

Hexakis(2-aminopyridinium) di- μ_6 -oxido-tetra- μ_3 -oxido-tetradeca- μ_2 -oxido-octa-oxidodecavanadium(V) dihydrate

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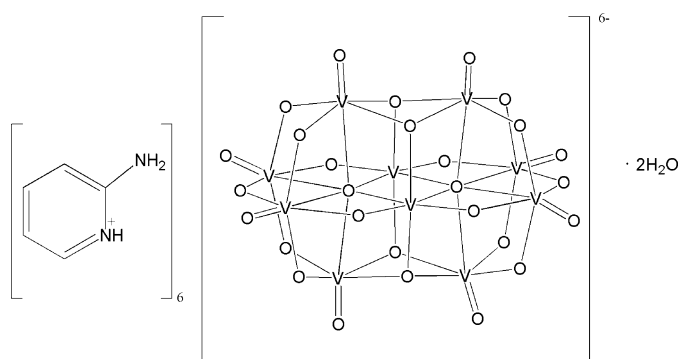
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.074; wR factor = 0.128; data-to-parameter ratio = 11.7.

In the title compound, $(\text{C}_5\text{H}_7\text{N}_2)_6[\text{V}_{10}\text{O}_{28}]\cdot 2\text{H}_2\text{O}$, the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion is generated by crystallographic inversion symmetry and each of the five vanadium centres adopts a distorted VO_6 octahedral geometry. In the crystal structure, a network of $\text{N}-\text{H}\cdots\text{O}$, $\text{N}-\text{H}\cdots(\text{O},\text{O})$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds helps to establish the packing.

Related literature

For a related structure, see: Gong *et al.* (2006). For background to the biological activity of oxovanadates and peroxovanadium compounds, see: Pacigová *et al.* (2007).



Experimental

Crystal data

$(\text{C}_5\text{H}_7\text{N}_2)_6[\text{V}_{10}\text{O}_{28}]\cdot 2\text{H}_2\text{O}$

$M_r = 1564.19$

Monoclinic, $P2_1/c$

$a = 9.840$ (3) Å

$b = 18.180$ (6) Å

$c = 14.299$ (5) Å

$\beta = 97.416$ (4)°

$V = 2536.6$ (14) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 1.86$ mm⁻¹

$T = 298$ (2) K

$0.40 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.523$, $T_{\max} = 0.707$

9858 measured reflections

4341 independent reflections

3949 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.074$

$wR(F^2) = 0.128$

$S = 1.29$

4341 reflections

370 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.53$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.45$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|---------------------|-----------|---------------------|-----------|
| V1—O7 | 1.616 (4) | V3—O6 | 1.891 (4) |
| V1—O3 | 1.767 (4) | V3—O5 | 2.045 (4) |
| V1—O8 | 1.842 (4) | V3—O1 | 2.305 (4) |
| V1—O2 | 1.991 (4) | V4—O4 | 1.676 (4) |
| V1—O12 | 2.038 (4) | V4—O5 ⁱ | 1.680 (4) |
| V1—O1 | 2.250 (4) | V4—O12 ⁱ | 1.921 (4) |
| V2—O9 | 1.608 (4) | V4—O2 | 1.953 (4) |
| V2—O6 | 1.794 (4) | V4—O1 ⁱ | 2.097 (4) |
| V2—O10 | 1.823 (4) | V4—O1 | 2.111 (4) |
| V2—O12 ⁱ | 2.015 (4) | V5—O13 | 1.590 (5) |
| V2—O2 ⁱ | 2.017 (4) | V5—O14 | 1.835 (4) |
| V2—O1 | 2.243 (4) | V5—O10 | 1.864 (4) |
| V3—O11 | 1.594 (4) | V5—O3 | 1.881 (4) |
| V3—O14 | 1.827 (4) | V5—O4 | 2.045 (4) |
| V3—O8 | 1.871 (4) | V5—O1 | 2.318 (4) |

Symmetry code: (i) $-x + 2, -y + 2, -z + 2$.

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|------------------------------------|--------------|--------------------|-------------|----------------------|
| N1—H1A \cdots O4 ⁱⁱ | 0.86 | 2.44 | 3.217 (9) | 150 |
| N1—H1A \cdots O5 ⁱⁱⁱ | 0.86 | 2.55 | 3.286 (8) | 144 |
| N1—H1B \cdots O10 ^{iv} | 0.86 | 2.21 | 3.058 (8) | 169 |
| N2—H2A \cdots O2 ⁱⁱ | 0.86 | 1.85 | 2.697 (7) | 168 |
| N3—H3A \cdots O9 ^{iv} | 0.86 | 2.17 | 2.969 (7) | 155 |
| N3—H3A \cdots O7 ^v | 0.86 | 2.48 | 3.017 (7) | 122 |
| N3—H3B \cdots O14 | 0.86 | 2.09 | 2.908 (7) | 158 |
| N4—H4A \cdots O12 ^v | 0.86 | 1.84 | 2.698 (6) | 174 |
| N5—H5A \cdots O7 ^v | 0.86 | 2.23 | 3.085 (8) | 175 |
| N5—H5B \cdots O9 | 0.86 | 2.22 | 3.057 (8) | 164 |
| N6—H6 \cdots O8 ^v | 0.86 | 1.87 | 2.709 (7) | 166 |
| O15—H15A \cdots O6 ^{vi} | 0.85 | 2.09 | 2.926 (8) | 166 |
| O15—H15B \cdots O7 ⁱⁱ | 0.85 | 2.13 | 2.977 (8) | 180 |

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL/PC* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2897).

