simeq 13.5$ is a medium-sized cubic suboxide. Two of the four crystallographically independent Ba atoms form a network of face-sharing octahedra with O atoms occupying the central position of these octahedra, giving a network resembling the pyrochlore structure. Two of three O-atom positions are fully occupied and the third partially occupied. The remainder of the Ba atoms and the Pd atoms are distributed in another network residing in the channels of the network of face-sharing $O–Ba_6$ octahedra.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Ba–O) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.029
wR factor = 0.041
Data-to-parameter ratio = 15.3

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

Comment

The title compound was synthesized as part of a search for intermetallic compounds for use as hydrogen storage materials. The compound is composed of a network of face-sharing $O–Ba_6$ octahedra with the residual Ba atoms and all Pd atoms located in the tunnels of the octahedra network. O atoms were assigned to model quite large residual densities in the centre of the octahedra. This network of $O–Ba_6$ is closely related to the pyrochlore structure (Gaertner, 1930). Removing the O1 atom (Fig. 1) gives a good resemblance between the pyrochlore $Nb–O_6$ octahedra and the network of $O2–Ba2_6$ octahedra in the title compound. Barium suboxides, with similar arrangements of O–Ba octahedra, have been observed earlier (Röhr, 1995). The main difference in the present compound are the slightly longer Ba—O and Ba—Ba distances. This may be due to partial occupation of the O-atom positions giving a weaker attraction but may also be an effect of the excess Ba and Pd in the structure. In addition to the network of $O–Ba_6$ octahedra as shown in Fig. 2, one can construct a complementary network of tetrahedraly coordinated Ba3 around Ba4 with an extra tetrahedron of Pd1 around Ba4 connected to each other through squares of 2 × Ba3 and 2 × Pd2. This additional network is shown in Fig. 3. It must be emphasized that the only indication that the title compound contains oxygen is the much better fit of the diffraction data when the model includes O atoms. Removing the O atoms from the structure model gives a pure intermetallic compound with the composition $Ba_{68}Pd_{32}$. This is, however, probably not correct. The oxygen stoichiometry cannot be stated with particularly high accuracy as it is a result from refinement.

Experimental

The compound was crystallized from a solid-state reaction between a mixture of BaH_2 (Ba rods 99.9+%, Aldrich Chemical Company Inc.; heated under 50 bar of H_2 pressure at 723 K for 4 h) and Pd (powder

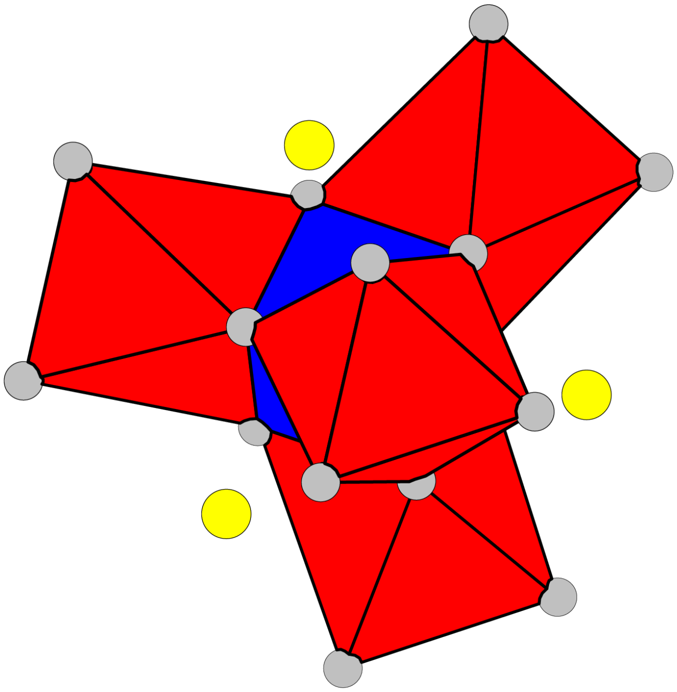

Figure 1
Part of the network of O–Ba_6 octahedra. The octahedra with O1 in its centre is blue and the ones with O3 in the centres are red. The Pd atoms are shown as yellow unconnected circles and the Ba atoms are shown with small grey circles at the apices of the octahedra. The surrounding of O2 is very similar to the surrounding of O1.

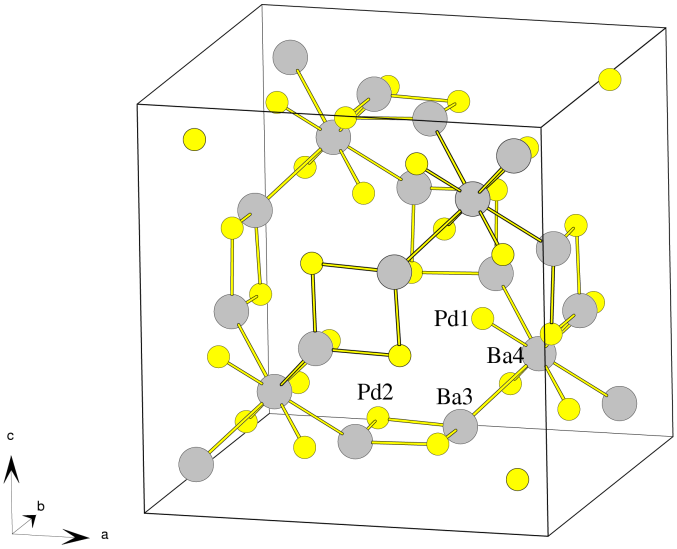

Figure 3
The unit-cell content with the complementary network to the O–Ba_6 network. The Ba atoms are shown as grey circles and Pd with yellow circles. The orientation of this picture is equivalent to Fig. 2.

