

catena-Poly[2,2',2''-nitrilotris(ethan-aminium) [tri- μ -oxido-tris[dioxido-vanadate(V)] monohydrate]

Kelvin B. Chang,^a Matthew D. Smith,^a Matthias Zeller^b and Alexander J. Norquist^{a*}

^aDepartment of Chemistry, Haverford College, 370 Lancaster Avenue, Haverford, PA 19041, USA, and ^bDepartment of Chemistry, Youngstown State University, 1 University Plaza, Youngstown, OH 44555, USA
Correspondence e-mail: anorquis@haverford.edu

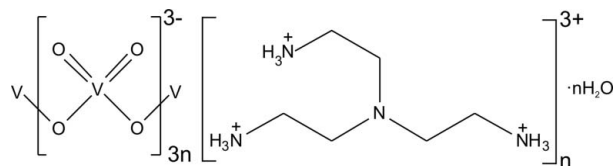
Received 31 July 2013; accepted 20 September 2013

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.052; wR factor = 0.094; data-to-parameter ratio = 13.8.

The title compound, $\{(\text{C}_6\text{H}_{21}\text{N}_4)[\text{V}_3\text{O}_9]\cdot\text{H}_2\text{O}\}_n$, crystallizes as a salt with $[\text{trenH}_3]^{3+}$ cations [tren is tris(2-aminoethyl)amine], and one-dimensional anionic $\{[\text{V}^{\text{V}}\text{O}_3]^{-}\}_n$ (metavanadate) chains along the c -axis direction. Three crystallographically distinct V^{V} sites and one occluded water molecule are present for every $[\text{trenH}_3]^{3+}$ cation in the unit cell. The $\{[\text{V}^{\text{V}}\text{O}_3]^{-}\}_n$ chains are composed of vertex-sharing $[\text{VO}_4]$ tetrahedra and have a repeat unit of six tetrahedra. Each tetrahedron in the chain contains two terminal and two μ^2 -bridging oxide ligands. The $[\text{trenH}_3]^{3+}$ cations, $\{[\text{V}^{\text{V}}\text{O}_3]^{-}\}_n$ anions and occluded water molecules participate in an extensive three-dimensional hydrogen-bonding network. The three terminal ammonium sites of the $[\text{trenH}_3]^{3+}$ cations each form strong $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds to terminal oxide ligands on the $\{[\text{V}^{\text{V}}\text{O}_3]^{-}\}_n$ chain. Each occluded water molecule also donates two $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to the terminal oxide ligands.

Related literature

For properties of organically templated metal oxides, see: Cheetham *et al.* (1999). A host of amine-templated metavanadate chains with connectivities identical to the title compound have been reported previously, for examples, see: Riou & Ferey (1996); Roman *et al.* (1991); Smith *et al.* (2012). Metavanadate chains with repeat units of six tetrahedra are known to exist, see: Lin *et al.* (2003); Tyrselová *et al.* (1995). For details of the H-atom treatment in the refinement, see: Cooper *et al.* (2010).



Experimental

Crystal data

$(\text{C}_6\text{H}_{21}\text{N}_4)[\text{V}_3\text{O}_9]\cdot\text{H}_2\text{O}$
 $M_r = 464.09$
Monoclinic, $P2_1/c$
 $a = 9.6624$ (14) Å
 $b = 10.9179$ (15) Å
 $c = 15.768$ (2) Å
 $\beta = 100.565$ (2)°

$V = 1635.2$ (4) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 1.73$ mm⁻¹
 $T = 100$ K
 $0.26 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.623$, $T_{\max} = 0.746$

14279 measured reflections
4719 independent reflections
3195 reflections with $I > 2.0\sigma(I)$
 $R_{\text{int}} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.094$
 $S = 1.00$
2860 reflections

208 parameters
H-atom parameters not refined
 $\Delta\rho_{\max} = 1.44$ e Å⁻³
 $\Delta\rho_{\min} = -0.68$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|-------|-------------|--------------------|-----------|
| V1—O1 | 1.613 (3) | V2—O6 | 1.623 (4) |
| V1—O2 | 1.651 (3) | V2—O7 | 1.778 (3) |
| V1—O3 | 1.773 (4) | V3—O3 ⁱ | 1.769 (4) |
| V1—O4 | 1.793 (3) | V3—O7 | 1.793 (3) |
| V2—V3 | 3.2585 (11) | V3—O8 | 1.651 (4) |
| V2—O4 | 1.793 (3) | V3—O9 | 1.632 (3) |
| V2—O5 | 1.654 (3) | | |

