Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(dabconium) vanadium arsenate octahydrate, $(N_2C_6H_{14})_2[V_4As_6O_{30}H_6]\cdot 8H_2O$

Colin A. Bremner and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

Received 13 May 2002
Accepted 27 May 2002
Online 8 June 2002

Key indicators

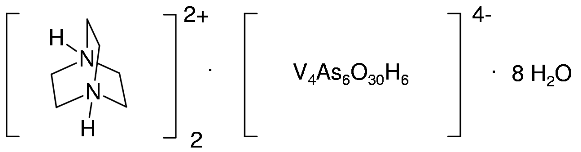
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.028
wR factor = 0.071
Data-to-parameter ratio = 20.6

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

The title compound contains a network of $[V_4As_6O_{30}H_6]^{4-}$ clusters, each of which is accompanied by two dabconium (doubly protonated 1,4-diazabicyclo[2.2.2]octane) cations and eight water molecules. A complex hydrogen-bonding network stabilizes the crystal packing.

Comment

The $[V_4As_6O_{30}H_6]^{4-}$ cluster (Fig. 1) of the title compound, (I), has already been observed, accompanied by other molecular cations (Durif & Averbuch-Pouchot, 1979; Nenoff *et al.*, 1994; Bremner & Harrison, 2002). In particular, it complements bis(dabconium) vanadium arsenate tetrahydrate, $(N_2C_6H_{14})_2$-$[V_4As_6O_{30}H_6]\cdot 4H_2O$, (I) (Nenoff *et al.*, 1994).



(I)

The cluster contains two pairs of VO_6 octahedra sharing an edge (*via* O4 and O5). The distorted VO_6 groups both contain a short (d < 1.59 Å) V=O 'vanadyl' group and a long (d > 2.24 Å) *trans* V—O bond. The four remaining V—O bonds are

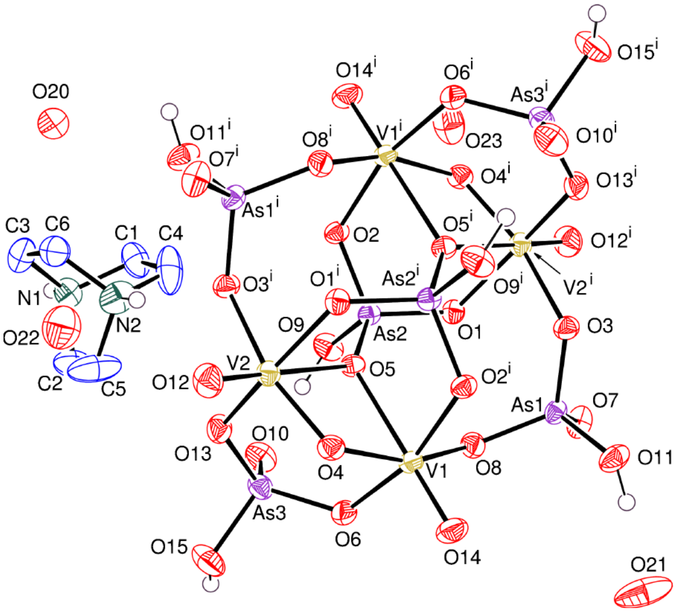


Figure 1
The structure of (I) (50% displacement ellipsoids for the non-H atoms). H atoms from C—H and water O—H groups have been omitted for clarity. [Symmetry code: (i) 1−*x*, 1−*y*, 1−*z*.]