References

Bruker (2000). *SMART*, *SAINTE* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Gong, Y., Hu, C., Li, H., Tang, W., Huang, K. & Hou, W. B. (2006). *J. Mol. Struct.* **784**, 228–238.

Pacigová, S., Rakovský, E., Sivák, M. & Žák, Z. (2007). *Acta Cryst.* **C63**, m419–m422.

Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2009). E65, m267-m268 [doi:10.1107/S1600536809004334]

**Hexakis(2-aminopyridinium)
octaoxidodecavanadium(V) dihydrate**

di- μ_6 -oxido-tetra- μ_3 -oxido-tetradeca- μ_2 -oxido-

C. Yuan, L. Lu, M. Zhu, Q. Ma and Y. Wu

Comment

Oxovanadates and peroxovanadium compounds are of great interest in biochemistry and medicine because of their diverse biological activities (Pacigová *et al.*, 2007). Of them, decavanadates have shown high affinity for selected kinases and phosphorylase and has been used to facilitate crystallization of proteins. Herein, we report the structure of the title compound, (I), containing decavanadate anions, 2-aminopyridinium cations and water molecules (Fig. 1).

Compound (I) consists of a centrosymmetric $[\text{V}_{10}\text{O}_{28}]^{6-}$ polyanion, two distinct 2-aminopyridinium cations and a water molecule (Fig. 1). The $[\text{V}_{10}\text{O}_{28}]^{6-}$ unit is constructed by ten VO_6 octahedra connected with each other *via* edge-sharing oxygen atoms. The different coordination of the oxygen atoms in the molecule results in different V—O bond distances (Table 1). The V—O (one coordinated oxygen) double bond distances range from 1.590 (5) to 1.616 (4) Å; the V—O (two coordinated oxygen) single bond distances range from 1.676 (4) to 2.045 (4) Å; the V—O (three coordinated oxygen) single bond distances range from 1.921 (4) to 2.038 (4) Å and the V—O (six coordinated oxygen) single bond distances are even longer (2.097 (4) to 2.318 (4) Å). These V—O bond types are similar to those in related compounds (Gong *et al.*, 2006).

A three-dimensional supramolecular hydrogen-bonding network is observed in the crystal structure of (I); details are given in Table 2. All the $(\text{C}_5\text{H}_7\text{N}_2)^+$ cations and water molecules are involved in hydrogen bonds with either terminal or bridging O atoms in the $[\text{V}_{10}\text{O}_{28}]^{6-}$ anion (Fig. 2).

Experimental

A hot aqueous VOSO_4 solution (1 mmol) was added dropwise to a stirred solution of 2-aminopyridine (1 mmol), which was dissolved in 20 ml of ethanol and refluxed for 4 h. Then the filtrate was kept open to slowly evaporate for a few days, depositing yellow blocks of (I).

Refinement

The H atoms were placed in geometrically idealized positions (C—H = 0.93 Å, N—H = 0.86 Å, O—H = 0.85 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Figures

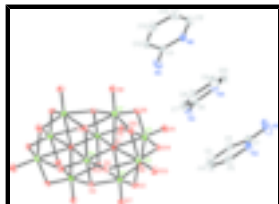


Fig. 1. A view of the structure of (I) with displacement ellipsoids drawn at the 30% probability level; H atoms and the water molecule are omitted for clarity.

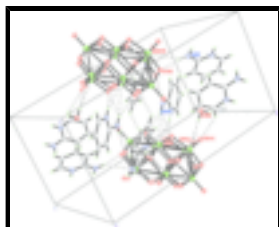


Fig. 2. The packing in (I), with hydrogen bonds indicated by dashed lines.

Hexakis(2-aminopyridinium) di- μ_6 -oxido-tetra- μ_3 -oxido- tetradeca- μ_2 -oxido-octaoxidodecavanadium(V) di-hydrate

Crystal data

$(C_5H_7N_2)_6[V_{10}O_{28}] \cdot 2H_2O$

$M_r = 1564.19$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 9.840$ (3) Å

$b = 18.180$ (6) Å

$c = 14.299$ (5) Å

$\beta = 97.416$ (4)°

$V = 2536.6$ (14) Å³

$Z = 2$

$F_{000} = 1560$

$D_x = 2.048$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 3889 reflections

$\theta = 2.2$ – 27.0 °

$\mu = 1.86$ mm⁻¹

$T = 298$ K

Block, yellow

$0.40 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART 1K CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ K

ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2000)

