

Sodium magnesium bis(vanadate)  
pyrovanadate:  $\text{Na}_6\text{Mg}_2(\text{VO}_4)_2(\text{V}_2\text{O}_7)$ Alexander Mitiaev, Andrei Mironov, Roman  
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The crystal structure of the new complex vanadium oxide  $\text{Na}_6\text{Mg}_2(\text{VO}_4)_2(\text{V}_2\text{O}_7)$  was solved from X-ray single-crystal data. The structure contains  $\text{VO}_4$  tetrahedra and  $\text{MgO}_6$  octahedra, linked by corners and forming a complex three-dimensional framework. A half of the  $\text{VO}_4$  tetrahedra are connected only to  $\text{MgO}_6$  octahedra, whereas the others are corner-sharing, forming  $\text{V}_2\text{O}_7$  pyrovanadate groups with statistically random orientations. One unique Mg atom is located at an inversion centre, while the other Mg atom, one unique V atom and five unique O atoms lie on mirror planes.

## Comment

Complex vanadium oxides have drawn the attention of researchers because of the possible application of these compounds as secondary current sources and catalysts in oxidation processes (Zavalij & Whittingham, 1999; Schindler *et al.*, 2000). The existence of a variety of vanadium oxidation states and coordination polyhedra gives numerous opportunities for the synthesis of new compounds.

To date, only two compounds have been reported in the Na/Mg/V/O system. The crystal structure of  $\text{NaMg}_4(\text{VO}_4)_3$  (Murashova *et al.*, 1988) contains isolated  $\text{V}^{5+}\text{O}_4$  tetrahedra and  $\text{MgO}_6$  octahedra, linked in a three-dimensional framework. Na and Mg atoms adopt ordered positions in the structural interstices. The crystal structure of  $\text{Na}_6\text{Mg}_3\text{V}_4\text{O}_{16}$  (Slobodin *et al.*, 1987) is unknown; moreover, the X-ray diffraction powder pattern of this compound was not indexed.

The crystal structure of the title compound is shown in Fig. 1. The three-dimensional framework is built up of corner-sharing  $\text{V}^{5+}\text{O}_4$  tetrahedra and  $\text{MgO}_6$  octahedra. The  $\text{MgO}_6$  octahedra are close to regular, with Mg—O bonds in the range 2.072 (2)–2.248 (2) Å (Table 1), and every octahedron is corner-linked to six  $\text{VO}_4$  tetrahedra. Atoms Na1, Na2 and Na3 have five O-atom neighbours, and atom Na4 has six, the Na—O range of bond lengths being 2.288 (3)–2.668 (3) Å.

There are three symmetry-independent vanadium sites in the structure, all of which are tetrahedrally coordinated and contain  $\text{V}^{5+}$  cations. The bond-valence sums (BVSs) for the V1-, V2- and V3-atom positions are 5.05, 5.18 and 4.77, respectively. The  $\text{V1O}_4$  and  $\text{V2O}_4$  tetrahedra are essentially undistorted and have four V—O distances close to 1.70 Å, which is typical for vanadate groups. The  $\text{V3O}_4$  tetrahedron is strongly distorted, with a noticeable elongation of the V3—O9 bond length to 1.933 (3) Å. Atom V3 partially (0.5) occupies an *8d* site, which results from the splitting of a *4c* site along the *b* axis, the separation between atoms V3a and V3b being 1.064 (1) Å. Only one of the two  $\text{V3O}_4$  tetrahedra can be occupied at any one time.