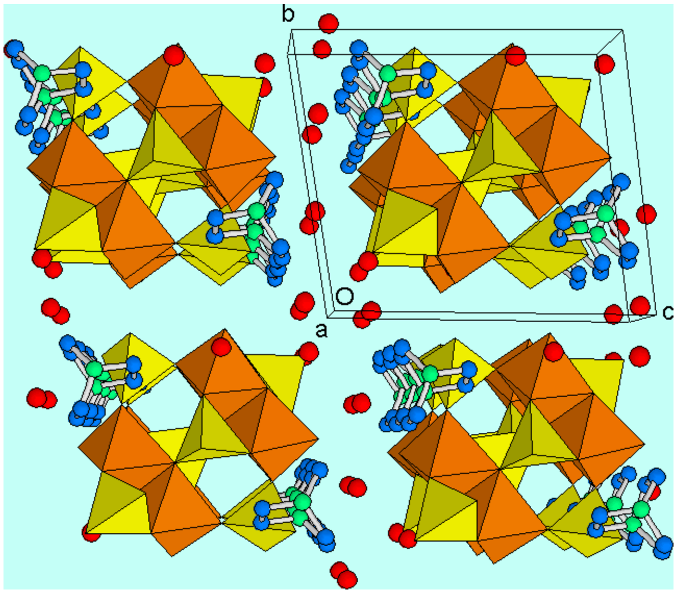


Figure 2
Packing diagram for (I), viewed approximately down [100], with the cluster anions represented by polyhedra and H atoms omitted for clarity. Colour key: VO_6 octahedra orange, AsO_4 tetrahedra yellow, C atoms blue, N atoms green, O (water) atoms red.

intermediate in length between these extremes. The three distinct arsenate tetrahedra bridge the two octahedral pairs into a discrete anionic cluster. The As1- and As3-centred groups both make two As—O—V links and have two terminal As—O vertices, one of which is protonated. The As2 group makes three As—O—V bonds and has one terminal As—OH grouping. The 15 distinct O atoms in the cluster divide into terminal vanadyl O atoms (O12 and O14), terminal As—O atoms [O7 and O10; d_{av}(As—O) = 1.651 (2) Å], terminal As—OH species [O9, O11 and O15; d_{av}(As—O) = 1.703 (2) Å], As—O—V bridges (O1, O2, O3, O6, O8 and O13; average V—O—As bond angle = 125.6°), a V—O—V bridge (O4) and the three coordinate (to two V and one As) O5 species. The locations of the cluster H atoms (one As—OH moiety per arsenate tetrahedron) are similar to those seen in $(C_2H_7N_4O)_4[V_4As_6O_{30}H_6]$ (Bremner & Harrison, 2002). The geometrical parameters for the doubly protonated dabconium cation are unexceptional (Cascales *et al.*, 2002). Eight water molecules of crystallization per cluster complete the structure.

Here, and also in $(C_2N_4OH_7)_4[V_4As_6O_{30}H_6]$, the complete cluster is generated by inversion symmetry. Similar clusters may also show $2/m$ or mmm symmetry (Durif & Averbuch-Pouchot, 1979; Nenoff *et al.*, 1994).

The hydrogen-bonding interactions in (I) include cluster-to-cluster O—H···O and cation-to-cluster N—H···O links (one of which is bifurcated), as well as numerous O—H···O bonds involving the water molecules. A [100] view (Fig. 2) of the resulting crystal packing shows stacks of clusters and dabconium cations interspersed by a sheet-like array of water molecules in the (010) plane.

Experimental

25 ml of 1.0 *M* H_3AsO_4 solution was added to 0.502 g $VOSO_4\cdot nH_2O$ with gentle agitation, resulting in a light-blue solution. Then, 0.501 g dabco (1,4-diazabicyclo[2.2.2]octane) was slowly added to the mixture, which was left to stand until effervescence ceased, at which point the solution was orange with a yellow precipitate. The mixture was transferred to an evaporating basin. After 5 d, clumps of rhombic orange crystals were recovered from the green supernatant liquors by vacuum filtration and washing with water.

Crystal data

$(C_6H_{14}N_2)_2[V_4As_6O_{30}H_6]\cdot 8H_2O$
M_r = 755.91
Triclinic, $P\overline{1}$
a = 9.6824 (5) Å
b = 11.0733 (7) Å
c = 11.8967 (7) Å
α = 94.546 (2)°
β = 101.557 (2)°
γ = 114.193 (2)°
V = 1121.16 (11) Å^3

Z = 2
D_x = 2.239 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3766 reflections
θ = 2.1–30.1°
μ = 5.32 mm^{-1}
T = 293 (2) K
Chunk, orange
0.50 × 0.40 × 0.40 mm

Data collection

Bruker SMART1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
T_{min} = 0.176, T_{max} = 0.225
7764 measured reflections

6021 independent reflections
4987 reflections with $I > 2\sigma()$'
R_{int} = 0.015
θ_{max} = 30.2°
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 15$
$l = -16 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.071
S = 0.97
6021 reflections
292 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.041P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.60 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0025 (4)

Table 1
Selected geometric parameters (Å, °).

