

Guanylurea vanadium arsenate

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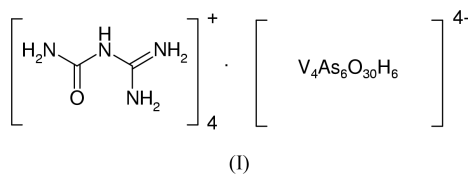
Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{N}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.024
 wR factor = 0.064
Data-to-parameter ratio = 20.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The title compound consists of anionic $[\text{V}_4\text{As}_6\text{O}_{30}\text{H}_6]^{4-}$ clusters, each accompanied by four guanylurea ($\text{C}_2\text{N}_4\text{OH}_7^+$) cations. An extensive hydrogen-bonding network stabilizes the crystal packing.

Comment

The $[\text{V}_4\text{As}_6\text{O}_{30}\text{H}_6]^{4-}$ cluster seen here, (I) (Fig. 1), has been observed previously (Durif & Averbuch-Pouchot, 1979; Nenoff *et al.*, 1994), accompanied by other molecular cations. It contains two pairs of VO_6 octahedra sharing an edge (*via* O5 and O8). The VO_6 groups are highly distorted and each shows a short ($d < 1.60\text{ \AA}$) $\text{V}=\text{O}$ 'vanadyl' group and a long ($d > 2.30\text{ \AA}$) *trans*- $\text{V}-\text{O}$ bond, as typically seen for V^{V} (Durif & Averbuch-Pouchot, 1979). The four remaining $\text{V}-\text{O}$ bonds are intermediate in length between these extremes. The three distinct arsenate tetrahedra bridge the two octahedral pairs into a discrete cluster. The As1- and As3-centred groups both make two $\text{As}-\text{O}-\text{V}$ links and have two terminal $\text{As}-\text{O}$ vertices, one of which is protonated. The As2 group makes three $\text{As}-\text{O}-\text{V}$ bonds and has one terminal $\text{As}-\text{OH}$ grouping. The 15 distinct O atoms in the cluster divide into terminal vanadyl O atoms (O2 and O7), terminal $\text{As}-\text{O}$ atoms (O11 and O15), terminal $\text{As}-\text{OH}$ species (O6, O13 and O14), $\text{As}-\text{O}-\text{V}$ bridges (O1, O3, O4, O9, O10 and O12; average $\text{V}-\text{O}-\text{As}$ bond angle 125.5°), a $\text{V}-\text{O}-\text{V}$ bridge (O5) and the three-coordinate (to two V and one As) O8 species. The O8/V1/V2/As2 grouping is almost flat [sum of $X-\text{O8}-X$ ($X = \text{V}, \text{As}$) bond angles = 359.8°]. This study has located the H atoms in this type of cluster for the first time. As predicted (Nenoff *et al.*, 1994), they are all associated with terminal $\text{As}-\text{O}$ vertices. The $\text{As}-\text{O}$ terminal bonds [$d_{\text{av}} = 1.658(2)\text{ \AA}$] are significantly shorter than the $\text{As}-\text{OH}$ [$d_{\text{av}} = 1.718(2)\text{ \AA}$] bonds.



Here, the complete cluster is generated by inversion symmetry. In $(\text{NH}_4)_6[\text{V}_4\text{As}_6\text{O}_{30}\text{H}_6]$ (Durif & Averbuch-Pouchot, 1979) and $(\text{N}_2\text{C}_6\text{H}_{14})_2[\text{V}_4\text{As}_6\text{O}_{30}\text{H}_6]\cdot 4\text{H}_2\text{O}$ (Nenoff *et al.*, 1994), the equivalent cluster possesses $2/m$ symmetry, whereas in $[\text{N}(\text{CH}_3)_4]_2[\text{V}_4\text{As}_6\text{O}_{30}\text{H}_8]\cdot 5.33\text{H}_2\text{O}$ (Nenoff *et al.*, 1994), it has mmm symmetry.

