SHORT-FORMAT PAPERS

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Redetermination of the Structure of PNb_9O_{25}

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Abstract. Nonaniobium phosphorus pentacosaoxide, PNb_9O_{25}, $M_r = 1267{\cdot}11$, tetragonal, $I4/m$, $a = 15{\cdot}639\ (2)$, $c = 3{\cdot}8317\ (4)$ Å, $V = 937{\cdot}1\ (3)$ Å^3, $Z = 2$, $D_x = 4{\cdot}49$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 5·27 mm^{-1}, $F(000) = 584$, $T = 294$ K, 316 reflections with $I > 3\sigma(I)$, $R = 0{\cdot}033$, $wR = 0{\cdot}031$. The framework is composed of ReO_3-type $3 \times 3 \times \infty$ columns. Each column shares edges with the four neighboring columns and corners with the PO_4 tetrahedra.

Experimental. During the study of the K–Nb–P–O system single crystals of PNb_9O_{25} were isolated. The crystal structure of this compound had already been determined by Roth, Wadsley & Anderson (1965) using integrated Weissenberg photographs. However, the R factor remained rather high (0·093), some atoms had negative thermal factors and some problems remain with the choice of the space group. So we performed a new data collection on an automatic diffractometer in order to obtain better accuracy on the atomic positions.

Crystal: 0·252 × 0·012 × 0·012 mm, mounted along the needle axis b. Weissenberg films: $4/m$ symmetry with systematic absences $h + k + l = 2n + 1$. Enraf–Nonius diffractometer. Unit cell: least-squares on 25 reflections $\pm 2\theta$, $18 \le \theta \le 22°$. Intensity measurements up to $\theta = 45°$ with an ω–$5/3\theta$ scan of width $(0{\cdot}8 + 0{\cdot}35\tan\theta)°$ and a counter slit aperture of $(1 + \tan\theta)$ mm, values determined by a study of some reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I < 0{\cdot}018$ or to approach it in a time limited to 60 s. Three standards for counting (14,2,0, 2,13,1, 004) every 2000 s and orientation (14,2,0, 903, 004) every 600 reflections, no appreciable trends. 316 reflections with $I > 3\sigma(I)$ used to solve and refine the structure. No correction made for extinction or absorption. $2\theta_{max} = 90°$; $0 \le h \le 27$, $0 \le k \le 29$, $0 \le l \le 6$. The usual f's from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations performed with a MicroVAX II with the *SDP* system (B. A. Frenz & Associates, Inc., 1982). The structure was first refined in space group $I4/m$ with anisotropic thermal factors for the Nb atoms and isotropic factors for the other atoms in regard to the small number of reflections. This led to $R = 0{\cdot}034$ and $wR = 0{\cdot}032$ [$w = 1/\sigma^2(F)$]. The B_{eq} factor of Nb(2) and Nb(3) was about 0·4 Å^2 and that of Nb(1) was about 1·2 Å^2 with a β_{33} component more than three times the β_{33} of the other Nb atoms. This indicated a splitting of Nb(1) in two positions along the fourfold axis near the symmetry center. The refinement of the structure with an isotropic thermal factor for the split Nb(1) atom led to $R = 0{\cdot}033$, $wR = 0{\cdot}031$, $\Delta\rho = 0{\cdot}8$ e Å^{-3}, $\Delta/\sigma \simeq 0{\cdot}05$, $S = 1{\cdot}6$ and B_{eq} values of about 0·4 Å^2 for all Nb atoms (Table 1).†

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53590 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters and their e.s.d.'s*

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
Nb(1)	0·000	0·000	0·043 (1)	0·40 (6)‡
Nb(2)	0·1086 (1)	0·2178 (1)	0·000	0·44 (2)
Nb(3)	0·3291 (1)	0·1158 (1)	0·000	0·40 (2)
P	0·500	0·000	0·250	0·7 (2)‡
O(1)	0·0461 (9)	0·115 (1)	0·000	1·0 (2)‡
O(2)	0·2204 (9)	0·1733 (9)	0·000	1·3 (3)‡
O(3)	0·1557 (8)	0·3553 (8)	0·000	0·6 (2)‡
O(4)	0·2852 (8)	0·0112 (8)	0·000	0·5 (2)‡
O(5)	0·4491 (8)	0·0685 (8)	0·000	0·9 (2)‡
O(6)	0·3872 (8)	0·2469 (8)	0·000	0·6 (2)‡
O(7)	0·000	0·000	0·500	1·4 (5)‡

‡ Refined isotropically.

