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**Rb<sub>3</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub> from X-ray powder data**

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**Key indicators**

Powder X-ray study

*T* = 295 K

Mean  $\sigma(\text{P}-\text{O}) = 0.012 \text{ \AA}$

*R* factor = 0.038

*wR* factor = 0.050

Data-to-parameter ratio = 5.1

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

The crystal structure of trirubidium phosphate dodecatungstate, Rb<sub>3</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub>, has been refined from X-ray powder diffraction data using the Rietveld method. The compound was obtained under hydrothermal conditions and is isotopic with K<sub>2.4</sub>(H<sub>3</sub>O)<sub>0.6</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub>. The regular PO<sub>4</sub> tetrahedron ( $\bar{4}3m$  symmetry) is surrounded by 12 WO<sub>6</sub> octahedra, building the heteropolymetallate anion. By close packing of these heteropolyanionic units, orthogonally intersecting channels are formed where the Rb atoms are located. The alkali metal ion is surrounded by 12 O atoms to give a polyhedron with  $\bar{4}2.m$  symmetry.

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**Comment**

In connection with our systematic studies of heteropoly compounds of tungsten (Kang *et al.*, 2004), a new phosphate tungstate, Rb<sub>3</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub>, (I), has been synthesized under hydrothermal conditions at low pH in the form of a polycrystalline material.

The crystal structure of (I) is isotopic with that of K<sub>2.4</sub>(H<sub>3</sub>O)<sub>0.6</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub> (Kang *et al.*, 2004) and with the solid solutions of general formula K<sub>3</sub>P(Mo<sub>1-x</sub>W<sub>x</sub>)<sub>12</sub>O<sub>40</sub> (*x* = 0–1; Goubin *et al.*, 2004). The polyoxometallate anions in all these compounds are of the Keggin type (Boeyens *et al.*, 1976). The interatomic distances and angles in the isotopic Keggin structures are very similar. Compound (I) has a larger unit-cell parameter *a* than that of K<sub>2.4</sub>(H<sub>3</sub>O)<sub>0.6</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub> [*a* = 11.5621 (8) Å and *V* = 1545.6 (3) Å<sup>3</sup>], because the Rb<sup>+</sup> cation is larger than K<sup>+</sup>/H<sub>3</sub>O<sup>+</sup> (Shannon, 1976). Compared with (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>Mo<sub>12</sub>O<sub>36</sub> (Boeyens *et al.*, 1976), the unit-cell parameter is nearly the same (*a* = 11.666 Å and *V* = 1587.7 Å<sup>3</sup>), although Rb<sup>+</sup> is larger than the ammonium cation. This is caused by the different metal atoms of the polymetallate anions in both compounds, and the resulting Mo–O and W–O bonds are slightly different.

For (I), the observed and calculated intensities, and their difference plot after the final Rietveld refinement, are shown in Fig. 1, and the crystal structure of the compound is illustrated in Fig. 2. The regular phosphate group is situated at a site of  $\bar{4}3m$  symmetry and is at the centre of 12 surrounding WO<sub>6</sub> octahedra, to establish the polyanion with composition [PO<sub>4</sub>WO<sub>12</sub>O<sub>36</sub>]<sup>3-</sup>. By close packing of these polyanionic units, orthogonally intersecting channels are formed where the Rb atoms reside. They are surrounded by 12 O atoms to give a polyhedron with  $\bar{4}2.m$  symmetry.

**Experimental**

All starting materials were of analytical grade and were used without further purification. Compound (I) was synthesized hydrothermally

from a mixture of Na<sub>2</sub>WO<sub>4</sub> (0.828 g), RbNO<sub>3</sub> (1.851 g), H<sub>3</sub>BO<sub>3</sub> (0.925 g) and H<sub>3</sub>PO<sub>4</sub> (0.5 ml, 85 wt %) in the molar ratio W:Rb:B = 1:5:6:2.7. The mixture was dissolved in distilled water (2.5 ml); the resulting pH of the solution was about 1.5. The reaction mixture was heated at 423 K for 3 d under autogenous pressure in a 20 ml Teflon-lined autoclave filled to 20% capacity. The chemical composition of (I) was confirmed by a semi-quantitative energy-dispersive X-ray fluorescence analysis (Oxford Instruments). Calculated (at %): O 71.43, P 1.79, Rb 5.35, W 21.43; observed: O 72.5, P 2.0, Rb 5.3, W 20.2.