The guanylurea (1-carbamoylguanidinium) moieties show typical behaviour (Zaman & Darlow, 1986) and are essentially planar (r.m.s. deviations from the least-squares plane = 0.018

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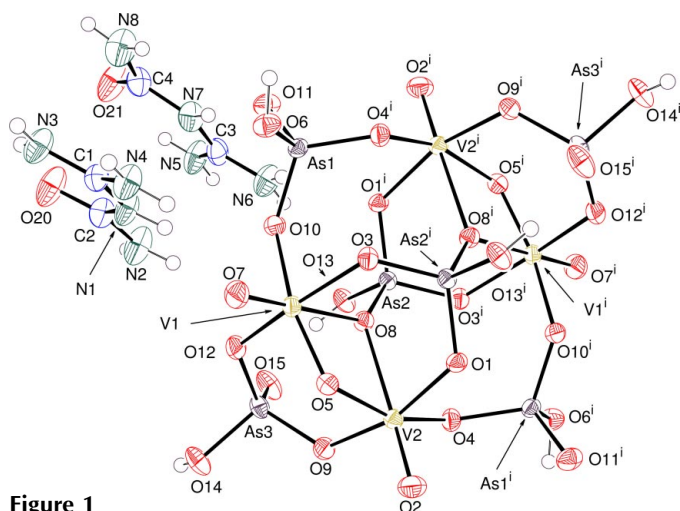


Figure 1
The structure of (I) (50% displacement ellipsoids, arbitrary spheres for the H atoms). Symmetry code: (i) $-x, -y, 1-z$.

and 0.006 Å for the non-H atoms of the C1- and C3-containing molecules, respectively).

The hydrogen-bonding interactions include cluster-to-cluster $O-H \cdots O$ and cation-to-cluster $N-H \cdots O$ links as well as cation-to-cation $N-H \cdots O$ and both intramolecular and intermolecular cluster-to-cluster $O-H \cdots O$ bonds. A [100] view (Fig. 2) of the resulting crystal packing shows a square network of clusters with the organic cations forming double stacks in the channel-like interstices, somewhat like the situation in $(N(CH_3)_4)_2[V_4As_6O_{30}H_8] \cdot 5.33H_2O$ (Nenoff *et al.*, 1994).

Experimental

25 ml of 1.0 M H_3AsO_4 solution was added to 0.501 g $VOSO_4 \cdot nH_2O$ with gentle agitation until the solid dissolved. Then, 0.500 g dicyandiamide was slowly added to the mixture, accompanied by vigorous effervescence, during which time the solution changed colour from pale blue to olive green. The mixture was transferred to an evaporating basin and chunky orange crystal masses were manually recovered from the olive-green gel/sludge after standing for 7 d in air. The starting dicyandiamide was transformed to guanyurea by slow acid hydrolysis.

Crystal data

$(C_2H_7N_4O)_4[As_6V_4O_{30}H_6]$	$Z = 1$
$M_r = 1551.8$	$D_x = 2.360 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.5376$ (4) Å	Cell parameters from 5166 reflections
$b = 11.0544$ (5) Å	$\theta = 2.5\text{--}30.0^\circ$
$c = 12.4672$ (5) Å	$\mu = 5.46 \text{ mm}^{-1}$
$\alpha = 83.144$ (1) $^\circ$	$T = 293$ (2) K
$\beta = 82.652$ (1) $^\circ$	Block, orange
$\gamma = 69.848$ (1) $^\circ$	$0.30 \times 0.30 \times 0.20 \text{ mm}$
$V = 1091.94$ (8) Å 3	

Data collection

Bruker SMART1000 CCD diffractometer	6216 independent reflections
ω scans	5186 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 1999)	$R_{\text{int}} = 0.014$
$T_{\text{min}} = 0.291, T_{\text{max}} = 0.408$	$\theta_{\text{max}} = 30.1^\circ$
8831 measured reflections	$h = -11 \rightarrow 12$
	$k = -12 \rightarrow 15$
	$l = -16 \rightarrow 17$

