

Youjun Kang,^a Manrong Li,^b
Jingtai Zhao^b and Shaoyu Mao^{a*}^aDepartment of Chemistry, Xiamen University, Xiamen 361005, People's Republic of China, and ^bChinese Academy of Sciences, Shanghai Institute of Ceramics, State Key Laboratory of High Performance Ceramics and Superfine Microstructure, 1295 Dingxi Road, Shanghai 200050, People's Republic of ChinaCorrespondence e-mail:
symao@jingxian.xmu.edu.cn

Key indicators

Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{P-O}) = 0.010$ Å
H-atom completeness 0%
Disorder in solvent or counterion
 R factor = 0.038
 wR factor = 0.091
Data-to-parameter ratio = 12.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.The Keggin-type potassium/hydronium
12-tungstophosphate, $\text{K}_{2.4}(\text{H}_3\text{O})_{0.6}\text{PO}_4\text{W}_{12}\text{O}_{36}$

The crystal structure of a new potassium/hydronium tungstophosphate, potassium hydronium phosphate tungstate, $\text{K}_{2.4}(\text{H}_3\text{O})_{0.6}\text{PO}_4\text{W}_{12}\text{O}_{36}$, obtained by hydrothermal synthesis at low pH, has been determined by single-crystal X-ray diffraction. Regular PO_4 tetrahedra are located on sites of $\bar{4}3m$ symmetry. 12 W atoms are in a shell around the phosphate anion and are surrounded by O atoms in a distorted octahedral coordination. The close packing of the heteropoly-anionic units forms orthogonally intersecting channels where the statistically distributed potassium/hydronium ions are situated.

Received 7 June 2004
Accepted 24 June 2004
Online 17 July 2004

Comment

Heteropoly compounds of tungsten and molybdenum and their salts, such as $M_3\text{PO}_4\text{W}_{12}\text{O}_{36}$ ($M = \text{H}^+, \text{NH}_4^+, \text{K}^+$; Ito *et al.*, 1997; Uchida *et al.*, 2000; Benedetto *et al.*, 1996; Song *et al.*, 2002), $\text{K}_3\text{PO}_4\text{Mo}_{12}\text{O}_{36}$ and $(\text{NH}_4)_x\text{K}_y\text{PO}_4\text{Mo}_{12}\text{O}_{36}$ (Boeyens *et al.*, 1976) have drawn much attention as catalysts owing to their versatility and environmental compatibility. Many scientists have made great efforts to investigate their applications in industry and pharmaceutical chemistry. The structures of some compounds with such structural features have been determined. Most of them have Keggin-type structures (Boeyens *et al.*, 1976), others show Dawson-, Anderson-,

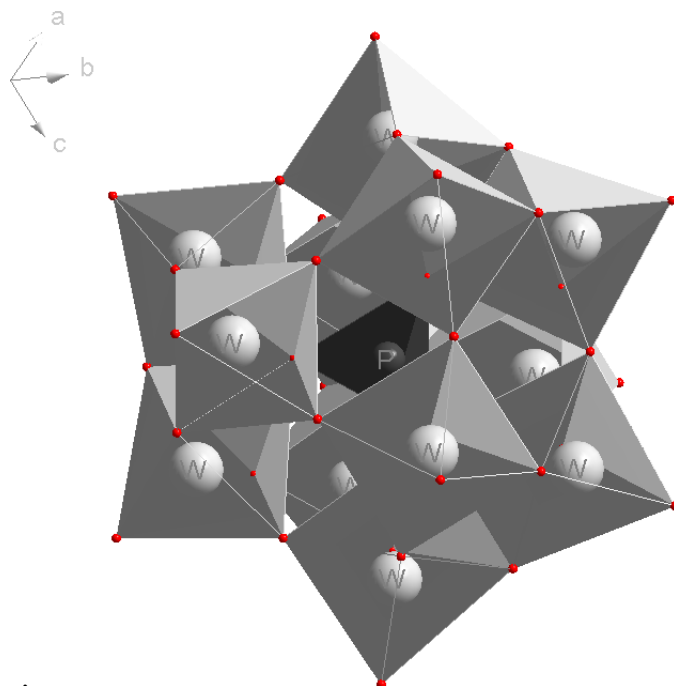


Figure 1
The Keggin-type heteropoly anion, with 12 interconnected WO_6 octahedra around the PO_4 group.

