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## K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)].6H<sub>2</sub>O

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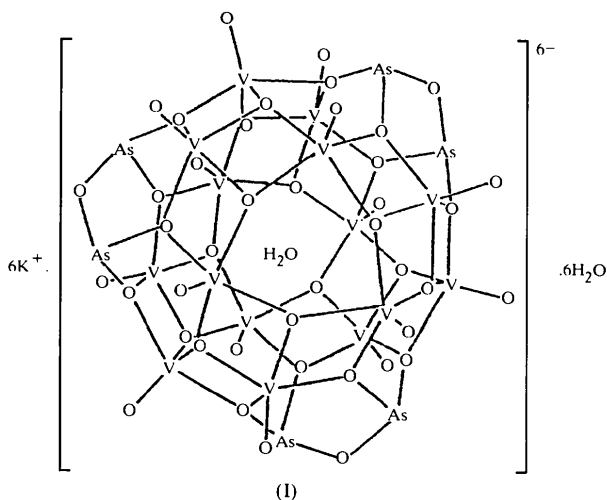
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### Abstract

The crystal structure of hexapotassium dotetracontaoxo-(hexaarsenio)pentadecavanadate(IV) heptahydrate, K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)].6H<sub>2</sub>O, is composed of an [As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>6-</sup> anion, which has *D*<sub>3</sub> symmetry, and six seven-coordinate potassium ions. There is an H<sub>2</sub>O molecule at the centre of the heteropolyanion. This anion consists of VO<sub>5</sub> pyramids linked by As<sub>2</sub>O<sub>5</sub> units through shared O atoms. The V—O distances range from 1.604 (4) to 2.009 (4) Å, As—O from 1.772 (4) to 1.793 (3) Å, and K···O from 2.676 (6) to 3.311 (4) Å.

### Comment

Iso- and heteropolyvanadates usually contain molecular anions with interesting cage structures. These polyanion cage anions form inclusion compounds with neutral molecules and anions, among which are [V<sub>12</sub>O<sub>32</sub>(MeCN)]<sup>4-</sup> (Day *et al.*, 1989), [V<sub>18</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>12-</sup> (Johnson & Schlemper, 1978), [V<sub>18</sub>O<sub>42</sub>H<sub>9</sub>(VO<sub>4</sub>)]<sup>6-</sup>, [V<sub>18</sub>O<sub>42</sub>(SO<sub>4</sub>)]<sup>8-</sup>, [As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>6-</sup>, [As<sub>8</sub>V<sub>14</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>4-</sup>, [As<sub>8</sub>V<sub>14</sub>O<sub>42</sub>(X)]<sup>6-</sup> (X = SO<sub>3</sub><sup>2-</sup> or SO<sub>4</sub><sup>2-</sup>; Müller & Döring, 1991) and [As<sub>8</sub>V<sub>14</sub>O<sub>42</sub>(H<sub>2</sub>O)<sub>1/2</sub>]<sup>4-</sup> (Huan *et al.*, 1991). The crystal structure has been reported for an [As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>6-</sup> anion with H<sub>2</sub>O at the centre in K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)].8H<sub>2</sub>O (Müller & Döring, 1988, 1991). The present study concerns the phase K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)].6H<sub>2</sub>O, (I), which contains a similar anion to that found in K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)].8H<sub>2</sub>O (Müller & Döring, 1988, 1991).



The [As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>6-</sup> anion has *D*<sub>3</sub> symmetry, and consists of 15 distorted VO<sub>5</sub> square pyramids and six AsO<sub>3</sub> triangular pyramids, with a statistically disordered H<sub>2</sub>O molecule at its centre. Two AsO<sub>3</sub> groups are joined to each other *via* an oxygen bridge and form an As<sub>2</sub>O<sub>5</sub> unit. Every VO<sub>5</sub> consists of one terminal O and four bridging O atoms. The VO<sub>5</sub> pyramids are joined through vertices and edges to their neighbouring VO<sub>5</sub> pyramids, but the AsO<sub>3</sub> groups are connected by VO<sub>5</sub> pyramids only through vertices. The 15 VO<sub>5</sub> pyramids linked with one another through vertices and edges are connected by As<sub>2</sub>O<sub>5</sub> units through shared O atoms, and form a ball-like structure.