All tetrahedra in the structure are corner-linked. The  $\text{V1O}_4$  tetrahedron has four neighbouring  $\text{MgO}_6$  octahedra, while the  $\text{V2O}_4$  group shares three corners with  $\text{MgO}_6$  octahedra and one with a  $\text{V3O}_4$  tetrahedron. The latter is also connected to two  $\text{Mg1O}_6$  octahedra. The coordinating atom, O2, belongs only to the  $\text{V3O}_4$  tetrahedron. Fig. 2 shows that the corner-linked  $\text{V2O}_4$  and  $\text{V3aO}_4$  (or  $\text{V3bO}_4$ ) tetrahedra together form randomly oriented  $\text{V}_2\text{O}_7$  pyrovanadate groups. Hence, the structural formula for the title compound can be written as  $\text{Na}_6\text{Mg}_2(\text{VO}_4)_2(\text{V}_2\text{O}_7)$ .

The random orientation of the pyrovanadate groups explains the statistical populations of the coordinated Na3 and Na4 sites, which are only half occupied. We suggest that in each particular unit cell these atoms should be situated opposite to any of the  $\text{V3aO}_4$  or  $\text{V3bO}_4$  tetrahedra present in the structure.

Although a trigonal bipyramidal coordination can be realized for a  $\text{V}^{5+}$  cation, no such configuration is realized in the  $\text{Na}_6\text{Mg}_2(\text{VO}_4)_2(\text{V}_2\text{O}_7)$  structure. A shift of atom V3 to the

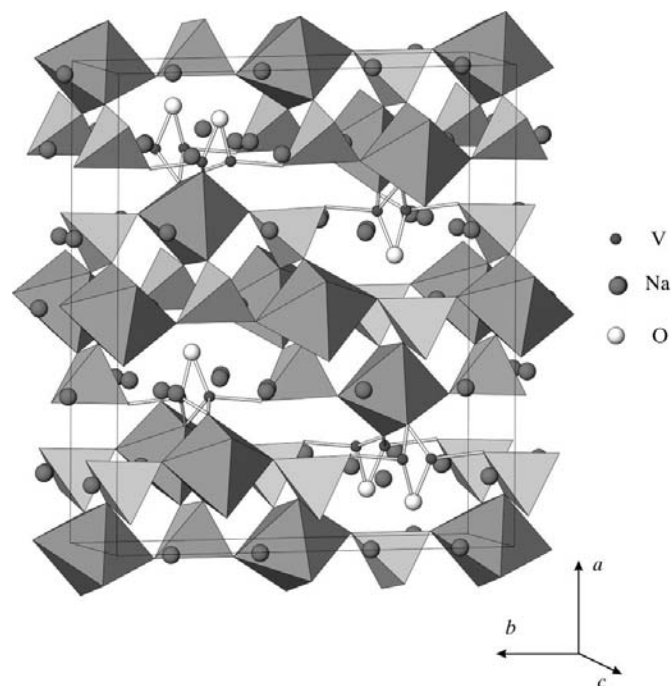
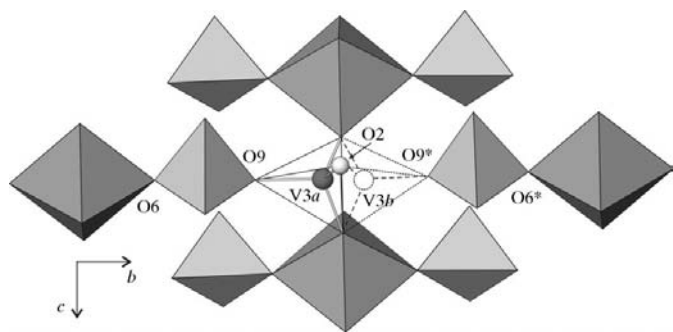


Figure 1  
The crystal structure of  $\text{Na}_6\text{Mg}_2(\text{VO}_4)_2(\text{V}_2\text{O}_7)$ .

centre of the O4/O2/O5 plane of a hypothetical bipyramid (4c position) results in enormous V—O9 distances (~2.46 Å), which can be considered to be non-bonding. A BVS calculation indicates a vanadium oxidation state of +5.46 for this configuration, which is much higher than the maximum possible vanadium valence.