$T_{\min} = 0.523$, $T_{\max} = 0.707$

9858 measured reflections

4341 independent reflections

3949 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\text{max}} = 25.0$ °

$\theta_{\text{min}} = 2.9$ °

$h = -11 \rightarrow 11$

$k = -21 \rightarrow 18$

$l = -16 \rightarrow 12$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.074$ | H-atom parameters constrained |
| $wR(F^2) = 0.128$ | $w = 1/[\sigma^2(F_o^2) + (0.0095P)^2 + 8.6635P]$ |
| $S = 1.29$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4341 reflections | $(\Delta/\sigma)_{\max} = 0.002$ |
| 370 parameters | $\Delta\rho_{\max} = 0.53 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$ |
| | Extinction correction: none |

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|-------------|----------------------------------|
| V1 | 0.92911 (10) | 1.06195 (6) | 0.82727 (7) | 0.0219 (3) |
| V2 | 0.93856 (11) | 0.85376 (6) | 0.99424 (7) | 0.0223 (3) |
| V3 | 1.01726 (11) | 0.90023 (6) | 0.79935 (8) | 0.0261 (3) |
| V4 | 0.84711 (10) | 1.01767 (6) | 1.02703 (7) | 0.0207 (3) |
| V5 | 0.72947 (11) | 0.93367 (6) | 0.84923 (8) | 0.0248 (3) |
| O1 | 0.9456 (4) | 0.9637 (2) | 0.9237 (3) | 0.0187 (9) |
| O2 | 0.8818 (4) | 1.1018 (2) | 0.9486 (3) | 0.0200 (9) |
| O3 | 0.7620 (4) | 1.0262 (2) | 0.7977 (3) | 0.0260 (10) |
| O4 | 0.6972 (4) | 0.9938 (2) | 0.9652 (3) | 0.0257 (10) |
| O5 | 1.1928 (4) | 0.9330 (2) | 0.8810 (3) | 0.0262 (10) |
| O6 | 1.0166 (4) | 0.8267 (2) | 0.8929 (3) | 0.0258 (10) |
| O7 | 0.9299 (4) | 1.1366 (2) | 0.7659 (3) | 0.0302 (10) |
| O8 | 1.0138 (4) | 0.9970 (2) | 0.7546 (3) | 0.0244 (10) |
| O9 | 0.9418 (5) | 0.7791 (2) | 1.0547 (3) | 0.0307 (11) |
| O10 | 0.7627 (4) | 0.8570 (2) | 0.9357 (3) | 0.0263 (10) |
| O11 | 1.0796 (5) | 0.8564 (3) | 0.7182 (3) | 0.0357 (11) |
| O12 | 1.1132 (4) | 1.0743 (2) | 0.9091 (3) | 0.0196 (9) |
| O13 | 0.5753 (5) | 0.9180 (3) | 0.8055 (3) | 0.0356 (11) |