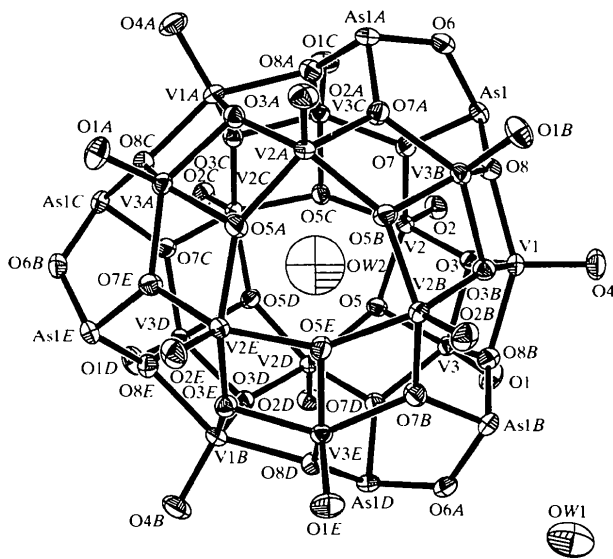


Fig. 1. View of the [As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]<sup>6-</sup> anion, with displacement ellipsoids at the 50% probability level.

In the crystal lattice, the VO<sub>5</sub> pyramids can be divided into three different types. The first V site (V1, V1A, V1B) contains three VO<sub>5</sub> pyramids, which are joined to four VO<sub>5</sub> and two As<sub>2</sub>O<sub>5</sub> units. The second V site includes six VO<sub>5</sub> pyramids, each of which is joined to its neighbouring five VO<sub>5</sub> pyramids and one AsO<sub>3</sub> group. Finally, the third V site contains six VO<sub>5</sub> pyramids, which are joined through three VO<sub>5</sub> pyramids and two AsO<sub>3</sub> groups.

The anions are linked by hydrated potassium ions, which themselves have a distorted sevenfold coordination sphere composed of one bridging and four terminal O atoms from the anions, and two O atoms from the water molecules. Within the anion, a V atom is bound to one terminal O atom at distances of 1.604 (4)–1.615 (6) Å and one O atom shared with two other V atoms, at distances of 1.910 (4)–1.955 (4) Å. The K···O and As—O distances are 2.676 (6)–3.311 (4) and 1.772 (4)–1.793 (3) Å, respectively. The V···V distances are in the range 2.8758 (15)–3.0592 (15) Å. These distances are comparable to those found in similar structures (Müller & Döring, 1988, 1991). The largest difference between K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]·6H<sub>2</sub>O and K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]·8H<sub>2</sub>O is cell type: the former is a hexagonal cell and the latter is rhombohedral. In both structures, the anion has D<sub>3</sub> symmetry.

## Experimental

The synthesis of the title compound was carried out by hydrothermal reaction of H<sub>2</sub>O, V<sub>2</sub>O<sub>5</sub>, As<sub>2</sub>O<sub>3</sub>, H<sub>3</sub>PO<sub>3</sub> (25%), H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub> and KOH (molar ratio 800:6:6:20:6:12) in a 30 ml Teflon-lined stainless steel autoclave for 3 d at 433 K. The dark-green crystals were isolated from the solution once it had been cooled to room temperature.

### Crystal data

K<sub>6</sub>[As<sub>6</sub>V<sub>15</sub>O<sub>42</sub>(H<sub>2</sub>O)]·6H<sub>2</sub>O  
M<sub>r</sub> = 2246.33

Trigonal

R $\bar{3}c$

a = 17.942 (3) Å

c = 28.450 (6) Å

V = 7932 (2) Å<sup>3</sup>

Z = 6

D<sub>x</sub> = 2.822 Mg m<sup>-3</sup>

D<sub>m</sub> not measured

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å

Cell parameters from 30 reflections

$\theta$  = 4.99–12.48°

$\mu$  = 6.825 mm<sup>-1</sup>

T = 293 (2) K

Polyhedron

0.52 × 0.36 × 0.24 mm

Dark green

### Data collection

Siemens P4 diffractometer  
 $\omega/2\theta$  scans

Absorption correction:  
empirical via  $\psi$  scans  
(North *et al.*, 1968)

