

Poly[4,4'-iminodipyridinium [tetra- μ_3 -oxido-tetraoxido-di- μ_4 -phosphato- κ^4 O:O':O'':O''']-tetravanadium(V)]

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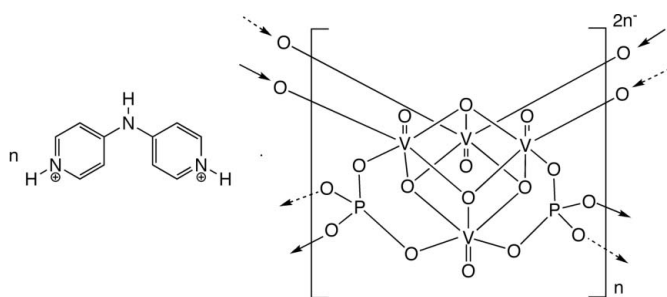
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 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.038; wR factor = 0.101; data-to-parameter ratio = 14.3.

In the title salt, $\{(\text{C}_{10}\text{H}_{11}\text{N}_3)[\text{V}_4\text{O}_8(\text{PO}_4)_2]\}_n$, cubane-like $[\text{V}_4\text{O}_8]^{4+}$ clusters are connected by phosphate anions into anionic $[\text{V}_4\text{P}_2\text{O}_{16}]^{2n-}$ layers. These aggregate into the three-dimensional structure *via* $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding mechanisms imparted by 4,4'-iminodipyridinium dications situated between the layers.

Related literature

For a nickel vanadate phase incorporating 4,4'-dipyridylamine, see: LaDuca *et al.* (2001). For a related layered vanadium phosphate solid containing doubly protonated 4,4'-bipyridine cations, see: Shi *et al.* (2004).



Experimental

Crystal data

 $(\text{C}_{10}\text{H}_{11}\text{N}_3)[\text{V}_4\text{O}_8(\text{PO}_4)_2]$
 $M_r = 694.92$

 Monoclinic, $P2_1/n$
 $a = 7.4431$ (10) Å

 $b = 14.524$ (2) Å
 $c = 18.825$ (3) Å
 $\beta = 94.363$ (2)°
 $V = 2029.1$ (5) Å³
 $Z = 4$

 Mo $K\alpha$ radiation
 $\mu = 2.04$ mm⁻¹
 $T = 173$ (2) K
 $0.20 \times 0.20 \times 0.04$ mm

Data collection

 Bruker SMART 1K diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.786$, $T_{\max} = 0.922$

 21687 measured reflections
 4652 independent reflections
 3678 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.101$
 $S = 1.09$
 4652 reflections
 325 parameters
 3 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 1.03$ e Å⁻³
 $\Delta\rho_{\min} = -0.76$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1N}\cdots\text{O10}$	0.93 (4)	2.14 (4)	2.885 (4)	136 (4)
$\text{N1}-\text{H1N}\cdots\text{O9}^i$	0.93 (4)	2.45 (4)	3.018 (5)	119 (4)
$\text{N2}-\text{H2N}\cdots\text{O2}^{ii}$	0.862 (19)	2.35 (2)	3.195 (4)	166 (4)
$\text{N3}-\text{H3N}\cdots\text{O8}^{iii}$	0.90 (5)	2.02 (5)	2.902 (4)	164 (4)

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *CrystalMaker* (Palmer, 2007); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2326).

References

- Bruker (2003). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- LaDuca, R. L., Rarig, R. S. & Zubieta, J. (2001). *Inorg. Chem.* **40**, 607–612.
- Palmer, D. (2007). *CrystalMaker*. CrystalMaker Software Ltd, Bicester, Oxfordshire, England.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Shi, F.-N., Paz, F. A. A., Rocha, J., Klinowski, J. & Trindade, T. (2004). *Eur. J. Inorg. Chem.* pp.3031–3037.

supplementary materials

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Poly[4,4'-iminodipyridinium [tetra- μ_3 -oxido-tetraoxido-di- μ_4 -phosphato- $\kappa^4 O:O':O'':O'''$ -tetravanadium(V)]]

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Comment

The kinked and hydrogen-bonding capable imine 4,4'-dipyridylamine has proven useful in the construction of novel mixed metal oxide phases (LaDuca *et al.*, 2001). In an attempt to extend this chemistry into a metal phosphate oxide system, yellow plate-like crystals of the title compound (I) were obtained.

The asymmetric unit of (I) comprises a cluster of four pentavalent V atoms, four terminal O atoms, four triply bridging O atoms, two phosphate anions and an unligated 4,4'-iminodipyridinium dication (Fig. 1). Each V atom is octahedrally coordinated, with three μ_3 O atom donors, two O atoms from two different phosphate anions, and one terminal O atom with a formal V=O double bond. The four V=O groups and four μ_3 O atoms form a cubane-type $[V_4O_8]^{4+}$ cluster.

