

K₂NaH[GeW₁₂O₄₀]·7H₂O, with a Keggin-type heteropolyoxoanionQiu-Xia Han,^a Jing-Ping Wang^{b*}
and Li-Hua Song^a^aBasic Experiment Teaching Centre, Henan University, Kaifeng 475001, People's Republic of China, and ^bCollege of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, People's Republic of China

Correspondence e-mail: hdhqx@henu.edu.cn

Key indicatorsSingle-crystal X-ray study
T = 293 K
Mean $\sigma(\text{Na}-\text{O}) = 0.04 \text{ \AA}$
H-atom completeness 54%
Disorder in solvent or counterion
R factor = 0.036
wR factor = 0.076
Data-to-parameter ratio = 15.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

During experiments aimed at the crystal growth of tetrapotassium dodecatungstogermanate, K₄[GeW₁₂O₄₀] \cdot *x*H₂O, the title compound, dipotassium sodium hydrogen dodecatungstogermanate heptahydrate, K₂NaH[GeW₁₂O₄₀] \cdot 7H₂O, (I), was obtained serendipitously. The [GeW₁₂O₄₀]⁴⁻ units in (I) are interconnected by K⁺ cations to establish a three-dimensional network, with large channels running along the *c* axis. Disordered Na⁺ cations and water molecules reside on the outside of these channels, leaving empty pores with a diameter of *ca* 9.2 Å. The heteropolyoxoanion is of the Keggin-type, with a central Ge atom situated on a position with 222 symmetry.

Received 16 July 2006
Accepted 26 August 2006**Comment**

In the past, several structures of tungsten- or molybdenum-containing heteropolyoxoanions have been solved by X-ray diffraction, particularly those belonging to the series with general formula [X*M*₁₂O₄₀]^{(8-*n*)-}, where *X* is the heteroatom, *n* is its oxidation number, and *M* is Mo or W. The synthesis of several of these phases is described in the literature (Rocchiccioli-Deltcheff *et al.*, 1983), and recently the structure of a complex based on the dodecatungstogermanate anion, *viz.* H₄[GeW₁₂O₄₀] \cdot 5C₆H₇N \cdot CH₃CN, has been described (Niu *et al.*, 1996). During experiments aimed at the crystal growth of

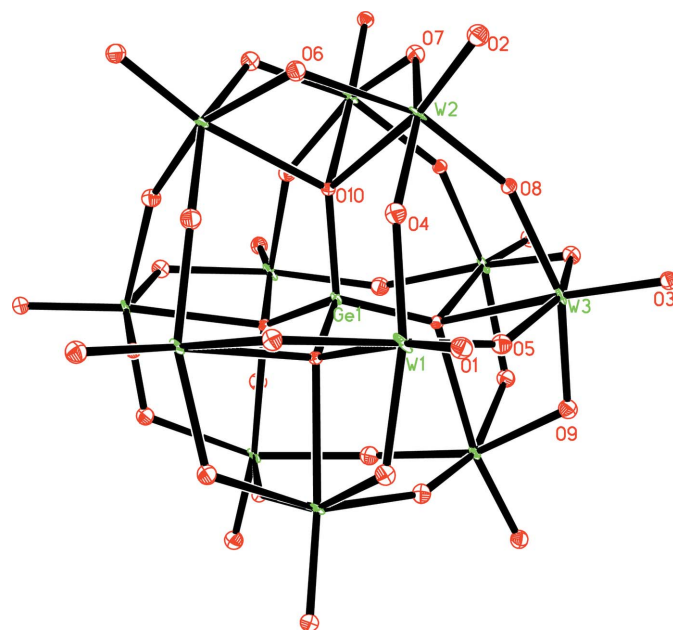


Figure 1
The Keggin-type heteropolyanion in (I), displayed with anisotropic displacement ellipsoids at the 30% probability level.