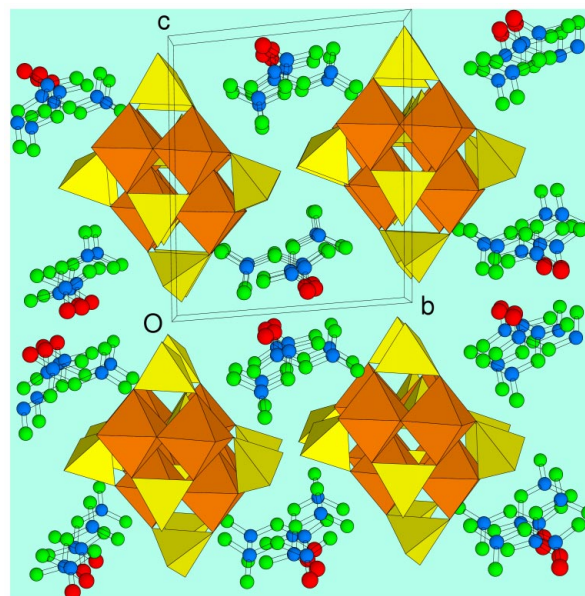


Figure 2
Packing diagram for (I), viewed approximately down [100], with the cluster anions represented by polyhedra and H atoms omitted for clarity. Colour key: VO_6 octahedra orange, AsO_4 tetrahedra yellow, C atoms blue, N atoms green, and O atoms red.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.024$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.78 \text{ e \AA}^{-3}$
6216 reflections	$\Delta\rho_{\text{min}} = -0.64 \text{ e \AA}^{-3}$
308 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.0018 (3)

Table 1

Selected geometric parameters (Å, $^\circ$).

V1—O7	1.5960 (18)	As2—O1 ⁱ	1.6921 (16)
V1—O5	1.7541 (16)	As2—O13	1.7143 (17)
V1—O3	1.9498 (17)	As3—O15	1.6611 (18)
V1—O12	1.9678 (18)	As3—O12	1.6855 (18)
V1—O10	1.9864 (17)	As3—O9	1.6969 (17)
V1—O8	2.3145 (16)	As3—O14	1.7247 (17)
V2—O2	1.5782 (17)	O20—C2	1.224 (3)
V2—O5	1.8773 (17)	N1—C1	1.362 (3)
V2—O9	1.9154 (17)	N1—C2	1.405 (3)
V2—O4	1.9155 (17)	N2—C2	1.330 (4)
V2—O1	1.9314 (16)	N3—C1	1.307 (3)
V2—O8	2.3401 (16)	N4—C1	1.314 (3)
As1—O11	1.6546 (16)	O21—C4	1.211 (3)
As1—O10	1.6805 (17)	N5—C3	1.307 (4)
As1—O4 ⁱ	1.7023 (16)	N6—C3	1.323 (3)
As1—O6	1.7164 (17)	N7—C3	1.348 (4)
As2—O8	1.6677 (15)	N7—C4	1.395 (4)
As2—O3 ⁱ	1.6895 (16)	N8—C4	1.328 (4)
As2 ⁱ —O1—V2	123.98 (9)	As2—O8—V2	136.64 (8)
As2 ⁱ —O3—V1	120.66 (9)	V1—O8—V2	85.55 (5)
As1 ⁱ —O4—V2	126.80 (10)	As3—O9—V2	127.28 (10)
V1—O5—V2	120.99 (9)	As1—O10—V1	130.33 (10)
As2—O8—V1	137.38 (9)	As3—O12—V1	124.11 (9)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O6—H6...O11 ⁱ	0.93	1.68	2.597 (2)	166
O13—H13...O15	0.84	1.72	2.548 (2)	168
O14—H14...O15 ⁱⁱ	0.92	1.71	2.617 (3)	169
N1—H1...O10	0.86	2.37	3.101 (3)	143
N1—H1...O7	0.86	2.41	3.165 (3)	147
N2—H2A...O20 ⁱⁱⁱ	0.86	2.07	2.904 (3)	165
N2—H2B...O12	0.86	2.40	3.191 (3)	154
N2—H2B...O10	0.86	2.58	3.254 (3)	136
N3—H3A...O13 ^{iv}	0.86	2.10	2.947 (3)	167
N3—H3B...O20	0.86	2.01	2.649 (3)	130
N4—H4A...O3 ^v	0.86	2.12	2.952 (3)	161
N4—H4B...O7	0.86	2.33	3.105 (3)	149
N5—H5A...O14 ^{vi}	0.86	2.31	3.147 (3)	163
N5—H5B...O21	0.86	2.06	2.685 (3)	128
N5—H5B...O21 ^{vii}	0.86	2.12	2.829 (3)	140
N6—H6B...O1 ^{viii}	0.86	2.39	3.058 (3)	135
N6—H6B...O11	0.86	2.49	3.171 (4)	137
N7—H7...O11	0.86	1.85	2.685 (3)	163
N8—H8A...O15 ^{ix}	0.86	2.46	3.312 (4)	171
N8—H8B...O4 ^{ix}	0.86	2.38	3.051 (3)	135

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SMART*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

References

- Bruker (1999). *SMART* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Durif, A. & Averbuch-Pouchot, M. T. (1979). *Acta Cryst.* **B35**, 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). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Zaman, N. & Darlow, S. F. (1986). *J. Bangladesh Acad. Sci.* **10**, 79–84.