Acta Crystallographica Section E
**Structure Reports Online**
ISSN 1600-5368

# Poly[4,4′-iminodipyridinium [tetra-$\mu_3$-oxido-tetraoxido-di-$\mu_4$-phosphato-$\kappa^4O:O':O'':O'''$-tetravanadium(V)]]

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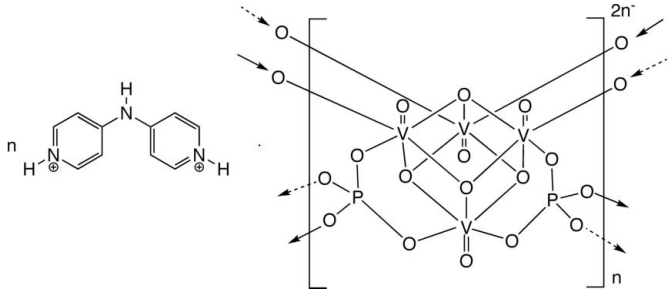
Received 7 November 2008; accepted 17 November 2008

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

In the title salt, $\{(C_{10}H_{11}N_3)[V_4O_8(PO_4)_2]\}_n$, cubane-like $[V_4O_8]^{4+}$ clusters are connected by phosphate anions into anionic $[V_4P_2O_{16}]_n^{2n-}$ layers. These aggregate into the three-dimensional structure *via* N—H···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

$(C_{10}H_{11}N_3)[V_4O_8(PO_4)_2]$
$M_r$ = 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) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 2.04 mm$^{-1}$
$T$ = 173 (2) K
0.20 × 0.20 × 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 $I > 2\sigma(I)$
$R_{int}$ = 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, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N1—H1N···O10 | 0.93 (4) | 2.14 (4) | 2.885 (4) | 136 (4) |
| N1—H1N···O9$^{i}$ | 0.93 (4) | 2.45 (4) | 3.018 (5) | 119 (4) |
| N2—H2N···O2$^{ii}$ | 0.862 (19) | 2.35 (2) | 3.195 (4) | 166 (4) |
| N3—H3N···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*.

We gratefully acknowledge the donors of the American Chemical Society Petroleum Research Fund for funding this work.

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.* A**64**, 112–122.
Shi, F.-N., Paz, F. A. A., Rocha, J., Klinowski, Ja. & Trindade, T. (2004). *Eur. J. Inorg. Chem.* pp.3031–3037.

# supporting information

*Acta Cryst.* (2008). E**64**, m1602 [doi:10.1107/S1600536808038348]

# Poly[4,4′-iminodipyridinium [tetra-$\mu_3$-oxido-tetraoxido-di-$\mu_4$-phosphato-$\kappa^4O:O':O'':O'''$-tetravanadium(V)]]

**Gregory A. Farnum and Robert L. LaDuca**

## S1. 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 $\mu_3$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 $\mu_3$ 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).

## S2. 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 $H_2O$ (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.

## S3. 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 $U_{iso}$ = 1.2$U_{eq}$(C). All H atoms bound to N atoms were found *via* Fourier difference map, restrained with N—H = 0.89 Å, and refined with $U_{iso}$=1.2$U_{eq}$(N). The largest residual electron density peak of 1.03 e$^-$ Å$^{-3}$ was located 2.25 Å from the H2 atom.

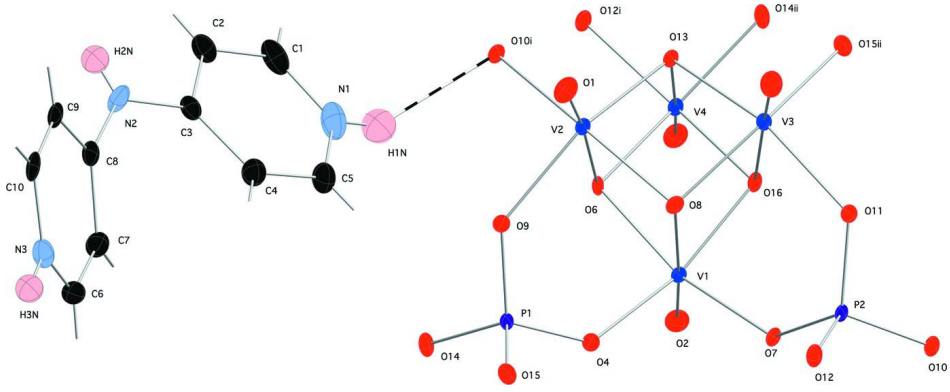



**Figure 1**

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.