Quadruply bridging phosphate anions bridge these cationic clusters into anionic $[V_4O_8(PO_4)_2]_n^{2n-}$ layers that are situated parallel to the *bc*-planes (Fig. 2). The phosphate groups bracket rhomboid apertures within the layers, with through-space P...P contact distances of 7.2685 (2) and 7.4431 (2) Å. Adjacent $[V_4O_8(PO_4)_2]_n^{2n-}$ layers stack in an *AB* pattern into the 3-D structure by N—H...O hydrogen bonding mediated by the protonated pyridyl-N atoms and the central amine groups of the 4,4'-iminodipyridinium cations situated in the interlamellar regions (Fig. 3).

The overall structure of (I) is very similar to a related phase incorporating doubly protonated 4,4'-bipyridine cations (Shi *et al.*, 2004).

Experimental

All chemicals were obtained commercially. Vanadium(V) oxide (140 mg, 0.77 mmol) and 4,4'-dipyridylamine (132 mg, 0.77 mmol) and phosphoric acid (526 mg of an 85.5% aqueous solution, 4.56 mmol) were placed into H₂O (10 ml) in a 23 ml Teflon-lined Parr acid digestion bomb. The bomb was heated at 393 K for 72 h and was then allowed to cool to room temperature. Yellow plates of (I) were obtained along with a reddish-brown amorphous solid.

Refinement

All H atoms bound to C atoms were placed in calculated positions with C—H = 0.95 Å and refined in riding mode with $U_{iso} = 1.2U_{eq}(C)$. All H atoms bound to N atoms were found *via* Fourier difference map, restrained with N—H = 0.89 Å, and refined with $U_{iso} = 1.2U_{eq}(N)$. The largest residual electron density peak of 1.03 e⁻ Å⁻³ was located 2.25 Å from the H2 atom.

Figures



Fig. 1. Asymmetric unit of (I), showing 50% probability ellipsoids and atom numbering scheme. Most H atom positions are shown as gray sticks. Color code: dark blue V, violet P, light blue N, red O, black C, pink H.

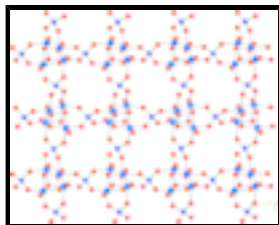


Fig. 2. A single $[V_4P_2O_{16}]_n^{2n-}$ layer in (I).

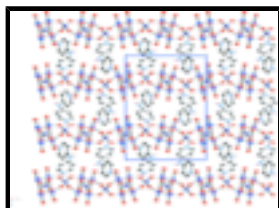


Fig. 3. Packing diagram illustrating the *ABAB* layer stacking pattern, which forms the 3-D crystal structure of (I) through hydrogen bonding between the inorganic layers and 4,4'-iminodipyridinium cations.

Poly[4,4'-iminodipyridinium [tetra- μ_3 -oxido-tetraoxidodi- μ_4 -phosphato- $\kappa^4 O:O':O'':O'''$ -tetravanadium(V)]]

Crystal data

(C₁₀H₁₁N₃)[V₄O₈(PO₄)₂]

$M_r = 694.92$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 7.4431 (10) \text{ \AA}$

$b = 14.524 (2) \text{ \AA}$

$c = 18.825 (3) \text{ \AA}$

$\beta = 94.363 (2)^\circ$

$V = 2029.1 (5) \text{ \AA}^3$

$Z = 4$

$F_{000} = 1368$

$D_x = 2.275 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 21687 reflections

$\theta = 1.8\text{--}28.2^\circ$

$\mu = 2.04 \text{ mm}^{-1}$

$T = 173 (2) \text{ K}$

Plate, yellow

$0.20 \times 0.20 \times 0.04 \text{ mm}$

Data collection

Bruker SMART 1K
diffractometer

4652 independent reflections

Radiation source: fine-focus sealed tube

3678 reflections with $I > 2\sigma(I)$

Monochromator: graphite

$R_{\text{int}} = 0.047$

$T = 173(2) \text{ K}$

$\theta_{\text{max}} = 28.2^\circ$

ω scans

$\theta_{\text{min}} = 1.8^\circ$

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$h = -9 \rightarrow 9$

$T_{\text{min}} = 0.786$, $T_{\text{max}} = 0.922$

$k = -19 \rightarrow 19$

21687 measured reflections

$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 6.7132P]$
$S = 1.09$	where $P = (F_o^2 + 2F_c^2)/3$
4652 reflections	$(\Delta/\sigma)_{\max} = 0.001$
325 parameters	$\Delta\rho_{\max} = 1.03 \text{ e } \text{\AA}^{-3}$
3 restraints	$\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	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	0.62200 (8)	0.45521 (4)	0.16868 (3)	0.00774 (14)
V2	0.65671 (8)	0.54528 (4)	0.33252 (3)	0.00778 (14)
V3	0.91535 (8)	0.41272 (4)	0.30933 (3)	0.00822 (14)
V4	0.89067 (8)	0.58608 (4)	0.19276 (3)	0.00808 (14)
P1	0.27074 (12)	0.50073 (6)	0.25058 (5)	0.00875 (19)
P2	0.74459 (12)	0.25121 (6)	0.21337 (5)	0.00750 (19)
O1	0.6496 (4)	0.53003 (17)	0.41627 (14)	0.0146 (6)
O2	0.5880 (3)	0.47775 (17)	0.08568 (14)	0.0141 (6)
O3	0.9438 (4)	0.38002 (18)	0.38988 (14)	0.0157 (6)
O4	0.3769 (3)	0.45212 (17)	0.19477 (14)	0.0117 (5)
O5	0.8869 (3)	0.62016 (17)	0.11231 (14)	0.0144 (5)
O6	0.6464 (3)	0.57326 (16)	0.20696 (13)	0.0093 (5)
O7	0.6413 (3)	0.32294 (16)	0.16610 (13)	0.0095 (5)
O8	0.6626 (3)	0.42384 (16)	0.29886 (13)	0.0093 (5)
O9	0.3989 (3)	0.54901 (17)	0.30680 (14)	0.0115 (5)
O10	0.8333 (3)	0.18063 (16)	0.16577 (13)	0.0093 (5)