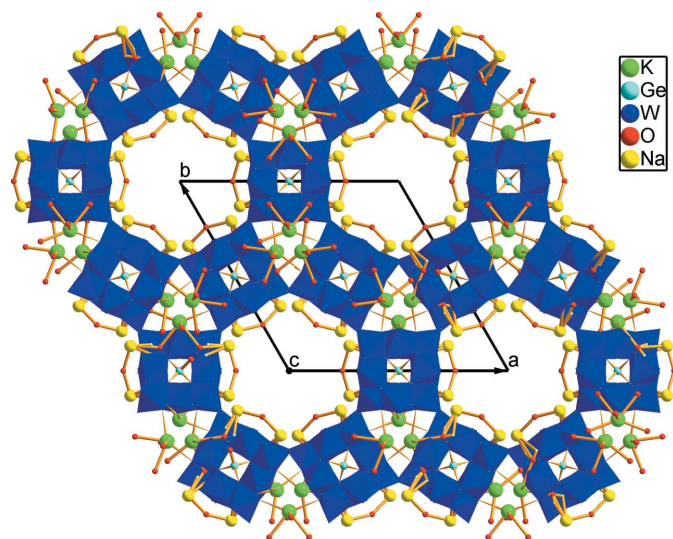


Figure 2
The empty channels in (I), viewed along the *c* axis.

$K_4[GeW_{12}O_{40}] \cdot xH_2O$ (Rocchiccioli-Deltcheff *et al.*, 1983), the title compound, $K_2NaH[GeW_{12}O_{40}] \cdot 7H_2O$, (I), was obtained serendipitously. As shown by the chemical analysis and structure refinement, in compound (I) not only K but also Na are incorporated as countercations, which can be explained by the experimental conditions, using Na_2WO_4 as an educt.

The $[GeW_{12}O_{40}]^{4-}$ unit in (I) shows the well known Keggin-type structure (Keggin, 1934) and it contains a central GeO_4 tetrahedron which exhibits 222 symmetry. The O atoms of the tetrahedron are part of the cage of the surrounding 12 WO_6 octahedra that are linked to each other by sharing corners and edges (Fig. 1). Within the Keggin anion, the $W=O$ distances of the formal double-bonded O atoms range from 1.697 (10) to 1.711 (11) Å (average 1.705 Å), the $W-O$ distances to the O atoms of the central GeO_4 tetrahedron lie between 2.268 (10) and 2.306 (10) Å (average 2.287 Å), and the $W-O$ distances to the bridging O atoms between the WO_6 octahedra vary from 1.893 (9) to 1.940 (10) Å (average 1.918 Å) (Table 1).

The heteropolyoxoanion is surrounded by K^+ cations which are coordinated by eight O atoms, resulting in distorted $[KO_8]$ polyhedra with 2 symmetry (Table 1). The packing of these building units leads to a three-dimensional network, with large hexagonal channels running along the *c* axis. The disordered Na^+ cation and the water molecules O2W and O3W reside on the outside of these channels, leaving empty pores with a diameter of *ca* 9.2 Å (Figs. 2 and 3).

Experimental

All reagents and solvents were used as obtained without further purification. $H_4GeW_{12}O_{40} \cdot nH_2O$ was prepared according to the literature method from Na_2WO_4 , Ge metal and NaOH (Rocchiccioli-Deltcheff *et al.*, 1983). On addition of KCl (0.13 g, 2 mmol) to a solution of $H_4GeW_{12}O_{40} \cdot nH_2O$ (3.160 g, 1 mmol) in water (50 ml), a

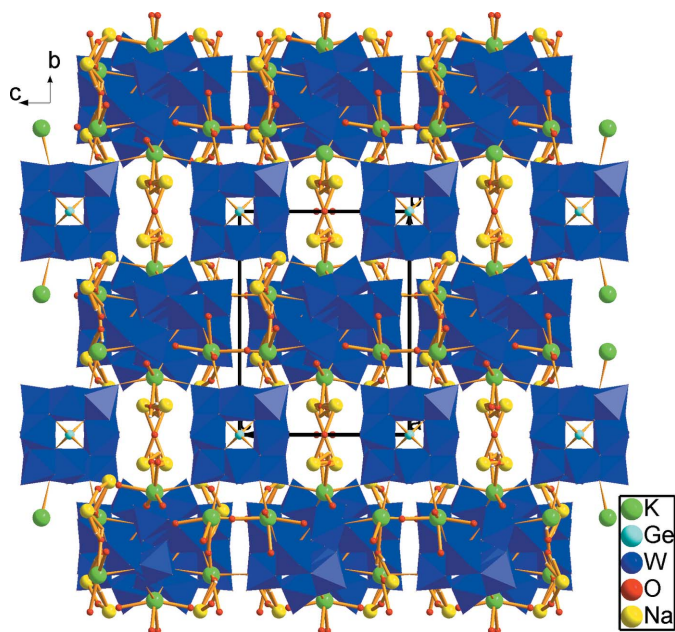


Figure 3
The structure of (I), in a projection along the *a* axis.

colourless polycrystalline powder was obtained. This powder was dissolved in a suitable amount of demineralized water, and the solution was filtered and left to evaporate at room temperature over a period of one week. Colourless block-like crystals of (I) were obtained. The content of K, Na, Ge and W was determined with an Ultima2 spectrometer. Analysis calculated (wt%): K 2.48, Na 0.70, Ge 2.31, W 70.10; found: K 2.4, Na 0.7, Ge 2.2, W 69.8.