V1—O14	1.5819 (19)	As2—O1	1.6894 (17)
V1—O6	1.8879 (19)	As2—O2	1.6945 (17)
V1—O8	1.8892 (19)	As2—O9	1.7027 (18)
V1—O4	1.8996 (18)	As3—O10	1.648 (2)
V1—O2^{i}	1.9576 (18)	As3—O13	1.6939 (18)
V1—O5	2.2443 (17)	As3—O15	1.696 (2)
V2—O12	1.585 (2)	As3—O6	1.7120 (19)
V2—O4	1.7661 (18)	N1—C2	1.478 (4)
V2—O13	1.9252 (19)	N1—C1	1.491 (4)
V2—O1^{i}	1.9469 (18)	N1—C3	1.495 (4)
V2—O3^{i}	2.0029 (19)	N2—C4	1.470 (5)
V2—O5	2.3272 (18)	N2—C6	1.490 (4)
As1—O7	1.6539 (18)	N2—C5	1.496 (5)
As1—O3	1.6852 (18)	C1—C4	1.519 (5)
As1—O8	1.6920 (18)	C2—C5	1.522 (5)
As1—O11	1.7098 (19)	C3—C6	1.510 (5)
As2—O5	1.6651 (17)		
As2—O1—V2^{i}	122.07 (9)	As2—O5—V2	138.98 (9)
As2—O2—V1^{i}	122.51 (10)	V1—O5—V2	87.86 (6)
As1—O3—V2^{i}	124.36 (10)	As3—O6—V1	127.43 (10)
V2—O4—V1	119.80 (10)	As1—O8—V1	132.74 (11)
As2—O5—V1	133.04 (9)	As3—O13—V2	124.54 (10)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9···O10	0.97	1.61	2.571 (3)	171
O11—H11···O21	0.88	1.75	2.629 (3)	173
O15—H15···O20^{i}	0.90	1.68	2.542 (3)	158
O20—H20···O7^{ii}	0.91	1.78	2.670 (3)	168
O20—H21···O23^{iii}	0.93	1.81	2.740 (4)	177
O21—H22···O10^{iv}	0.87	1.91	2.745 (3)	160
O21—H23···O2^{v}	0.89	1.99	2.868 (3)	170
O21—H23···O14^{vi}	0.89	2.65	3.125 (3)	115
O22—H24···O12	0.99	2.26	3.100 (3)	142
O22—H25···O23^{iii}	1.00	1.90	2.897 (4)	171
O23—H26···O4^{ii}	0.95	1.86	2.808 (3)	180
O23—H27···O20^{vii}	0.81	2.27	2.864 (3)	131
N1—H1···O7^{viii}	0.91	1.68	2.591 (3)	179
N2—H2···O3^{ii}	0.91	2.16	2.995 (3)	152
N2—H2···O22	0.91	2.52	3.114 (4)	123

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

References

Bremner, C. A. & Harrison, W. T. A. (2002). *Acta Cryst.* E**58**, m254–m256.

Bruker (1999). *SMART* and *SABADS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cascales, C., Gomez-Lor, B., Guitierrez-Puebla, E., Iglesias, M., Monge, M. A., Ruiz-Valero, C. & Snejko, N. (2002). *Chem. Mater.* **14**, 677–681.

Durif, A. & Averbuch-Pouchot, M. T. (1979). *Acta Cryst.* B**35**, 1441–1444.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.

Nenoff, T. M., Stucky, G. D. & Harrison, W. T. A. (1994). *Z. Kristallogr.* **209**, 892–898.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.