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O11	0.8977 (3)	0.29677 (16)	0.26015 (14)	0.0101 (5)
O12	0.6105 (3)	0.20382 (16)	0.25905 (14)	0.0104 (5)
O13	0.8962 (3)	0.54013 (16)	0.31834 (14)	0.0095 (5)
O14	0.1453 (3)	0.57446 (16)	0.21577 (14)	0.0114 (5)
O15	0.1609 (3)	0.42794 (16)	0.28734 (14)	0.0121 (5)
O16	0.8712 (3)	0.46004 (16)	0.18407 (13)	0.0096 (5)
N1	1.1851 (5)	0.2291 (3)	0.1230 (2)	0.0247 (8)
H1N	1.113 (5)	0.212 (3)	0.1588 (19)	0.030*
N2	1.5138 (4)	0.3207 (2)	-0.02781 (18)	0.0157 (7)
H2N	1.481 (6)	0.370 (2)	-0.050 (2)	0.019*
N3	1.9274 (4)	0.1840 (2)	-0.11738 (19)	0.0161 (7)
H3N	2.016 (6)	0.152 (3)	-0.136 (2)	0.019*
C1	1.1673 (5)	0.3154 (3)	0.0975 (2)	0.0215 (9)
H1	1.0813	0.3544	0.1146	0.026*
C2	1.2741 (5)	0.3461 (3)	0.0469 (2)	0.0174 (8)
H2	1.2593	0.4054	0.0287	0.021*
C3	1.4072 (5)	0.2878 (3)	0.0223 (2)	0.0128 (7)
C4	1.4197 (5)	0.1975 (3)	0.0485 (2)	0.0180 (8)
H4	1.5027	0.1566	0.0317	0.022*
C5	1.3089 (6)	0.1704 (3)	0.0990 (2)	0.0223 (9)
H5	1.3182	0.1110	0.1172	0.027*
C6	1.9152 (5)	0.1759 (3)	-0.0472 (2)	0.0183 (8)
H6	1.9969	0.1389	-0.0205	0.022*
C7	1.7833 (5)	0.2217 (3)	-0.0142 (2)	0.0159 (8)
H7	1.7759	0.2167	0.0347	0.019*
C8	1.6598 (5)	0.2760 (2)	-0.0557 (2)	0.0133 (7)
C9	1.6813 (5)	0.2865 (2)	-0.1276 (2)	0.0128 (7)
H9	1.6058	0.3257	-0.1553	0.015*
C10	1.8149 (5)	0.2386 (2)	-0.1577 (2)	0.0142 (8)
H10	1.8279	0.2440	-0.2063	0.017*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.0072 (3)	0.0038 (3)	0.0120 (3)	0.0000 (2)	-0.0006 (2)	-0.0003 (2)
V2	0.0073 (3)	0.0036 (3)	0.0125 (3)	-0.0003 (2)	0.0011 (2)	-0.0002 (2)
V3	0.0071 (3)	0.0039 (3)	0.0134 (3)	0.0005 (2)	-0.0003 (2)	0.0008 (2)
V4	0.0074 (3)	0.0041 (3)	0.0128 (3)	-0.0002 (2)	0.0014 (2)	0.0002 (2)
P1	0.0057 (4)	0.0041 (4)	0.0165 (5)	0.0002 (3)	0.0008 (3)	-0.0012 (3)
P2	0.0070 (4)	0.0027 (4)	0.0130 (4)	0.0005 (3)	0.0012 (3)	-0.0002 (3)
O1	0.0196 (14)	0.0111 (13)	0.0135 (14)	-0.0002 (10)	0.0040 (11)	-0.0003 (10)
O2	0.0155 (13)	0.0113 (13)	0.0151 (14)	0.0003 (10)	-0.0013 (10)	0.0011 (10)
O3	0.0179 (14)	0.0113 (13)	0.0174 (15)	0.0027 (10)	-0.0014 (11)	0.0018 (10)
O4	0.0079 (12)	0.0092 (12)	0.0181 (14)	-0.0003 (10)	0.0007 (10)	-0.0043 (10)
O5	0.0172 (13)	0.0104 (13)	0.0160 (14)	-0.0013 (10)	0.0033 (11)	0.0007 (10)
O6	0.0069 (11)	0.0049 (11)	0.0159 (13)	0.0026 (9)	0.0003 (9)	-0.0015 (9)
O7	0.0102 (12)	0.0027 (11)	0.0155 (14)	0.0013 (9)	-0.0006 (10)	-0.0007 (9)
O8	0.0090 (12)	0.0044 (11)	0.0147 (13)	-0.0019 (9)	0.0021 (10)	-0.0006 (9)