Crystal data

Rb<sub>3</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub>  
*M<sub>r</sub>* = 3133.54  
 Cubic, *Pn* $\bar{3}$ *m*  
*a* = 11.66078 (13) Å  
*V* = 1585.56 (5) Å<sup>3</sup>  
*Z* = 2  
*D<sub>x</sub>* = 6.563 Mg m<sup>-3</sup>  
 Cu *K*α<sub>1</sub> Cu *K*α<sub>2</sub> radiation

*T* = 295 (2) K  
 Specimen shape: flat sheet  
 10 × 10 × 0.1 mm  
 Specimen prepared at 101.3 kPa  
 Specimen prepared at 294 K  
 Particle morphology: spherical,  
 white

Data collection

PANalytical X'pert PRO  
 diffractometer  
 Specimen mounting: packed powder  
 sample container

Specimen mounted in reflection  
 mode  
 Scan method: continuous  
 2θ<sub>min</sub> = 5.0, 2θ<sub>max</sub> = 90.0°  
 Increment in 2θ = 0.017°

Refinement

Refinement on *I*<sub>net</sub>  
*R<sub>p</sub>* = 0.038  
*R<sub>wp</sub>* = 0.050  
*R<sub>exp</sub>* = 0.049  
*R<sub>B</sub>* = ?  
*S* = 1.01  
 Wavelength of incident radiation:  
 1.5405 and 1.5443 Å  
 Excluded region(s): none  
 Profile function: CW Profile  
 function number 3 with 19 terms.  
 Pseudovoigt profile coefficients

as parameterized in Thompson *et al.* (1987). Asymmetry correction of Finger *et al.* (1994). Peak tails are ignored where the intensity is below 0.0010 times the peak. Anisotropic broadening axis 0.0 0.0 1.0  
 285 reflections  
 56 parameters  
 (Δσ)<sub>max</sub> = 0.03  
 Preferred orientation correction:  
 none

Table 1

Selected geometric parameters (Å, °).

W—O1	1.913 (7)	P—O4	1.483 (20)
W—O2 <sup>i</sup>	1.659 (16)	Rb—O1 <sup>ii</sup>	3.267 (25)
W—O3	1.907 (11)	Rb—O2 <sup>iii</sup>	3.050 (15)
W—O4	2.469 (12)	Rb—O3 <sup>iii</sup>	3.200 (22)
O1—W—O1	86.2 (14)	O1 <sup>ii</sup> —Rb—O3 <sup>iii</sup>	111.2 (5)
O1—W—O2 <sup>i</sup>	103.1 (9)	O1 <sup>ii</sup> —Rb—O3	170.6 (8)
O1—W—O3	86.2 (7)	O1 <sup>ii</sup> —Rb—O3	47.62 (33)
O2 <sup>i</sup> —W—O3	101.8 (9)	O2 <sup>iii</sup> —Rb—O2	174.0 (10)
O3—W—O3	90.8 (13)	O2 <sup>iii</sup> —Rb—O2	90.15 (5)
O4—P—O4 <sup>iv</sup>	109.4712 (4)	O2 <sup>iii</sup> —Rb—O3 <sup>iii</sup>	53.9 (7)
O1 <sup>ii</sup> —Rb—O1 <sup>v</sup>	138.9 (6)	O2 <sup>iii</sup> —Rb—O3	132.1 (8)
O1 <sup>ii</sup> —Rb—O1	59.5 (9)	O2 <sup>iii</sup> —Rb—O3	87.7 (4)
O1 <sup>ii</sup> —Rb—O2 <sup>iii</sup>	57.3 (6)	O3 <sup>iii</sup> —Rb—O3	78.2 (10)
O1 <sup>ii</sup> —Rb—O2	92.6 (5)	O3 <sup>iii</sup> —Rb—O3	127.1 (6)

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

The crystal structure was refined using the atomic coordinates of the isotopic compound K<sub>2.4</sub>(H<sub>3</sub>O)<sub>0.6</sub>PO<sub>4</sub>W<sub>12</sub>O<sub>36</sub> (Kang *et al.*, 2004) as the starting parameters. A total of 56 independent parameters were refined, including the zero point, scale factor, 36 background poly-