Crystal data

$K_2NaH[GeW_{12}O_{40}] \cdot 7H_2O$
 $M_r = 3147.12$
Hexagonal, $P6_322$
 $a = 19.057$ (3) Å
 $c = 12.557$ (3) Å
 $V = 3949.3$ (13) Å³
 $Z = 3$

$D_x = 3.973$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 26.92$ mm⁻¹
 $T = 293$ (2) K
Block, colourless
0.10 × 0.08 × 0.06 mm

Data collection

Bruker *P4* diffractometer
 ω scans
Absorption correction: multi-scan
(*SHELXTL*; Bruker, 2000)
 $T_{min} = 0.174$, $T_{max} = 0.295$
(expected range = 0.117–0.199)
12980 measured reflections

2318 independent reflections
2165 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.091$
 $\theta_{max} = 25.1^\circ$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.076$
 $S = 1.11$
2318 reflections
155 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.73$ e Å⁻³
 $\Delta\rho_{min} = -1.25$ e Å⁻³
Absolute structure: Flack (1983)
Flack parameter: 0.61 (3)

Table 1
Selected geometric parameters (Å, °).

K1—O3 ⁱ	2.708 (9)	W2—O4	1.915 (10)
K1—O7 ⁱⁱ	2.819 (11)	W2—O7	1.929 (10)
K1—O1W	2.822 (15)	W2—O6	1.940 (10)
K1—O3 ⁱⁱⁱ	3.127 (10)	W2—O10	2.306 (10)
Ge1—O10	1.734 (10)	W3—O3	1.706 (10)
W1—O1	1.697 (10)	W3—O9	1.911 (10)
W1—O5	1.893 (11)	W3—O8	1.914 (9)
W1—O4	1.903 (10)	W3—O7 ⁱⁱ	1.917 (10)
W1—O6 ^{iv}	1.921 (10)	W3—O5	1.937 (11)
W1—O9 ^v	1.938 (10)	W3—O10 ⁱⁱ	2.268 (10)
W1—O10 ^{iv}	2.286 (10)	Na1—O3W	2.39 (4)
W2—O2	1.711 (11)	Na1—O6 ^{vi}	2.89 (4)
W2—O8	1.893 (9)		
O10 ^v —Ge1—O10	108.3 (6)	O10—Ge1—O10 ^{iv}	110.5 (6)
O10 ^v —Ge1—O10 ^{iv}	109.6 (7)		

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

The crystal structure was refined from a racemically twinned crystal. Atoms OW2, OW3 and Na are disordered and were refined with constrained site-occupancy factors of 0.5 for OW3 and OW2, and 0.25 for Na. The H atoms of one water molecule (OW1) were located in a difference Fourier map. They were then constrained to ideal geometry, with an O—H distance of 0.85 Å, and refined with a common U_{iso} parameter. The H atoms of the other water molecules

could not be located or positioned geometrically and were excluded from the refinement. The highest peak and deepest hole in the final difference Fourier map are 3.22 and 0.64 Å, respectively, from O6.

Data collection: *XSCANS* (Bruker, 2000); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL* (Bruker, 2000) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

The authors thank the Natural Science Foundation of Henan University for financial support (grant No. XK04YBRW057).

References

- Brandenburg, K. (2006). *DIAMOND*. Release 3.1c. Crystal Impact GbR, Bonn, Germany.
- Bruker (2000). *XSCANS* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Keggin, J. F. (1934). *Proc. R. Soc. London Ser. A*, **144**, 75–100.
- Niu, J. Y., You, X. Z. & Duan, C. Y. (1996). *Inorg. Chem.* **14**, 4211–4216.
- Rocchiccioli-Deltcheff, C., Fournier, M., Franck, R. & Thouvenot, R. (1983). *Inorg. Chem.* **22**, 207–216.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.