T<sub>min</sub> = 0.098, T<sub>max</sub> = 0.194

3480 measured reflections

1395 independent reflections

1105 reflections with

$I > 2\sigma(I)$

R<sub>int</sub> = 0.029

$\theta_{\max}$  = 25°

h = -1 → 19

k = -20 → 1

l = -3 → 32

3 standard reflections

every 97 reflections

intensity decay: 1%

## Refinement

Refinement on F<sup>2</sup>

R[F<sup>2</sup> > 2 $\sigma$ (F<sup>2</sup>)] = 0.031

wR(F<sup>2</sup>) = 0.088

S = 1.143

1392 reflections

118 parameters

H atoms not located

w = 1/[ $\sigma^2(F_o^2) + (0.0377P)^2$ ]

where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

( $\Delta/\sigma$ )<sub>max</sub> < 0.001

$\Delta\rho_{\max}$  = 1.069 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.529 e Å<sup>-3</sup>

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.00015 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a'_i a'_j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U <sub>eq</sub>
As1	0.46372 (4)	0.41868 (4)	0.04994 (2)	0.0213 (2)
V1	2/3	0.55562 (8)	1/12	0.0193 (4)
V2	0.60754 (7)	0.41094 (6)	-0.02096 (3)	0.0180 (3)
V3	0.77689 (7)	0.54205 (7)	0.00742 (3)	0.0190 (3)
K	0.96522 (12)	0.77970 (11)	-0.05348 (6)	0.0486 (5)
O1	0.8223 (3)	0.6205 (3)	-0.02903 (15)	0.0217 (12)
O2	0.5805 (3)	0.4387 (3)	-0.06872 (14)	0.0273 (10)
O3	0.6595 (3)	0.5094 (2)	0.02174 (14)	0.0206 (9)
O4	2/3	0.6456 (3)	1/12	0.033 (2)
O5	0.7236 (3)	0.4351 (3)	-0.02693 (13)	0.0218 (10)
O6	0.3796 (3)	1/3	1/12	0.0274 (15)
O7	0.5044 (3)	0.3582 (3)	0.02134 (14)	0.0230 (10)
O8	0.5434 (3)	0.4648 (3)	0.09429 (14)	0.0230 (10)
OW1	1.0336 (4)	0.8092 (4)	0.0328 (2)	0.069 (2)
OW2	0	0	3/4	0.164 (11)

Table 2. Selected bond lengths (Å)

As1—O8	1.772 (4)	V3—O1	1.605 (4)
As1—O7	1.778 (4)	V3—O3	1.926 (4)
As1—O6	1.793 (3)	V3—O5	1.928 (4)
V1—O4	1.615 (6)	V3—O7 <sup>iii</sup>	1.977 (4)
V1—O3	1.915 (4)	V3—O8 <sup>i</sup>	1.989 (4)
V1—O3 <sup>i</sup>	1.915 (4)	K···OW1	2.676 (6)
V1—O8 <sup>i</sup>	2.009 (4)	K···O2 <sup>ii</sup>	2.768 (5)
V1—O8	2.009 (4)	K···O4 <sup>i</sup>	2.805 (5)
V2—O2	1.604 (4)	K···O1	2.809 (5)
V2—O5	1.910 (4)	K···OW1 <sup>ii</sup>	2.820 (7)
V2—O5 <sup>ii</sup>	1.939 (4)	K···O1 <sup>iii</sup>	2.847 (5)
V2—O3	1.955 (4)	K···O5 <sup>iii</sup>	3.311 (4)
V2—O7	2.004 (4)		

Symmetry codes: (i)  $\frac{1}{3} - x, \frac{2}{3} - x + y, \frac{1}{6} - z$ ; (ii)  $1 - y, x - y, z$ ; (iii)  $1 - x + y, 1 - x, z$ ; (iv)  $\frac{2}{3} + y, \frac{1}{3} + x, -\frac{1}{6} - z$ ; (v)  $1 + x - y, x, -z$ ; (vi)  $y, 1 - x + y, -z$ ; (vii)  $\frac{2}{3} + x - y, \frac{1}{3} - y, -\frac{1}{6} - z$ .