< 60 µm, claimed purity 99.9+%, Chempur) in a nominal molar ratio Ba:Pd = 2:1 mixed and heated ($T \simeq 973$ K) in an Al_2O_3 crucible in a stainless-steel reactor under a H_2 pressure of 35 bar. All materials were handled in an argon-filled glove-box. The reason for using hydrogen was that the initial intention was to synthesize hydrides. The most probable sources of oxygen are either residual impurities in the glove-box atmosphere or a solid-state reaction with the crucible material (Al_2O_3). Assuming the conditions of Ellingham diagrams (Wulfsberg, 1987) to be true, one can imagine that the reduction of Al_2O_3 with Ba metal would be spontaneous at the synthesis temperature, thus a possible source of oxygen is the crucible material. Small single crystals were obtained from the solidified reaction product.

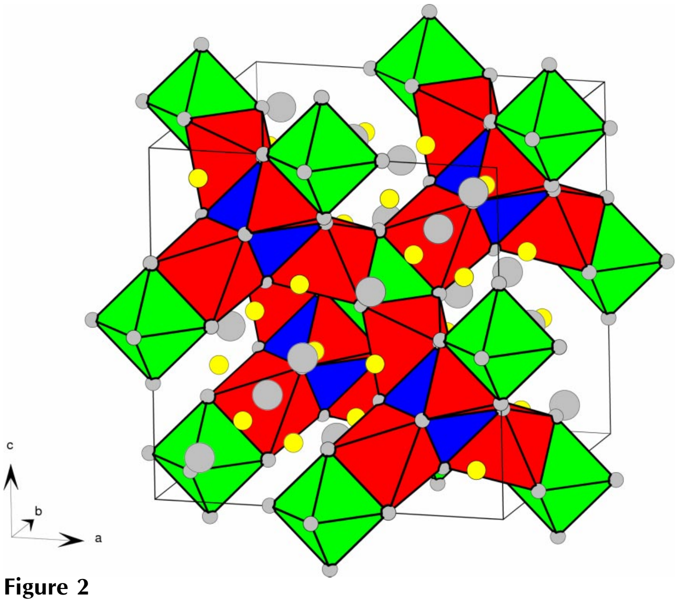

Figure 2
Slightly more than the unit cell content with the network of O–Ba_6 octahedra shown blue around O1, green around O2 and red around O3. Pd atoms are yellow and Ba grey. The Ba atoms that form the octahedra are shown with small circles.

Crystal data

$Ba_{2.125}PdO_{0.422}$
$M_r = 404.91$
Cubic, $F\bar{4}3m$
$a = 15.878$ (1) Å
$V = 4003.0$ (4) Å^3
$Z = 32$
$D_x = 5.340$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 32 reflections
$\theta = 15.0$–$19.2°$
$\mu = 19.89$ mm^{-1}
$T = 293$ (2) K
Prism, metallic light grey
0.14 × 0.09 × 0.07 mm

Data collection

Stoe AED-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1997)
$T_{\min} = 0.060$, $T_{\max} = 0.259$
1671 measured reflections
336 independent reflections
270 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$
$\theta_{\max} = 27.9°$
$h = -1 \rightarrow 20$
$k = -1 \rightarrow 20$
$l = -1 \rightarrow 20$
3 standard reflections frequency: 240 min intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.042$
$S = 1.16$
336 reflections
22 parameters
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.65$ e Å^{-3}
$\Delta\rho_{\min} = -1.32$ e Å^{-3}
Absolute structure: Flack (1983), 45 Friedel pairs
Flack parameter = −0.08 (11)

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Table 1
Selected distances (Å).

$Ba1—O1^{i}$	2.7999 (16)	$Ba2—Ba2^{vii}$	3.8225 (18)
$Ba1—O3$	3.00 (4)	$Ba2—Ba3$	4.2849 (11)
$Ba1—Pd2^{ii}$	3.255 (2)	$Ba3—Pd2^{viii}$	3.2825 (17)
$Ba1—Ba1^{iii}$	3.960 (2)	$Ba3—Ba4$	4.1393 (18)
$Ba1—Ba2^{iv}$	4.3277 (6)	$Ba3—Ba1^{ix}$	4.3567 (11)
$Ba2—O2^{i}$	2.7029 (13)	$Ba3—Ba3^{x}$	4.468 (3)
$Ba2—O3^{v}$	2.82 (3)	$Ba4—Pd1$	2.888 (3)
$Ba2—Pd1^{vi}$	3.280 (2)		

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

The O atoms in the centre of the barium octahedra were located from difference-density maps. Without the O atoms, residual densities of 12.2, 7.4 and 2.9 e Å^{-3} were located in the centre of the Ba octahedra. Adding the O atoms further decreased the conventional R1 from 0.040 to 0.029. All O atoms were refined with a common isotropic displacement parameter and the occupancy of O3 was left free to refine. Adding hydrogen as central atoms to describe the residual intensities invariably led to negative displacement parameters and the only reasonable model that fitted the diffraction data was the one described with the O atoms in the centre of the octahedra. The corresponding refinement of the occupancy parameters of O1 and O2 did not yield any significant deviation from full occupancy, thus they were fixed at full occupancy. The use of a common isotropic displacement parameter was found to be the model that gave the most stable refinement. No chemical analysis of the O content was performed; thus the only indication of the presence of O atoms is the better fit to the structural data.

Data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1988); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996).

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