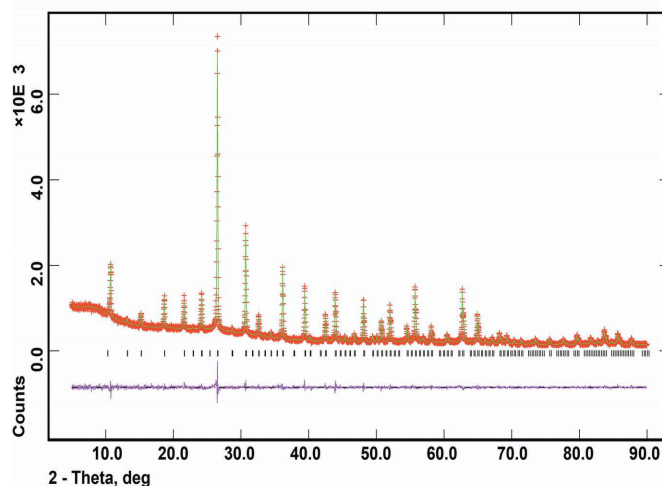


Figure 1

Comparison of observed (red crosses) and calculated (solid green line) intensity profiles for (I). The difference plot appears below (purple solid line) and allowed Bragg reflections (tick marks) are also shown.

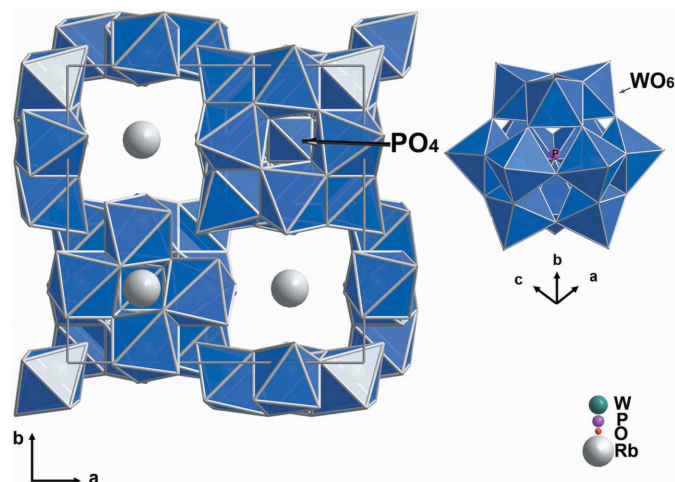


Figure 2

The 12 interconnected WO<sub>6</sub> octahedra around the PO<sub>4</sub> group in (I). The close-packing of the anionic units forms an orthogonally intersecting channel.

nomial coefficients, lattice parameter, half-width and asymmetry parameters for the peak shape, and atomic coordinates. No anisotropic displacement parameters were refined, and corrections for texture effects (preferred orientation) and absorption were not applied.

Data collection: *X'pert Data Collector* (PANalytical, 2003); cell refinement: *GSAS* (Larson & Von Dreele, 2000) and *EXPGUI* (Toby, 2001); data reduction: *X'pert Data Collector*; program(s) used to solve structure: coordinates taken from an isotopic compound; program(s) used to refine structure: *GSAS* and *EXPGUI*; molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

References

Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.

- Boeyens, J. C. A., McDougal, G. J. & Van Smit, J. (1976). *J. Solid State Chem.* **18**, 191–199.
- Brandenburg, K. (2004). *DIAMOND*. Version 3.0. Crystal Impact GbR, Bonn, Germany.
- Finger, L. W., Cox, D. E. & Jephcoat, A. P. (1994). *J. Appl. Cryst.* **27**, 892–900.
- Goubin, F., Guénée, L., Deniard, P., Koo, H. J., Whangbo, M.-H., Montardi, Y. & Jobic, S. (2004). *J. Solid State Chem.* **177**, 4528–4534.
- Kang, Y., Li, M., Zhao, J. & Mao, S. (2004). *Acta Cryst.* **E60**, i97–i99.
- Larson, A. C. & Von Dreele, R. B. (2000). *GSAS*. Report LAUR 86-748. Los Alamos National Laboratory, New Mexico, USA.
- PANalytical (2003). *X'pert Data Collector*. Version 1.0. PANalytical BV, Almelo, The Netherlands.
- Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
- Thompson, P., Cox, D. E. & Hastings, J. B. (1987). *J. Appl. Cryst.* **20**, 79–83.
- Toby, B. H. (2001). *J. Appl. Cryst.* **34**, 210–213.