The highest peak in the difference map is 0.737 Å from O8, and the largest hole is 0.931 Å from OW1. The structure was refined by full-matrix least-squares techniques, using SHELXL93 (Sheldrick, 1993). All non-H atoms were assigned anisotropic displacement parameters in the refinement.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: SHELXTL-Plus (Sheldrick, 1990b). Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990a). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus. Software used to prepare material for publication: SHELXTL-Plus.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1192). Services for accessing these data are described at the back of the journal.

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## Inversion Symmetry in the Spin-Peierls Compound $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub>

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## Abstract

At room temperature, sodium pentaoxodivanadate, NaV<sub>2</sub>O<sub>5</sub>, was found to have the centrosymmetric space group *Pmmn*. This space group implies the presence

of only one kind of V site, in contrast with previous reports [Carp & Galy (1975). *Acta Cryst.* **B31**, 1481–1483] of the non-centrosymmetric *P2<sub>1</sub>mn* counterpart. This indicates a non-integer valence state of vanadium. Furthermore, this symmetry has consequences for the interpretation of the transition at 34 K, which was ascribed to a spin-Peierls transition of one-dimensional chains of V<sup>4+</sup> ions.

## Comment

In recent years, low-dimensional quantum systems have revealed many new properties in their magnetic and electronic transport behavior. In many respects, the vanadates complement the copper oxide systems, with spinless  $S = 0$ ,  $\frac{1}{2}$  and 1 states, obtained by V<sup>5+</sup> ( $d^0$ ), V<sup>4+</sup> ( $d^1$ ) and V<sup>3+</sup> ( $d^2$ ), or Cu<sup>+</sup> ( $d^{10}$ ), Cu<sup>2+</sup> ( $d^9$ ) and Cu<sup>3+</sup> ( $d^8$ ), respectively. Recently, the first observation (Hase *et al.*, 1993) of a spin-Peierls (SP) transition in an inorganic compound, CuGeO<sub>3</sub>, was complemented by the observation (Isobe & Ueda, 1996) of an SP transition in NaV<sub>2</sub>O<sub>5</sub>. Evidence for this one-dimensional magnetic behavior was found in the temperature dependence of the susceptibility, which can be accurately described at high temperatures by the Bonner–Fisher (Bonner & Fisher, 1964) model for an  $S = \frac{1}{2}$  linear chain. Below  $T_{SP} = 34$  K, an isotropic exponential decrease in the magnetic susceptibility is observed, evidence for a non-magnetic ground state. The magnetic behavior of the SP state is complemented by SP signatures in a number of other measurements.

The usual interpretation of the transition at 34 K as a spin-Peierls transition is based on the structure determination of Carpy & Galy (1975). Their refinement, based on photographic data, in the non-centrosymmetric space group *P2<sub>1</sub>mn*, allows for two V-atom positions in the asymmetric unit. These sites were interpreted with different valence states, *i.e.* V<sup>4+</sup> and V<sup>5+</sup>. In their model, the resulting one-dimensional  $S = \frac{1}{2}$  V<sup>4+</sup> chain can cause the observed Bonner–Fisher-like temperature dependence in the magnetic susceptibility, and a spin-Peierls transition at low temperature. However, the reported structure determination of Carpy & Galy (1975) yielded atomic coordinates with a pseudo-inversion center at (0.259, 0.25, 0.11) (Le Page, 1987, 1988). Therefore, we have undertaken a structure redetermination to investigate the (centro)symmetry.

The structure can be constructed from double rows of edge-sharing pyramids, one facing up and the other down. These double rows are connected by pyramid corner-sharing, yielding a planar material. These planes are stacked with the Na<sup>+</sup> ions in the channels of the pyramids, as shown in Fig. 1. The eightfold coordination of sodium is somewhat more symmetric [with Na—O distances of 2.4325(11)–2.6038(9) Å] than in the refinement of Carpy & Galy (1975) (Na—O 2.43–2.90 Å). The structure of NaV<sub>2</sub>O<sub>5</sub> is thus similar to that