The crystal structure of Na<sub>6</sub>Mg<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(V<sub>2</sub>O<sub>7</sub>) is similar to that of Na<sub>2</sub>Ca<sub>6</sub>(SiO<sub>4</sub>)<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>) (space group *P2<sub>1</sub>/c*; Armbruster & Roethlisberger, 1990). The latter has a monoclinic lattice with cell parameters close to those of Na<sub>6</sub>Mg<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(V<sub>2</sub>O<sub>7</sub>). In contrast to the title structure, Na<sub>2</sub>Ca<sub>6</sub>(SiO<sub>4</sub>)<sub>2</sub>(Si<sub>2</sub>O<sub>7</sub>) has one SiO<sub>4</sub> tetrahedra, the Si<sub>2</sub>O<sub>7</sub> groups are arranged in an orderly manner and the A cations (Na and Ca) jointly occupy their positions.



**Figure 2**  
Two possibilities for V<sub>2</sub>O<sub>7</sub>-group orientation. Mg<sub>2</sub>O<sub>6</sub> octahedra and V<sub>2</sub>O<sub>4</sub> tetrahedra are shown as filled polyhedra. Na atoms are not shown. O atoms marked with an asterisk (\*), as well as V<sub>3a</sub> and V<sub>3b</sub>, are mutually related by the  $(x, \frac{1}{2} - y, z)$  mirror plane.

The theoretical X-ray powder pattern for Na<sub>6</sub>Mg<sub>2</sub>V<sub>4</sub>O<sub>15</sub>, calculated from single-crystal data, coincides with the powder data reported by Slobodin *et al.* (1987), who assumed the composition Na<sub>6</sub>Mg<sub>3</sub>V<sub>4</sub>O<sub>16</sub>. Taking into account the similarity of the two compositions, we assert that the formula of the incompletely characterized phase was actually Na<sub>6</sub>Mg<sub>2</sub>V<sub>4</sub>O<sub>15</sub>.

## Experimental

A single-phase powder sample was obtained by the solid-state reaction of Na<sub>2</sub>CO<sub>3</sub>, MgO and V<sub>2</sub>O<sub>5</sub>. Before weighing, MgO was dried in a dynamic vacuum at 773 K to eliminate water. The starting materials were mixed in an agate mortar, ground under acetone, pressed into pellets and annealed in air at 773 K for 36 h. Single crystals of Na<sub>6</sub>Mg<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(V<sub>2</sub>O<sub>7</sub>) were obtained by melting the powder sample and then cooling it slowly in a furnace.

### Crystal data

Na<sub>6</sub>Mg<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>(V<sub>2</sub>O<sub>7</sub>)

*M<sub>r</sub>* = 630.3

Orthorhombic, *Pnma*

*a* = 17.080 (3) Å

*b* = 14.6910 (18) Å

*c* = 5.5356 (7) Å

*V* = 1389.0 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 3.013 (1) Mg m<sup>-3</sup>

Mo *K*α radiation

Cell parameters from 23 reflections

$\theta$  = 17.6–20.4°

$\mu$  = 2.97 mm<sup>-1</sup>

*T* = 293 K

Arbitrary, colourless

0.23 × 0.09 × 0.07 mm

### Data collection

Enraf–Nonius CAD-4

diffractometer

$\omega/\theta$  scans

Absorption correction:  $\psi$  scan

(*CAD-4 Manual*; Enraf–Nonius, 1988)

*T<sub>min</sub>* = 0.722, *T<sub>max</sub>* = 0.812

14 190 measured reflections

3546 independent reflections

1762 reflections with *I* > 3σ(*I*)

*R<sub>int</sub>* = 0.030

$\theta_{\max}$  = 36.9°

*h* = -28 → 28

*k* = -24 → 4

*l* = 0 → 9

2 standard reflections

frequency: 120 min

intensity decay: none

### Refinement

Refinement on *F*

*R* = 0.037

*wR* = 0.050

*S* = 1.71

1762 reflections

143 parameters

*w* = 1/[σ<sup>2</sup>(*F*) + 0.0004*F*<sup>2</sup>]

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 1.01 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.79 e Å<sup>-3</sup>

Extinction correction: Gaussian

(Becker & Coppens, 1974)

Extinction coefficient: 0.011 (3)

**Table 1**

Selected interatomic distances (Å).