O9	0.0069 (12)	0.0094 (12)	0.0183 (14)	-0.0010 (9)	0.0019 (10)	-0.0049 (10)
O10	0.0094 (12)	0.0039 (11)	0.0148 (14)	0.0007 (9)	0.0020 (10)	0.0005 (9)
O11	0.0084 (11)	0.0036 (11)	0.0180 (14)	0.0005 (9)	-0.0012 (10)	0.0002 (10)
O12	0.0095 (12)	0.0052 (11)	0.0171 (14)	0.0000 (9)	0.0046 (10)	0.0012 (10)
O13	0.0081 (12)	0.0030 (11)	0.0175 (14)	-0.0002 (9)	0.0005 (10)	-0.0013 (10)
O14	0.0076 (11)	0.0043 (11)	0.0229 (15)	-0.0003 (9)	0.0050 (10)	0.0035 (10)
O15	0.0080 (12)	0.0054 (12)	0.0227 (15)	0.0000 (9)	0.0004 (10)	0.0023 (10)
O16	0.0090 (12)	0.0043 (11)	0.0157 (13)	0.0016 (9)	0.0014 (10)	-0.0007 (10)
N1	0.0218 (19)	0.033 (2)	0.0203 (19)	-0.0092 (16)	0.0068 (15)	-0.0002 (16)
N2	0.0182 (16)	0.0098 (15)	0.0197 (18)	0.0021 (13)	0.0064 (13)	0.0039 (13)
N3	0.0143 (16)	0.0121 (16)	0.0224 (19)	-0.0020 (13)	0.0040 (14)	-0.0034 (13)
C1	0.0154 (19)	0.029 (2)	0.021 (2)	-0.0051 (17)	0.0042 (16)	-0.0103 (17)
C2	0.0147 (19)	0.017 (2)	0.021 (2)	-0.0027 (15)	0.0012 (15)	-0.0053 (16)
C3	0.0111 (17)	0.0165 (18)	0.0107 (18)	-0.0032 (15)	0.0006 (13)	-0.0017 (14)
C4	0.0168 (19)	0.018 (2)	0.019 (2)	-0.0013 (15)	0.0033 (16)	0.0012 (16)
C5	0.021 (2)	0.023 (2)	0.023 (2)	-0.0058 (17)	0.0041 (17)	0.0069 (17)
C6	0.0160 (19)	0.0130 (19)	0.025 (2)	-0.0007 (15)	-0.0037 (16)	0.0032 (16)
C7	0.0170 (19)	0.0152 (19)	0.015 (2)	-0.0017 (15)	0.0013 (15)	0.0018 (15)
C8	0.0133 (17)	0.0080 (17)	0.018 (2)	-0.0048 (14)	-0.0003 (15)	-0.0016 (14)
C9	0.0157 (18)	0.0069 (16)	0.0155 (19)	-0.0057 (14)	0.0001 (14)	0.0002 (14)
C10	0.0185 (19)	0.0073 (17)	0.0171 (19)	-0.0077 (14)	0.0030 (15)	-0.0013 (14)

Geometric parameters (Å, °)

V1—O2	1.598 (3)	P2—O11	1.536 (2)
V1—O16	1.857 (2)	P2—O7	1.538 (2)
V1—O6	1.863 (2)	P2—O10	1.543 (3)
V1—O4	1.925 (3)	N1—C1	1.345 (6)
V1—O7	1.927 (2)	N1—C5	1.357 (6)
V1—O8	2.488 (3)	N1—H1N	0.93 (4)
V2—O1	1.597 (3)	N2—C3	1.364 (5)
V2—O13	1.824 (2)	N2—C8	1.401 (5)
V2—O8	1.876 (2)	N2—H2N	0.862 (19)
V2—O9	1.944 (2)	N3—C6	1.336 (5)
V2—O10 ⁱ	1.967 (2)	N3—C10	1.346 (5)
V2—O6	2.394 (3)	N3—H3N	0.90 (5)
V3—O3	1.588 (3)	C1—C2	1.362 (6)
V3—O13	1.865 (2)	C1—H1	0.9300
V3—O8	1.883 (2)	C2—C3	1.408 (5)
V3—O15 ⁱⁱ	1.917 (3)	C2—H2	0.9300
V3—O11	1.921 (2)	C3—C4	1.402 (5)
V3—O16	2.454 (3)	C4—C5	1.363 (6)
V4—O5	1.592 (3)	C4—H4	0.9300
V4—O16	1.843 (2)	C5—H5	0.9300
V4—O6	1.867 (2)	C6—C7	1.373 (6)
V4—O14 ⁱⁱ	1.919 (2)	C6—H6	0.9300
V4—O12 ⁱ	1.936 (2)	C7—C8	1.404 (5)
V4—O13	2.454 (3)	C7—H7	0.9300