Waugh- or Silverton-type structures. In our systematic studies on phosphates and borophosphates, a new compound, *viz.* $K_{2.4}(H_3O)_{0.6}PO_4W_{12}O_{36}$, with a Keggin-type structure was synthesized and its structure determined by X-ray single-crystal diffraction.

The structure of the title compound contains seven crystallographically independent atomic sites. The regular phosphate group is centered on a site of $\bar{4}3m$ symmetry, and is surrounded by 12 interconnected WO_6 units. All of the W atoms are in a shell around the phosphate ion and are octahedrally surrounded by O atoms (Fig. 1). The close packing of the heteropolyanionic units forms orthogonally intersecting channels. The K^+ ions are partly replaced by hydronium ions and are located within the channels (Fig. 2). Atoms O1 and O3 act as bridges between tungsten atoms at an average W–O distance of 1.90 Å. Atom O2ⁱ is located 1.695 (11) Å from W (symmetry code as in Table 1), corresponding to a typical double-bond length. The distance between W and O4 is 2.436 (10) Å, which is considerably longer than usual W–O bond lengths. It may thus be considered as a weak coordination. Therefore, the formal $[WO_6]$ octahedron is significantly distorted.

Experimental

The title compound was obtained by a mild hydrothermal method. Starting materials were of analytical grade and used without further purification. A mixture of 0.165 g $Na_2WO_4 \cdot 2H_2O$, 1.850 g H_3BO_3 and 2.727 g KH_2PO_4 was prepared and dissolved in distilled water in the molar ratio of 1:6:4. The pH value of the solution was about 0.4. A 20 ml Teflon-lined autoclave was 70% filled with the mixture. The autoclave was then placed in an oven and heated at 403 K for 4 d before cooling to room temperature. Colorless prismatic crystals of the title compound were obtained.

Crystal data

$K_{2.4}(H_3O)_{0.6}PO_4W_{12}O_{36}$
 $M_r = 2983.48$
 Cubic, $Pn\bar{3}m$
 $a = 11.5621$ (8) Å
 $V = 1545.65$ (19) Å³
 $Z = 2$
 $D_x = 6.410$ Mg m⁻³
 Mo $K\alpha$ radiation

Cell parameters from 390 reflections
 $\theta = 3.6$ – 27.9°
 $\mu = 44.97$ mm⁻¹
 $T = 293$ (2) K
 Prism, colorless
 $0.04 \times 0.04 \times 0.03$ mm

Data collection

Bruker SMART APEX 2000 diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{min} = 0.173$, $T_{max} = 0.217$
 12441 measured reflections

390 independent reflections
 360 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.125$
 $\theta_{max} = 28.3^\circ$
 $h = -14 \rightarrow 14$
 $k = -15 \rightarrow 15$
 $l = -14 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.092$
 $S = 1.15$
 390 reflections
 31 parameters
 H atoms not located

$w = 1/[\sigma^2(F_o^2) + (0.0408P)^2 + 49.5098P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 2.22$ e Å⁻³
 $\Delta\rho_{min} = -2.74$ e Å⁻³