V1—O1	1.715 (3)	Na1—O3	2.515 (3)
V1—O3 <sup>i</sup>	1.716 (3)	Na1—O7 <sup>vi</sup>	2.592 (3)
V1—O7 <sup>ii</sup>	1.717 (2)	Na1—O8	2.469 (3)
V2—O6	1.693 (2)	Na1—O8 <sup>iii</sup>	2.668 (3)
V2—O8	1.698 (2)	Na2—O1	2.568 (3)
V2—O9 <sup>iii</sup>	1.730 (3)	Na2—O5	2.473 (3)
V2—O10 <sup>iv</sup>	1.714 (2)	Na2—O6 <sup>i</sup>	2.572 (3)
V3—V3 <sup>v</sup>	1.0642 (12)	Na2—O9	2.349 (3)
V3—O2	1.684 (3)	Na2—O10	2.358 (3)
V3—O4 <sup>vi</sup>	1.709 (3)	Na3—Na4	0.836 (5)
V3—O5	1.684 (3)	Na3—O4	2.436 (4)
V3—O9	1.933 (3)	Na3—O5 <sup>vii</sup>	2.599 (4)
Mg1—O7	2.248 (2)	Na3—O6	2.518 (4)
Mg1—O8 <sup>vii</sup>	2.072 (2)	Na3—O7	2.505 (4)
Mg1—O10 <sup>viii</sup>	2.074 (2)	Na3—O9 <sup>vii</sup>	2.624 (4)
Mg2—O1 <sup>iv</sup>	2.078 (4)	Na3—O10 <sup>iii</sup>	2.448 (4)
Mg2—O3	2.086 (4)	Na4—O4	2.288 (3)
Mg2—O4	2.117 (3)	Na4—O6	2.517 (4)
Mg2—O5 <sup>vii</sup>	2.127 (3)	Na4—O7	2.432 (4)
Mg2—O6	2.077 (2)	Na4—O9 <sup>iv</sup>	2.471 (4)
Mg2—O6 <sup>v</sup>	2.077 (2)	Na4—O10 <sup>iii</sup>	2.512 (4)
Na1—O2	2.338 (3)		

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

Analysis of the systematic reflection extinctions revealed the rules *0kl*: *k* + *l* = 2*n* and *hk0*: *h* = 2*n*, which correspond to the two possible space groups *Pnma* and *Pn2<sub>1</sub>a*. The former was used for structure solution. The occupancies of atoms Na3 and Na4 appeared to be almost equal and slightly higher than 0.5 (deviations were ~8–10σ). In this case, the formal oxidation number for vanadium would be higher than +5. Thus, in the final refinement, the occupancies for both Na atoms were fixed at 0.5. Since the structure refinement revealed disorder of atoms V3, Na3 and Na4, additional refinements were performed for space group *Pn2<sub>1</sub>a*, as well as for other subgroups (down to monoclinic symmetry), to check for possible ordering of the atomic positions. However, lowering the symmetry did not lead to ordering of the cation positions. Moreover, all symmetry-dependent atoms of the *Pnma* group produced high correlation coefficients (up to 0.99 in the corresponding atomic parameters), indicating orthorhombic symmetry of the unit cell.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988); cell refinement: *CAD-4 Manual*; data reduction: *CSD* (Akselrud *et al.*, 1993); program(s) used to solve structure: *CSD*; program(s) used to refine structure: *JANA2000* (Petricek & Dusek, 2000); molecular graphics: *ATOMS* (Dowty, 1998); software used to prepare material for publication: *JANA2000*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1039). Services for accessing these data are described at the back of the journal.

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