supplementary materials

| | | | | |
|------|------------|------------|------------|-------------|
| O14 | 0.8326 (4) | 0.8887 (2) | 0.7676 (3) | 0.0257 (10) |
| N1 | 0.4744 (8) | 0.6382 (4) | 0.4937 (6) | 0.075 (3) |
| H1A | 0.4151 | 0.6036 | 0.4825 | 0.090* |
| H1B | 0.5513 | 0.6357 | 0.4713 | 0.090* |
| N2 | 0.3280 (5) | 0.6980 (3) | 0.5806 (4) | 0.0319 (13) |
| H2A | 0.2685 | 0.6638 | 0.5665 | 0.038* |
| N3 | 0.8180 (6) | 0.7312 (3) | 0.7329 (4) | 0.0397 (15) |
| H3A | 0.8710 | 0.7189 | 0.6922 | 0.048* |
| H3B | 0.8259 | 0.7738 | 0.7591 | 0.048* |
| N4 | 0.7146 (5) | 0.6182 (3) | 0.7122 (4) | 0.0301 (13) |
| H4A | 0.7710 | 0.6077 | 0.6730 | 0.036* |
| C1 | 0.4480 (7) | 0.6944 (4) | 0.5460 (5) | 0.0361 (17) |
| C2 | 0.5431 (7) | 0.7514 (4) | 0.5687 (5) | 0.0387 (18) |
| H2 | 0.6274 | 0.7507 | 0.5459 | 0.046* |
| C3 | 0.5103 (8) | 0.8073 (4) | 0.6245 (6) | 0.0442 (19) |
| H3 | 0.5722 | 0.8456 | 0.6388 | 0.053* |
| C4 | 0.3861 (7) | 0.8082 (4) | 0.6606 (6) | 0.0424 (19) |
| H4 | 0.3651 | 0.8458 | 0.7003 | 0.051* |
| C5 | 0.2971 (7) | 0.7535 (4) | 0.6369 (5) | 0.0355 (17) |
| H5 | 0.2127 | 0.7538 | 0.6597 | 0.043* |
| C6 | 0.7244 (7) | 0.6848 (4) | 0.7549 (5) | 0.0291 (15) |
| C7 | 0.6326 (7) | 0.7000 (4) | 0.8184 (5) | 0.0418 (19) |
| H7 | 0.6362 | 0.7453 | 0.8489 | 0.050* |
| C8 | 0.5373 (7) | 0.6501 (5) | 0.8361 (5) | 0.045 (2) |
| H8 | 0.4777 | 0.6604 | 0.8798 | 0.054* |
| C9 | 0.5284 (8) | 0.5829 (5) | 0.7885 (6) | 0.048 (2) |
| H9 | 0.4607 | 0.5490 | 0.7979 | 0.057* |
| C10 | 0.6201 (7) | 0.5680 (4) | 0.7286 (5) | 0.0387 (18) |
| H10 | 0.6179 | 0.5226 | 0.6983 | 0.046* |
| N5 | 0.9609 (7) | 0.6459 (4) | 0.9265 (5) | 0.0518 (18) |
| H5A | 0.9958 | 0.6421 | 0.8746 | 0.062* |
| H5B | 0.9708 | 0.6859 | 0.9587 | 0.062* |
| N6 | 0.8778 (6) | 0.5280 (3) | 0.9057 (4) | 0.0324 (13) |
| H6 | 0.9138 | 0.5261 | 0.8540 | 0.039* |
| C11 | 0.8923 (7) | 0.5903 (4) | 0.9568 (5) | 0.0301 (15) |
| C12 | 0.8313 (8) | 0.5922 (4) | 1.0402 (5) | 0.0388 (18) |
| H12 | 0.8382 | 0.6344 | 1.0773 | 0.047* |
| C13 | 0.7629 (8) | 0.5333 (5) | 1.0668 (5) | 0.049 (2) |
| H13 | 0.7232 | 0.5351 | 1.1224 | 0.058* |
| C14 | 0.7509 (9) | 0.4700 (5) | 1.0124 (6) | 0.052 (2) |
| H14 | 0.7034 | 0.4293 | 1.0305 | 0.062* |
| C15 | 0.8107 (8) | 0.4690 (4) | 0.9313 (6) | 0.046 (2) |
| H15 | 0.8048 | 0.4270 | 0.8939 | 0.055* |
| O15 | 0.2400 (7) | 0.7219 (4) | 0.8838 (5) | 0.083 (2) |
| H15A | 0.1820 | 0.7567 | 0.8795 | 0.125* |
| H15B | 0.1917 | 0.6976 | 0.8409 | 0.125* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|--------------|--------------|--------------|
| V1 | 0.0254 (6) | 0.0199 (6) | 0.0200 (6) | -0.0005 (4) | 0.0013 (4) | 0.0038 (4) |
| V2 | 0.0268 (6) | 0.0164 (5) | 0.0237 (6) | -0.0012 (4) | 0.0038 (5) | 0.0001 (4) |
| V3 | 0.0308 (6) | 0.0240 (6) | 0.0242 (6) | -0.0007 (5) | 0.0068 (5) | -0.0047 (5) |
| V4 | 0.0211 (5) | 0.0193 (5) | 0.0223 (6) | 0.0022 (4) | 0.0047 (4) | 0.0013 (4) |
| V5 | 0.0229 (6) | 0.0272 (6) | 0.0238 (6) | -0.0033 (5) | 0.0008 (5) | -0.0018 (5) |
| O1 | 0.019 (2) | 0.018 (2) | 0.020 (2) | -0.0005 (16) | 0.0022 (17) | 0.0005 (17) |