supplementary materials

P1—O15	1.533 (3)	C8—C9	1.384 (5)
P1—O4	1.534 (3)	C9—C10	1.371 (5)
P1—O14	1.535 (3)	C9—H9	0.9300
P1—O9	1.539 (3)	C10—H10	0.9300
P2—O12	1.529 (3)		
O2—V1—O16	103.13 (13)	O12—P2—O11	111.02 (15)
O2—V1—O6	101.14 (12)	O12—P2—O7	108.15 (14)
O16—V1—O6	80.68 (10)	O11—P2—O7	110.88 (13)
O2—V1—O4	99.88 (13)	O12—P2—O10	110.73 (14)
O16—V1—O4	156.29 (11)	O11—P2—O10	106.72 (14)
O6—V1—O4	89.38 (11)	O7—P2—O10	109.35 (14)
O2—V1—O7	100.73 (12)	P1—O4—V1	135.36 (15)
O16—V1—O7	88.06 (10)	V1—O6—V4	95.95 (11)
O6—V1—O7	157.17 (11)	V1—O6—V2	102.74 (11)
O4—V1—O7	93.27 (11)	V4—O6—V2	101.53 (10)
O2—V1—O8	177.48 (11)	P2—O7—V1	134.08 (15)
O16—V1—O8	78.94 (10)	V2—O8—V3	95.40 (11)
O6—V1—O8	77.68 (10)	V2—O8—V1	98.99 (10)
O4—V1—O8	77.93 (10)	V3—O8—V1	99.46 (10)
O7—V1—O8	80.71 (9)	P1—O9—V2	135.01 (16)
O1—V2—O13	104.17 (13)	P2—O10—V2 ⁱⁱⁱ	132.20 (15)
O1—V2—O8	101.92 (12)	P2—O11—V3	132.42 (15)
O13—V2—O8	82.17 (10)	P2—O12—V4 ⁱⁱⁱ	133.42 (15)
O1—V2—O9	98.26 (13)	V2—O13—V3	97.83 (11)
O13—V2—O9	157.22 (12)	V2—O13—V4	100.65 (10)
O8—V2—O9	89.43 (10)	V3—O13—V4	100.26 (11)
O1—V2—O10 ⁱ	97.26 (12)	P1—O14—V4 ^{iv}	135.73 (15)
O13—V2—O10 ⁱ	90.42 (10)	P1—O15—V3 ^{iv}	136.61 (15)
O8—V2—O10 ⁱ	160.60 (11)	V4—O16—V1	97.02 (11)
O9—V2—O10 ⁱ	90.66 (10)	V4—O16—V3	100.90 (11)
O1—V2—O6	175.87 (11)	V1—O16—V3	101.46 (11)
O13—V2—O6	79.67 (10)	C1—N1—C5	121.2 (4)
O8—V2—O6	79.97 (10)	C1—N1—H1N	118 (3)
O9—V2—O6	78.02 (10)	C5—N1—H1N	121 (3)
O10 ⁱ —V2—O6	81.07 (9)	C3—N2—C8	127.3 (3)
O3—V3—O13	102.45 (13)	C3—N2—H2N	118 (3)
O3—V3—O8	100.68 (13)	C8—N2—H2N	114 (3)
O13—V3—O8	80.90 (10)	C6—N3—C10	121.6 (3)
O3—V3—O15 ⁱⁱ	100.40 (13)	C6—N3—H3N	117 (3)
O13—V3—O15 ⁱⁱ	89.19 (11)	C10—N3—H3N	122 (3)
O8—V3—O15 ⁱⁱ	158.20 (11)	N1—C1—C2	120.5 (4)
O3—V3—O11	101.38 (12)	N1—C1—H1	119.7
O13—V3—O11	155.60 (11)	C2—C1—H1	119.7
O8—V3—O11	89.63 (10)	C1—C2—C3	119.7 (4)
O15 ⁱⁱ —V3—O11	91.63 (11)	C1—C2—H2	120.1
O3—V3—O16	178.86 (12)	C3—C2—H2	120.1