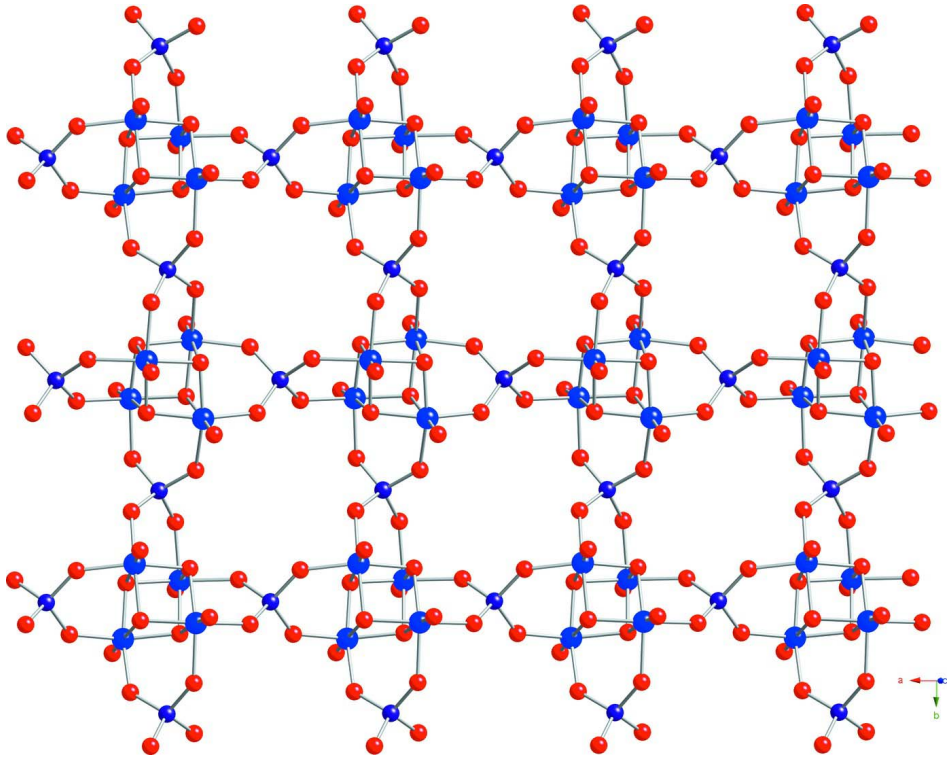


**Figure 2**

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

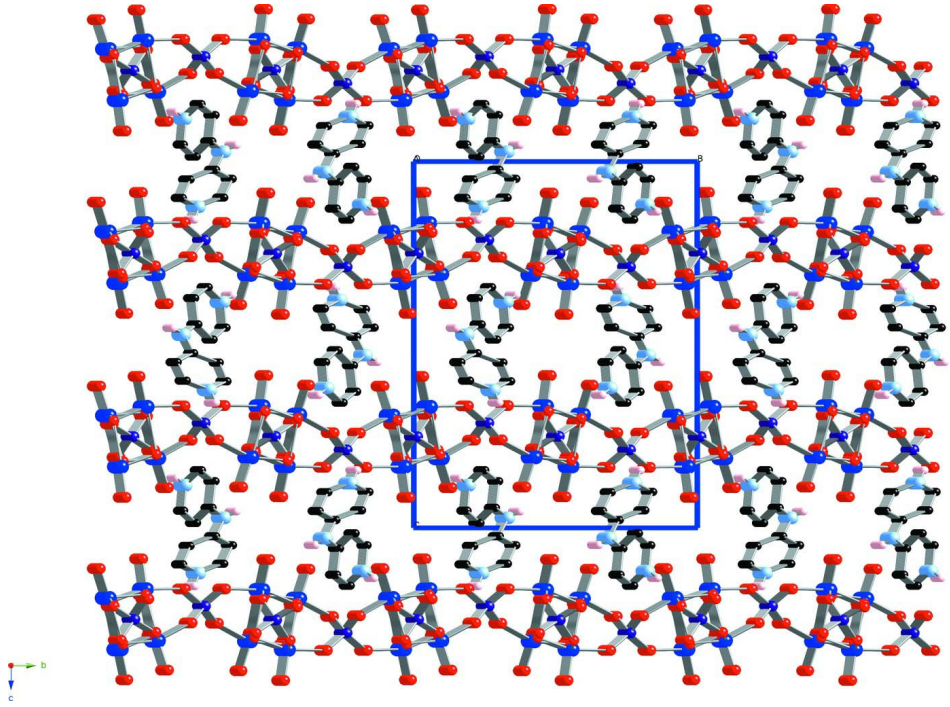


**Figure 3**

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-$\mu_3$-oxido-tetraoxidodi-$\mu_4$-phosphato- $\kappa^4O:O':O'':O'''$-tetravanadium(V)]]**

*Crystal data*

$(C_{10}H_{11}N_3)[V_4O_8(PO_4)_2]$
$M_r = 694.92$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.4431$ (10) Å
$b = 14.524$ (2) Å
$c = 18.825$ (3) Å
$\beta = 94.363$ (2)°
$V = 2029.1$ (5) Å$^3$
$Z = 4$
$F(000) = 1368$
$D_x = 2.275$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 21687 reflections
$\theta = 1.8$–$28.2°$
$\mu = 2.04$ mm$^{-1}$
$T = 173$ K
Plate, yellow
0.20 × 0.20 × 0.04 mm

*Data collection*

Bruker SMART 1K diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.786$, $T_{max} = 0.922$
21687 measured reflections
4652 independent reflections
3678 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 28.2°$, $\theta_{min} = 1.8°$
$h = -9 \rightarrow 9$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 24$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.101$
$S = 1.09$
4652 reflections
325 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0382P)^2 + 6.7132P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.03$ e Å$^{-3}$
$\Delta\rho_{min} = -0.76$ e Å$^{-3}$

*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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| 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) |
| 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 (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| 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, º)*

| | | | |
|---|---|---|---|
| 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 |
| 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) | | |

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| O2—V1—O16 | 103.13 (13) | O12—P2—O11 | 111.02 (15) |
| O2—V1—O6 | 101.14 (12) | O12—P2—O7 | 108.15 (14) |

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| 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 |

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| 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) | | |

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| 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) |
| 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) |

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| 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) |

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| 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 (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*N*···O10 | 0.93 (4) | 2.14 (4) | 2.885 (4) | 136 (4) |
| N1—H1*N*···O9$^{iii}$ | 0.93 (4) | 2.45 (4) | 3.018 (5) | 119 (4) |
| N2—H2*N*···O2$^{v}$ | 0.86 (2) | 2.35 (2) | 3.195 (4) | 166 (4) |
| N3—H3*N*···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.