| O2 | 0.022 (2) | 0.018 (2) | 0.021 (2) | 0.0030 (17) | 0.0057 (17) | 0.0021 (17) |
| O3 | 0.025 (2) | 0.028 (2) | 0.024 (2) | 0.0028 (18) | -0.0015 (19) | 0.0031 (19) |
| O4 | 0.019 (2) | 0.028 (2) | 0.031 (3) | 0.0003 (18) | 0.0050 (18) | 0.0031 (19) |
| O5 | 0.023 (2) | 0.027 (2) | 0.030 (3) | 0.0042 (18) | 0.0085 (19) | -0.0017 (19) |
| O6 | 0.034 (2) | 0.016 (2) | 0.029 (3) | 0.0033 (18) | 0.008 (2) | -0.0041 (18) |
| O7 | 0.032 (2) | 0.029 (3) | 0.030 (3) | -0.001 (2) | 0.003 (2) | 0.008 (2) |
| O8 | 0.032 (2) | 0.024 (2) | 0.018 (2) | -0.0013 (19) | 0.0040 (18) | -0.0012 (18) |
| O9 | 0.044 (3) | 0.022 (2) | 0.027 (3) | -0.005 (2) | 0.006 (2) | 0.0011 (19) |
| O10 | 0.030 (2) | 0.022 (2) | 0.028 (3) | -0.0047 (19) | 0.0069 (19) | -0.0013 (19) |
| O11 | 0.048 (3) | 0.033 (3) | 0.028 (3) | -0.001 (2) | 0.014 (2) | -0.005 (2) |
| O12 | 0.024 (2) | 0.017 (2) | 0.019 (2) | -0.0020 (17) | 0.0035 (17) | 0.0010 (17) |
| O13 | 0.031 (3) | 0.040 (3) | 0.033 (3) | 0.000 (2) | -0.006 (2) | -0.003 (2) |
| O14 | 0.032 (2) | 0.021 (2) | 0.023 (2) | -0.0006 (19) | 0.0014 (19) | -0.0029 (18) |
| N1 | 0.053 (4) | 0.072 (6) | 0.109 (7) | -0.026 (4) | 0.043 (4) | -0.056 (5) |
| N2 | 0.026 (3) | 0.032 (3) | 0.038 (4) | -0.011 (2) | 0.005 (3) | -0.013 (3) |
| N3 | 0.040 (3) | 0.034 (3) | 0.047 (4) | -0.002 (3) | 0.013 (3) | -0.013 (3) |
| N4 | 0.025 (3) | 0.036 (3) | 0.032 (3) | 0.002 (2) | 0.011 (2) | -0.002 (3) |
| C1 | 0.033 (4) | 0.040 (4) | 0.037 (4) | -0.005 (3) | 0.008 (3) | -0.009 (3) |
| C2 | 0.032 (4) | 0.049 (5) | 0.036 (4) | -0.018 (3) | 0.008 (3) | 0.002 (4) |
| C3 | 0.039 (4) | 0.033 (4) | 0.058 (5) | -0.017 (3) | -0.003 (4) | -0.001 (4) |
| C4 | 0.037 (4) | 0.031 (4) | 0.057 (5) | 0.001 (3) | 0.000 (4) | -0.012 (4) |
| C5 | 0.035 (4) | 0.031 (4) | 0.041 (4) | -0.002 (3) | 0.006 (3) | -0.002 (3) |
| C6 | 0.027 (3) | 0.033 (4) | 0.027 (4) | 0.005 (3) | -0.001 (3) | 0.000 (3) |
| C7 | 0.036 (4) | 0.048 (5) | 0.042 (5) | 0.012 (4) | 0.010 (4) | -0.014 (4) |
| C8 | 0.030 (4) | 0.067 (6) | 0.042 (5) | 0.001 (4) | 0.019 (3) | -0.010 (4) |
| C9 | 0.040 (4) | 0.049 (5) | 0.057 (5) | -0.013 (4) | 0.015 (4) | -0.010 (4) |
| C10 | 0.045 (4) | 0.032 (4) | 0.038 (4) | -0.008 (3) | 0.003 (4) | -0.014 (3) |
| N5 | 0.068 (5) | 0.035 (4) | 0.054 (5) | -0.001 (3) | 0.016 (4) | -0.005 (3) |
| N6 | 0.039 (3) | 0.037 (3) | 0.022 (3) | 0.008 (3) | 0.008 (3) | -0.008 (3) |
| C11 | 0.027 (3) | 0.037 (4) | 0.024 (4) | 0.011 (3) | -0.008 (3) | -0.005 (3) |
| C12 | 0.049 (5) | 0.044 (5) | 0.024 (4) | 0.016 (4) | 0.008 (3) | -0.006 (3) |
| C13 | 0.051 (5) | 0.066 (6) | 0.033 (5) | 0.007 (4) | 0.019 (4) | -0.001 (4) |
| C14 | 0.056 (5) | 0.051 (5) | 0.052 (5) | -0.009 (4) | 0.021 (4) | 0.003 (4) |
| C15 | 0.056 (5) | 0.036 (4) | 0.047 (5) | -0.004 (4) | 0.009 (4) | -0.014 (4) |
| O15 | 0.062 (4) | 0.098 (6) | 0.086 (5) | 0.022 (4) | -0.004 (4) | -0.013 (4) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|-------|-----------|--------|--------|
| V1—O7 | 1.616 (4) | N2—H2A | 0.8600 |
|-------|-----------|--------|--------|