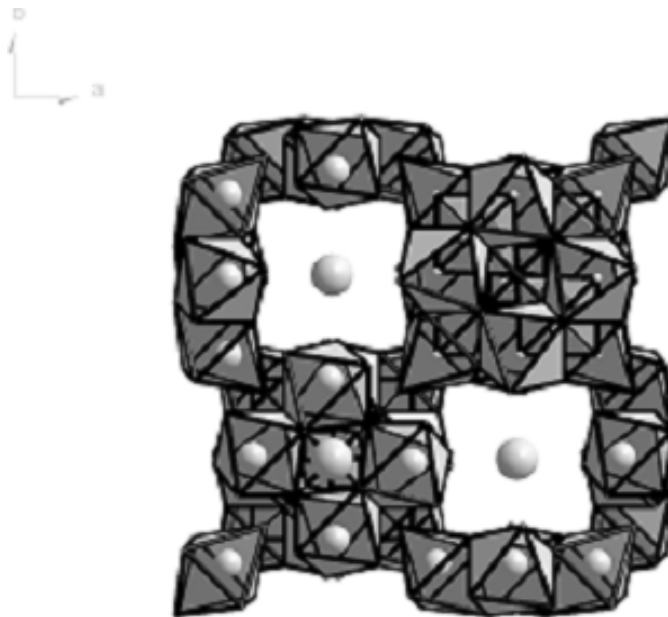


Figure 2

The potassium/hydronium ions situated in the channels, viewed along the [001] direction.

Table 1

Selected geometric parameters (Å, °).

W1–O2 ⁱ	1.695 (11)	W1–O3 ^v	1.907 (4)
W1–O1 ⁱⁱ	1.897 (3)	W1–O4	2.426 (10)
W1–O1 ⁱⁱⁱ	1.897 (3)	P1–O4	1.537 (18)
W1–O3 ^{iv}	1.907 (4)		
O2 ⁱ –W1–O1 ⁱⁱ	103.2 (4)	O3 ^{iv} –W1–O3 ^v	87.2 (6)
O1 ⁱⁱ –W1–O1 ⁱⁱⁱ	84.8 (7)	O2 ⁱ –W1–O4	171.5 (5)
O2 ⁱ –W1–O3 ^{iv}	102.2 (4)	O1 ⁱⁱ –W1–O4	83.0 (4)
O1 ⁱⁱ –W1–O3 ^{iv}	154.6 (4)	O3 ^{iv} –W1–O4	71.9 (3)
O1 ⁱⁱⁱ –W1–O3 ^{iv}	88.5 (5)		

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

Since the displacement parameters of the K^+ ion were considerably higher than those of the other atoms, the site-occupancy factor of potassium might be lower than unity. By considering the possible occupation of the same position by hydronium ions, the occupancy of both K^+ and H_3O^+ ions has been refined to an approximate K:O ratio of 0.82 (7):0.18 (7). This indicates that the title compound acts also as an ion exchanger at low pH values, as is the case in the ammonium/potassium 12-molybdophosphate system (Boeyens *et al.*, 1976). Qualitative IR spectroscopic measurements of dried samples support this conclusion. The ratio K:W:P was also roughly confirmed by chemical analysis (ICP–AES) to be 2.8:12:1.2. It was not possible to locate the H atoms and they were therefore omitted from the refinement. The highest peak and the deepest hole are located close to the W position; their distances from it are 0.80 and 0.07 Å, respectively.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: DIAMOND (Brandenburg, 1996–2001); software used to prepare material for publication: SHELXL97.

This study was supported by the Fund for Distinguished Young Scholars from the NNSF of China and the Fund for State '863' project.

References

- Benedetto, S. D., Chidichimo, G., Golemme, A. & Imbardelli, D. (1996). *J. Phys. Chem.* **100**, 8079–8084.
- Boeyens, J. C. A., McDougal, G. J. & Smit, J. Van R. (1976). *J. Solid State Chem.* **18**, 191–199.
- Brandenburg, K. (1996–2001). *DIAMOND*. Version 2.1a. Crystal Impact GbR, Bonn, Germany.
- Bruker (2001). *SAINT* and *SMART*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Ito, T., Inumaru, K. & Misono, M. (1997). *J. Phys. Chem. B*, **101**, 9958–9963.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Song, I. K., Shnitser, R. B., Cowan, J. J., Hill, C. L. & Barteau, M. A. (2002). *Inorg. Chem.* **41**, 1292–1298.
- Uchida, S., Inumaru, K. & Misono, M. (2000). *J. Phys. Chem. B*, **104**, 8108–8115.