O13—V3—O16	78.69 (10)	N2—C3—C4	123.0 (3)
O8—V3—O16	79.38 (10)	N2—C3—C2	118.5 (4)
O15 ⁱⁱ —V3—O16	79.66 (10)	C4—C3—C2	118.4 (4)
O11—V3—O16	77.48 (10)	C5—C4—C3	119.2 (4)
O5—V4—O16	103.23 (13)	C5—C4—H4	120.4
O5—V4—O6	102.74 (13)	C3—C4—H4	120.4
O16—V4—O6	80.95 (10)	N1—C5—C4	120.8 (4)
O5—V4—O14 ⁱⁱ	100.81 (13)	N1—C5—H5	119.6
O16—V4—O14 ⁱⁱ	90.13 (10)	C4—C5—H5	119.6
O6—V4—O14 ⁱⁱ	156.16 (12)	N3—C6—C7	120.6 (4)
O5—V4—O12 ⁱ	99.84 (12)	N3—C6—H6	119.7
O16—V4—O12 ⁱ	156.34 (11)	C7—C6—H6	119.7
O6—V4—O12 ⁱ	88.95 (10)	C6—C7—C8	118.8 (4)
O14 ⁱⁱ —V4—O12 ⁱ	90.67 (11)	C6—C7—H7	120.6
O5—V4—O13	177.67 (11)	C8—C7—H7	120.6
O16—V4—O13	79.09 (10)	C9—C8—N2	117.8 (3)
O6—V4—O13	77.30 (10)	C9—C8—C7	119.1 (4)
O14 ⁱⁱ —V4—O13	79.32 (10)	N2—C8—C7	123.1 (4)
O12 ⁱ —V4—O13	77.83 (10)	C10—C9—C8	119.3 (4)
O15—P1—O4	108.18 (14)	C10—C9—H9	120.3
O15—P1—O14	110.24 (14)	C8—C9—H9	120.3
O4—P1—O14	110.92 (15)	N3—C10—C9	120.4 (4)
O15—P1—O9	109.13 (15)	N3—C10—H10	119.8
O4—P1—O9	110.85 (14)	C9—C10—H10	119.8
O14—P1—O9	107.51 (14)		
O15—P1—O4—V1	-133.2 (2)	O8—V3—O11—P2	15.9 (2)
O14—P1—O4—V1	105.7 (2)	O15 ⁱⁱ —V3—O11—P2	-142.4 (2)
O2—V1—O4—P1	-125.5 (2)	O16—V3—O11—P2	-63.3 (2)
O16—V1—O4—P1	40.4 (4)	O11—P2—O12—V4 ⁱⁱⁱ	-81.1 (2)
O6—V1—O4—P1	-24.3 (2)	O7—P2—O12—V4 ⁱⁱⁱ	157.06 (19)
O7—V1—O4—P1	133.0 (2)	O10—P2—O12—V4 ⁱⁱⁱ	37.3 (3)
O8—V1—O4—P1	53.2 (2)	O1—V2—O13—V3	85.66 (14)
O2—V1—O6—V4	-84.30 (13)	O8—V2—O13—V3	-14.73 (11)
O16—V1—O6—V4	17.36 (11)	O9—V2—O13—V3	-84.0 (3)
O4—V1—O6—V4	175.75 (12)	O10 ⁱ —V2—O13—V3	-176.74 (12)
O7—V1—O6—V4	78.8 (3)	O6—V2—O13—V3	-95.89 (11)
O8—V1—O6—V4	97.97 (11)	O1—V2—O13—V4	-172.29 (11)
O2—V1—O6—V2	172.42 (11)	O8—V2—O13—V4	87.33 (11)
O16—V1—O6—V2	-85.91 (11)	O9—V2—O13—V4	18.0 (3)
O4—V1—O6—V2	72.48 (11)	O10 ⁱ —V2—O13—V4	-74.69 (10)
O7—V1—O6—V2	-24.5 (3)	O6—V2—O13—V4	6.16 (8)
O8—V1—O6—V2	-5.31 (8)	O3—V3—O13—V2	-84.30 (14)
O5—V4—O6—V1	84.15 (13)	O8—V3—O13—V2	14.72 (11)
O16—V4—O6—V1	-17.49 (11)	O15 ⁱⁱ —V3—O13—V2	175.22 (12)
O14 ⁱⁱ —V4—O6—V1	-86.7 (3)	O11—V3—O13—V2	83.1 (3)