supplementary materials

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|---------------------|-------------|------------------------|-------------|
| V1—O3 | 1.767 (4) | N3—C6 | 1.316 (9) |
| V1—O8 | 1.842 (4) | N3—H3A | 0.8600 |
| V1—O2 | 1.991 (4) | N3—H3B | 0.8599 |
| V1—O12 | 2.038 (4) | N4—C10 | 1.345 (9) |
| V1—O1 | 2.250 (4) | N4—C6 | 1.353 (8) |
| V2—O9 | 1.608 (4) | N4—H4A | 0.8599 |
| V2—O6 | 1.794 (4) | C1—C2 | 1.405 (9) |
| V2—O10 | 1.823 (4) | C2—C3 | 1.357 (11) |
| V2—O12 ⁱ | 2.015 (4) | C2—H2 | 0.9299 |
| V2—O2 ⁱ | 2.017 (4) | C3—C4 | 1.387 (11) |
| V2—O1 | 2.243 (4) | C3—H3 | 0.9300 |
| V3—O11 | 1.594 (4) | C4—C5 | 1.339 (10) |
| V3—O14 | 1.827 (4) | C4—H4 | 0.9300 |
| V3—O8 | 1.871 (4) | C5—H5 | 0.9300 |
| V3—O6 | 1.891 (4) | C6—C7 | 1.389 (9) |
| V3—O5 | 2.045 (4) | C7—C8 | 1.352 (11) |
| V3—O1 | 2.305 (4) | C7—H7 | 0.9300 |
| V4—O4 | 1.676 (4) | C8—C9 | 1.396 (11) |
| V4—O5 ⁱ | 1.680 (4) | C8—H8 | 0.9300 |
| V4—O12 ⁱ | 1.921 (4) | C9—C10 | 1.349 (10) |
| V4—O2 | 1.953 (4) | C9—H9 | 0.9300 |
| V4—O1 ⁱ | 2.097 (4) | C10—H10 | 0.9300 |
| V4—O1 | 2.111 (4) | N5—C11 | 1.319 (9) |
| V5—O13 | 1.590 (5) | N5—H5A | 0.8600 |
| V5—O14 | 1.835 (4) | N5—H5B | 0.8601 |
| V5—O10 | 1.864 (4) | N6—C15 | 1.335 (9) |
| V5—O3 | 1.881 (4) | N6—C11 | 1.346 (8) |
| V5—O4 | 2.045 (4) | N6—H6 | 0.8600 |
| V5—O1 | 2.318 (4) | C11—C12 | 1.403 (9) |
| O1—V4 ⁱ | 2.097 (4) | C12—C13 | 1.346 (11) |
| O2—V2 ⁱ | 2.017 (4) | C12—H12 | 0.9300 |
| O5—V4 ⁱ | 1.680 (4) | C13—C14 | 1.386 (11) |
| O12—V4 ⁱ | 1.921 (4) | C13—H13 | 0.9300 |
| O12—V2 ⁱ | 2.015 (4) | C14—C15 | 1.366 (11) |
| N1—C1 | 1.312 (9) | C14—H14 | 0.9300 |
| N1—H1A | 0.8599 | C15—H15 | 0.9300 |
| N1—H1B | 0.8600 | O15—H15A | 0.8499 |
| N2—C1 | 1.339 (8) | O15—H15B | 0.8496 |
| N2—C5 | 1.350 (8) | | |
| O7—V1—O3 | 104.4 (2) | V1—O1—V3 | 85.95 (14) |
| O7—V1—O8 | 101.4 (2) | V4 ⁱ —O1—V5 | 170.8 (2) |
| O3—V1—O8 | 95.96 (19) | V4—O1—V5 | 87.36 (14) |
| O7—V1—O2 | 100.7 (2) | V2—O1—V5 | 85.25 (13) |
| O3—V1—O2 | 91.58 (18) | V1—O1—V5 | 85.16 (14) |
| O8—V1—O2 | 154.05 (18) | V3—O1—V5 | 83.19 (13) |
| O7—V1—O12 | 98.8 (2) | V4—O2—V1 | 107.04 (19) |