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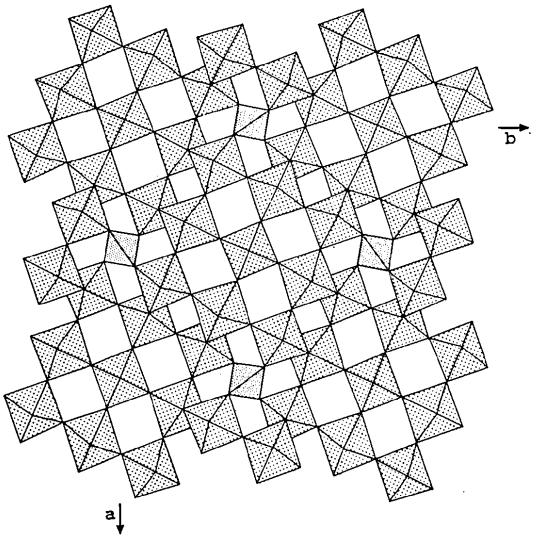

Fig. 1. Projection onto the *ab* plane of the structure of PNb_9O_{25}.

Thus, as well as the two P atoms statistically distributed over four positions as observed by Roth *et al.* (1965) there are also two Nb atoms split over four positions. In order to avoid the half-occupied positions, refinements were performed in the two possible noncentrosymmetric space groups $I\bar{4}$ and $I4$. In the first one the P atoms were ordered but not the Nb(1) atoms and in the second one the Nb(1) atoms were ordered but not the P atoms. In both cases the R and wR factors were higher and so it is proposed that in the 'Nb_8O_{25}' framework the P and the Nb(1) atoms occupy half of their sites, respectively, in such a way that the polarization of the whole crystal is zero giving a centrosymmetric mean unit cell.

Table 2. *Main atomic bond distances* (Å)

Nb(1)—O(1)	×4	1·95 (2)	Nb(3)—O(2)		1·92 (1)
Nb(1)—O(7)		1·753 (6)	Nb(3)—O(3)	×2	1·983 (3)
Nb(1)—O(7^{i})		2·079 (6)	Nb(3)—O(4)		1·78 (1)
Nb(2)—O(1)		1·88 (2)	Nb(3)—O(5)		2·02 (1)
Nb(2)—O(2)		1·88 (1)	Nb(3)—O(6)		2·24 (1)
Nb(2)—O(3)		2·27 (1)	P—O(5)	×4	1·64 (1)
Nb(2)—O(4)		2·15 (1)			
Nb(2)—O(6)	×2	1·995 (4)			

Symmetry code: (i) = $x-1, y, z$.

Related literature. The general features of the structure (Fig. 1) are very similar to those determined by Roth *et al* (1965). Some small differences appear in the interatomic distances (Table 2), principally arising from the splitting of Nb(1). The value of the thermal motion factor for phosphorus here indicates that there is no replacement of some of the P atoms by Nb atoms in the tetrahedral site in contrast to $K_7Nb_{14+x}P_{9-x}O_{60}$ (Leclaire, Benabbas, Borel, Grandin & Raveau, 1989).

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Structure of Tl_2SnTe_5

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Abstract. Dithallium tin pentatelluride, $M_r = 1165{\cdot}4$, tetragonal, $I4/mcm$, $a = 8{\cdot}306\ (2)$, $c = 15{\cdot}161\ (5)$ Å, $V = 1045{\cdot}9\ (8)$ Å^3, $Z = 4$, $D_x = 7{\cdot}40$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 47{\cdot}09$ mm^{-1}, $F(000) = 1888$, $T = 294$ K, final $R = 0{\cdot}041$ for 236 independent observed reflections. The

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