supplementary materials

O12 ⁱ —V4—O6—V1	-176.00 (12)	O16—V3—O13—V2	95.61 (11)
O13—V4—O6—V1	-98.25 (11)	O3—V3—O13—V4	173.31 (11)
O5—V4—O6—V2	-171.52 (11)	O8—V3—O13—V4	-87.67 (10)
O16—V4—O6—V2	86.85 (11)	O15 ⁱⁱ —V3—O13—V4	72.83 (11)
O14 ⁱⁱ —V4—O6—V2	17.6 (3)	O11—V3—O13—V4	-19.3 (3)
O12 ⁱ —V4—O6—V2	-71.67 (11)	O16—V3—O13—V4	-6.78 (8)
O13—V4—O6—V2	6.09 (8)	O16—V4—O13—V2	-91.04 (12)
O1—V2—O6—V1	-110.6 (16)	O6—V4—O13—V2	-7.98 (11)
O13—V2—O6—V1	90.76 (11)	O14 ⁱⁱ —V4—O13—V2	176.74 (12)
O8—V2—O6—V1	6.99 (11)	O12 ⁱ —V4—O13—V2	83.71 (11)
O9—V2—O6—V1	-84.57 (11)	O16—V4—O13—V3	9.03 (11)
O10 ⁱ —V2—O6—V1	-177.17 (12)	O6—V4—O13—V3	92.09 (11)
O13—V2—O6—V4	-8.13 (11)	O14 ⁱⁱ —V4—O13—V3	-83.19 (11)
O8—V2—O6—V4	-91.91 (11)	O12 ⁱ —V4—O13—V3	-176.22 (12)
O9—V2—O6—V4	176.53 (12)	O15—P1—O14—V4 ^{iv}	-13.6 (3)
O10 ⁱ —V2—O6—V4	83.94 (11)	O4—P1—O14—V4 ^{iv}	106.2 (2)
O12—P2—O7—V1	104.0 (2)	O9—P1—O14—V4 ^{iv}	-132.5 (2)
O11—P2—O7—V1	-18.0 (3)	O4—P1—O15—V3 ^{iv}	-129.8 (2)
O10—P2—O7—V1	-135.4 (2)	O14—P1—O15—V3 ^{iv}	-8.3 (3)
O2—V1—O7—P2	149.9 (2)	O9—P1—O15—V3 ^{iv}	109.6 (2)
O16—V1—O7—P2	46.9 (2)	O5—V4—O16—V1	-83.47 (14)
O6—V1—O7—P2	-13.3 (4)	O6—V4—O16—V1	17.59 (11)
O4—V1—O7—P2	-109.4 (2)	O14 ⁱⁱ —V4—O16—V1	175.38 (12)
O8—V1—O7—P2	-32.2 (2)	O12 ⁱ —V4—O16—V1	83.4 (3)
O1—V2—O8—V3	-88.41 (13)	O13—V4—O16—V1	96.29 (11)
O13—V2—O8—V3	14.51 (11)	O5—V4—O16—V3	173.38 (11)
O9—V2—O8—V3	173.26 (12)	O6—V4—O16—V3	-85.56 (11)
O10 ⁱ —V2—O8—V3	82.9 (3)	O14 ⁱⁱ —V4—O16—V3	72.23 (11)
O6—V2—O8—V3	95.33 (10)	O12 ⁱ —V4—O16—V3	-19.7 (3)
O1—V2—O8—V1	171.10 (11)	O13—V4—O16—V3	-6.86 (8)
O13—V2—O8—V1	-85.99 (11)	O2—V1—O16—V4	81.73 (13)
O9—V2—O8—V1	72.77 (10)	O6—V1—O16—V4	-17.64 (11)
O10 ⁱ —V2—O8—V1	-17.6 (4)	O4—V1—O16—V4	-84.0 (3)
O6—V2—O8—V1	-5.16 (8)	O7—V1—O16—V4	-177.70 (12)
O3—V3—O8—V2	86.84 (13)	O8—V1—O16—V4	-96.79 (11)
O13—V3—O8—V2	-14.23 (11)	O2—V1—O16—V3	-175.60 (11)
O15 ⁱⁱ —V3—O8—V2	-78.2 (3)	O6—V1—O16—V3	85.03 (11)
O11—V3—O8—V2	-171.65 (11)	O4—V1—O16—V3	18.7 (3)
O16—V3—O8—V2	-94.32 (10)	O7—V1—O16—V3	-75.03 (11)
O3—V3—O8—V1	-173.09 (11)	O8—V1—O16—V3	5.88 (8)
O13—V3—O8—V1	85.84 (10)	O13—V3—O16—V4	9.06 (11)
O15 ⁱⁱ —V3—O8—V1	21.9 (3)	O8—V3—O16—V4	91.79 (11)
O11—V3—O8—V1	-71.58 (10)	O15 ⁱⁱ —V3—O16—V4	-82.19 (11)
O16—V3—O8—V1	5.75 (8)	O11—V3—O16—V4	-176.21 (12)

O16—V1—O8—V2	89.44 (11)	O13—V3—O16—V1	-90.50 (12)
O6—V1—O8—V2	6.69 (10)	O8—V3—O16—V1	-7.77 (11)
O4—V1—O8—V2	-85.33 (11)	O15 ⁱⁱ —V3—O16—V1	178.25 (12)
O7—V1—O8—V2	179.27 (12)	O11—V3—O16—V1	84.23 (11)
O16—V1—O8—V3	-7.62 (10)	C5—N1—C1—C2	-0.2 (6)
O6—V1—O8—V3	-90.37 (11)	N1—C1—C2—C3	-1.5 (6)
O4—V1—O8—V3	177.60 (12)	C8—N2—C3—C4	-6.6 (6)
O7—V1—O8—V3	82.21 (11)	C8—N2—C3—C2	175.7 (4)
O15—P1—O9—V2	106.2 (2)	C1—C2—C3—N2	-179.2 (4)
O4—P1—O9—V2	-12.8 (3)	C1—C2—C3—C4	3.0 (5)
O14—P1—O9—V2	-134.2 (2)	N2—C3—C4—C5	179.5 (4)
O1—V2—O9—P1	-129.9 (2)	C2—C3—C4—C5	-2.8 (6)
O13—V2—O9—P1	40.0 (4)	C1—N1—C5—C4	0.3 (6)
O8—V2—O9—P1	-27.9 (2)	C3—C4—C5—N1	1.2 (6)
O10 ⁱ —V2—O9—P1	132.7 (2)	C10—N3—C6—C7	1.8 (6)
O6—V2—O9—P1	51.9 (2)	N3—C6—C7—C8	0.9 (6)
O12—P2—O10—V2 ⁱⁱⁱ	-14.4 (2)	C3—N2—C8—C9	141.3 (4)
O11—P2—O10—V2 ⁱⁱⁱ	106.6 (2)	C3—N2—C8—C7	-38.6 (6)
O7—P2—O10—V2 ⁱⁱⁱ	-133.43 (19)	C6—C7—C8—C9	-4.0 (5)
O12—P2—O11—V3	-82.1 (2)	C6—C7—C8—N2	175.9 (3)
O7—P2—O11—V3	38.1 (3)	N2—C8—C9—C10	-175.4 (3)
O10—P2—O11—V3	157.15 (19)	C7—C8—C9—C10	4.5 (5)
O3—V3—O11—P2	116.7 (2)	C6—N3—C10—C9	-1.3 (5)
O13—V3—O11—P2	-50.7 (4)	C8—C9—C10—N3	-1.9 (5)