| | | | |
|--------------------------------------|-------------|--------------------------------------|-------------|
| O3—V1—O12 | 155.27 (18) | V4—O2—V2 ⁱ | 106.87 (19) |
| O8—V1—O12 | 87.81 (17) | V1—O2—V2 ⁱ | 101.98 (17) |
| O2—V1—O12 | 75.49 (16) | V1—O3—V5 | 115.8 (2) |
| O7—V1—O1 | 173.8 (2) | V4—O4—V5 | 110.3 (2) |
| O3—V1—O1 | 81.16 (17) | V4 ⁱ —O5—V3 | 109.7 (2) |
| O8—V1—O1 | 80.48 (16) | V2—O6—V3 | 114.8 (2) |
| O2—V1—O1 | 76.19 (15) | V1—O8—V3 | 113.5 (2) |
| O12—V1—O1 | 75.36 (15) | V2—O10—V5 | 113.8 (2) |
| O9—V2—O6 | 102.8 (2) | V4 ⁱ —O12—V2 ⁱ | 107.03 (18) |
| O9—V2—O10 | 103.1 (2) | V4 ⁱ —O12—V1 | 106.72 (18) |
| O6—V2—O10 | 96.7 (2) | V2 ⁱ —O12—V1 | 100.42 (17) |
| O9—V2—O12 ⁱ | 99.71 (19) | V3—O14—V5 | 113.9 (2) |
| O6—V2—O12 ⁱ | 154.72 (18) | C1—N1—H1A | 119.8 |
| O10—V2—O12 ⁱ | 89.15 (18) | C1—N1—H1B | 120.1 |
| O9—V2—O2 ⁱ | 99.5 (2) | H1A—N1—H1B | 120.0 |
| O6—V2—O2 ⁱ | 89.59 (18) | C1—N2—C5 | 122.3 (6) |
| O10—V2—O2 ⁱ | 154.54 (18) | C1—N2—H2A | 119.0 |
| O12 ⁱ —V2—O2 ⁱ | 75.43 (16) | C5—N2—H2A | 118.7 |
| O9—V2—O1 | 173.9 (2) | C6—N3—H3A | 120.0 |
| O6—V2—O1 | 80.77 (17) | C6—N3—H3B | 120.0 |
| O10—V2—O1 | 81.23 (16) | H3A—N3—H3B | 120.0 |
| O12 ⁱ —V2—O1 | 75.85 (15) | C10—N4—C6 | 122.6 (6) |
| O2 ⁱ —V2—O1 | 75.47 (15) | C10—N4—H4A | 118.8 |
| O11—V3—O14 | 103.0 (2) | C6—N4—H4A | 118.6 |
| O11—V3—O8 | 102.3 (2) | N1—C1—N2 | 119.8 (7) |
| O14—V3—O8 | 92.79 (19) | N1—C1—C2 | 122.0 (7) |
| O11—V3—O6 | 101.5 (2) | N2—C1—C2 | 118.1 (6) |
| O14—V3—O6 | 90.05 (19) | C3—C2—C1 | 119.1 (7) |
| O8—V3—O6 | 154.81 (18) | C3—C2—H2 | 120.5 |
| O11—V3—O5 | 100.7 (2) | C1—C2—H2 | 120.4 |
| O14—V3—O5 | 156.20 (18) | C2—C3—C4 | 121.0 (7) |
| O8—V3—O5 | 84.18 (18) | C2—C3—H3 | 119.4 |
| O6—V3—O5 | 83.21 (18) | C4—C3—H3 | 119.6 |
| O11—V3—O1 | 175.1 (2) | C5—C4—C3 | 118.5 (7) |
| O14—V3—O1 | 81.71 (16) | C5—C4—H4 | 120.8 |
| O8—V3—O1 | 78.46 (16) | C3—C4—H4 | 120.8 |
| O6—V3—O1 | 77.20 (16) | C4—C5—N2 | 121.0 (7) |
| O5—V3—O1 | 74.55 (15) | C4—C5—H5 | 119.5 |
| O4—V4—O5 ⁱ | 105.8 (2) | N2—C5—H5 | 119.5 |
| O4—V4—O12 ⁱ | 97.83 (19) | N3—C6—N4 | 118.4 (6) |
| O5 ⁱ —V4—O12 ⁱ | 98.45 (19) | N3—C6—C7 | 124.3 (7) |
| O4—V4—O2 | 96.17 (19) | N4—C6—C7 | 117.3 (6) |
| O5 ⁱ —V4—O2 | 96.12 (19) | C8—C7—C6 | 120.9 (7) |
| O12 ⁱ —V4—O2 | 156.20 (17) | C8—C7—H7 | 119.4 |
| O4—V4—O1 ⁱ | 166.03 (18) | C6—C7—H7 | 119.7 |

supplementary materials

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|--------------------------------------|-------------|---------------|-----------|
| O5 ⁱ —V4—O1 ⁱ | 88.08 (18) | C7—C8—C9 | 119.9 (7) |
| O12 ⁱ —V4—O1 ⁱ | 81.50 (16) | C7—C8—H8 | 120.3 |
| O2—V4—O1 ⁱ | 80.29 (16) | C9—C8—H8 | 119.9 |
| O4—V4—O1 | 87.89 (18) | C10—C9—C8 | 118.7 (7) |
| O5 ⁱ —V4—O1 | 166.22 (19) | C10—C9—H9 | 120.7 |
| O12 ⁱ —V4—O1 | 81.02 (16) | C8—C9—H9 | 120.6 |
| O2—V4—O1 | 80.36 (16) | N4—C10—C9 | 120.5 (7) |
| O1 ⁱ —V4—O1 | 78.21 (17) | N4—C10—H10 | 119.7 |
| O13—V5—O14 | 104.4 (2) | C9—C10—H10 | 119.7 |
| O13—V5—O10 | 101.8 (2) | C11—N5—H5A | 120.0 |
| O14—V5—O10 | 91.43 (19) | C11—N5—H5B | 120.0 |
| O13—V5—O3 | 102.0 (2) | H5A—N5—H5B | 120.0 |
| O14—V5—O3 | 90.73 (19) | C15—N6—C11 | 123.3 (6) |
| O10—V5—O3 | 154.79 (19) | C15—N6—H6 | 118.4 |
| O13—V5—O4 | 100.0 (2) | C11—N6—H6 | 118.3 |
| O14—V5—O4 | 155.60 (18) | N5—C11—N6 | 119.3 (6) |
| O10—V5—O4 | 83.94 (18) | N5—C11—C12 | 123.6 (7) |
| O3—V5—O4 | 83.79 (18) | N6—C11—C12 | 117.1 (7) |
| O13—V5—O1 | 174.4 (2) | C13—C12—C11 | 120.4 (7) |
| O14—V5—O1 | 81.21 (17) | C13—C12—H12 | 119.8 |
| O10—V5—O1 | 78.41 (16) | C11—C12—H12 | 119.8 |
| O3—V5—O1 | 77.12 (16) | C12—C13—C14 | 120.8 (7) |
| O4—V5—O1 | 74.39 (15) | C12—C13—H13 | 119.6 |
| V4 ⁱ —O1—V4 | 101.79 (16) | C14—C13—H13 | 119.6 |
| V4 ⁱ —O1—V2 | 94.50 (15) | C15—C14—C13 | 118.2 (8) |
| V4—O1—V2 | 93.22 (15) | C15—C14—H14 | 120.9 |
| V4 ⁱ —O1—V1 | 93.87 (15) | C13—C14—H14 | 120.9 |
| V4—O1—V1 | 93.23 (15) | N6—C15—C14 | 120.3 (7) |
| V2—O1—V1 | 168.2 (2) | N6—C15—H15 | 119.9 |
| V4 ⁱ —O1—V3 | 87.65 (14) | C14—C15—H15 | 119.9 |
| V4—O1—V3 | 170.6 (2) | H15A—O15—H15B | 91.4 |
| V2—O1—V3 | 86.07 (14) | | |

Symmetry codes: (i) $-x+2, -y+2, -z+2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| N1—H1A \cdots O4 ⁱⁱ | 0.86 | 2.44 | 3.217 (9) | 150 |
| N1—H1A \cdots O5 ⁱⁱⁱ | 0.86 | 2.55 | 3.286 (8) | 144 |
| N1—H1B \cdots O10 ^{iv} | 0.86 | 2.21 | 3.058 (8) | 169 |
| N2—H2A \cdots O2 ⁱⁱ | 0.86 | 1.85 | 2.697 (7) | 168 |
| N3—H3A \cdots O9 ^{iv} | 0.86 | 2.17 | 2.969 (7) | 155 |
| N3—H3A \cdots O7 ^v | 0.86 | 2.48 | 3.017 (7) | 122 |
| N3—H3B \cdots O14 | 0.86 | 2.09 | 2.908 (7) | 158 |
| N4—H4A \cdots O12 ^v | 0.86 | 1.84 | 2.698 (6) | 174 |

| | | | | |
|-----------------------------|------|------|-----------|-----|
| N5—H5A···O7 ^v | 0.86 | 2.23 | 3.085 (8) | 175 |
| N5—H5B···O9 | 0.86 | 2.22 | 3.057 (8) | 164 |
| N6—H6···O8 ^v | 0.86 | 1.87 | 2.709 (7) | 166 |
| O15—H15A···O6 ^{vi} | 0.85 | 2.09 | 2.926 (8) | 166 |
| O15—H15B···O7 ⁱⁱ | 0.85 | 2.13 | 2.977 (8) | 180 |

Symmetry codes: (ii) $-x+1, y-1/2, -z+3/2$; (iii) $x-1, -y+3/2, z-1/2$; (iv) $x, -y+3/2, z-1/2$; (v) $-x+2, y-1/2, -z+3/2$; (vi) $x-1, y, z$.

Fig. 1

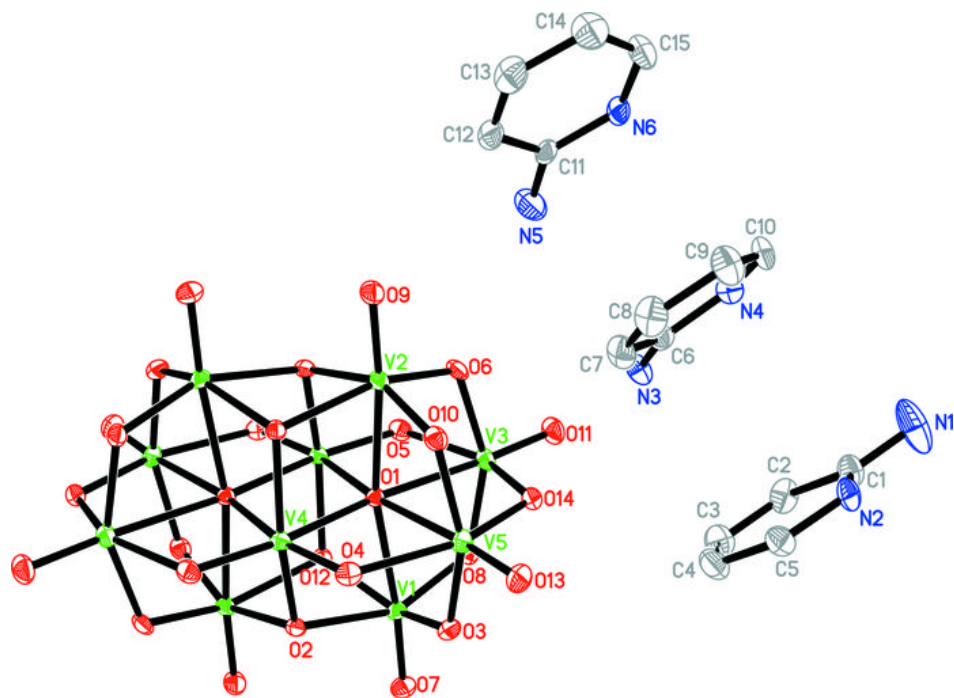


Fig. 2