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

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—H1N \cdots O10	0.93 (4)	2.14 (4)	2.885 (4)	136 (4)
N1—H1N \cdots O9 ⁱⁱⁱ	0.93 (4)	2.45 (4)	3.018 (5)	119 (4)
N2—H2N \cdots O2 ^v	0.862 (19)	2.35 (2)	3.195 (4)	166 (4)
N3—H3N \cdots O8 ^{vi}	0.90 (5)	2.02 (5)	2.902 (4)	164 (4)

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

Fig. 1

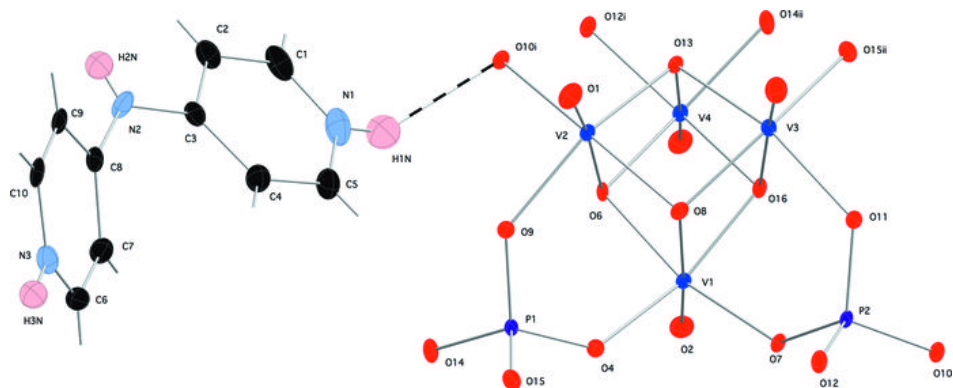


Fig. 2

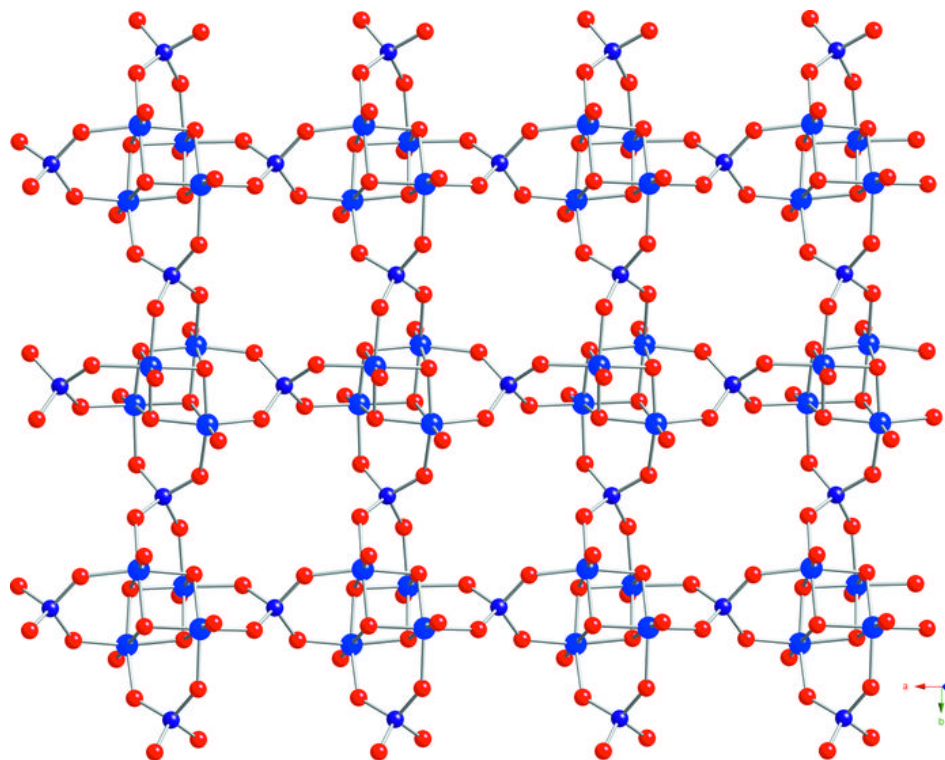


Fig. 3