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

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| O10—H1 ⁱ ···O1 ⁱ | 0.95 | 2.06 | 2.997 (6) | 170 (1) |
| O10—H2 ⁱ ···O9 ⁱⁱ | 0.95 | 1.83 | 2.739 (6) | 160 (1) |
| N2—H7 ⁱ ···O8 ⁱⁱⁱ | 0.95 | 1.97 | 2.864 (6) | 155 (1) |
| N2—H8 ⁱ ···O1 ⁱⁱⁱ | 0.95 | 2.18 | 2.951 (6) | 138 (1) |
| N2—H9 ⁱ ···O5 ^{iv} | 0.95 | 1.98 | 2.850 (6) | 152 (1) |
| C4—H13 ⁱ ···O9 ⁱⁱⁱ | 0.97 | 2.50 | 3.447 (6) | 167 (1) |
| N3—H14 ⁱ ···O5 ^{iv} | 0.95 | 2.00 | 2.912 (6) | 162 (1) |
| N3—H15 ⁱ ···O2 ^{iv} | 0.95 | 1.87 | 2.819 (6) | 176 (1) |
| N3—H16 ⁱ ···O6 ^v | 0.95 | 2.03 | 2.853 (6) | 144 (1) |
| N3—H16 ⁱ ···O10 ^v | 0.95 | 2.23 | 2.925 (6) | 129 (1) |
| C6—H19 ⁱ ···O6 ^v | 0.97 | 2.54 | 3.222 (6) | 127 (1) |
| N4—H21 ⁱ ···O4 ^v | 0.95 | 2.14 | 3.013 (6) | 152 (1) |
| N4—H22 ⁱ ···O2 ^{vi} | 0.95 | 1.94 | 2.796 (6) | 150 (1) |
| N4—H23 ⁱ ···O5 ^{iv} | 0.95 | 1.90 | 2.803 (6) | 157 (1) |

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; program(s) used to solve

structure: *SHELXS86* (Sheldrick, 2008); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

The authors acknowledge support from the NSF (Award No. CHE-0911121), the Henry Dreyfus Teacher-Scholar Awards Program, and grants to Haverford College from the HHMI Undergraduate Science Education Program. MZ acknowledges support for the purchase of a diffractometer from the NSF Grant 0087210, the Ohio Board of Regents Grant CAP-491, and Youngstown State University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HP2060).

References

- Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.
- Bruker (2008). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2009). *SAINTE* and *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cheetham, A. K., Ferey, G. & Loiseau, T. (1999). *Angew. Chem. Int. Ed.* **38**, 3268–3292.
- Cooper, R. I., Thompson, A. L. & Watkin, D. J. (2010). *J. Appl. Cryst.* **43**, 1100–1107.
- Lin, B. Z., Li, Z., Pei, X. K. & Liu, P. D. (2003). *J. Mol. Struct.* **660**, 181–186.
- Riou, D. & Ferey, G. (1996). *J. Solid State Chem.* **124**, 151–154.
- Roman, P., Aranzabe, A., Luque, A. & Gutierrez-Zorrilla, J. (1991). *Mater. Res. Bull.* **26**, 19–27.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Smith, M. D., Blau, S. M., Chang, K. B., Tran, T. T., Zeller, M., Halasyamani, P. S., Schrier, J. & Norquist, A. J. (2012). *J. Solid State Chem.* **195**, 86–93.
- Tyrselová, J., Kuchta, L. & Pavelčík, F. (1995). *Acta Cryst.* **C51**, 1752–1754.
- Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, Oxford, England.

supporting information

Acta Cryst. (2013). E69, m570–m571 [doi:10.1107/S1600536813026056]

catena-Poly[2,2',2''-nitrilotris(ethanaminium) [tri- μ -oxido-tris-dioxidovanadate(V)]] monohydrate**Kelvin B. Chang, Matthew D. Smith, Matthias Zeller and Alexander J. Norquist****S1. Comment**

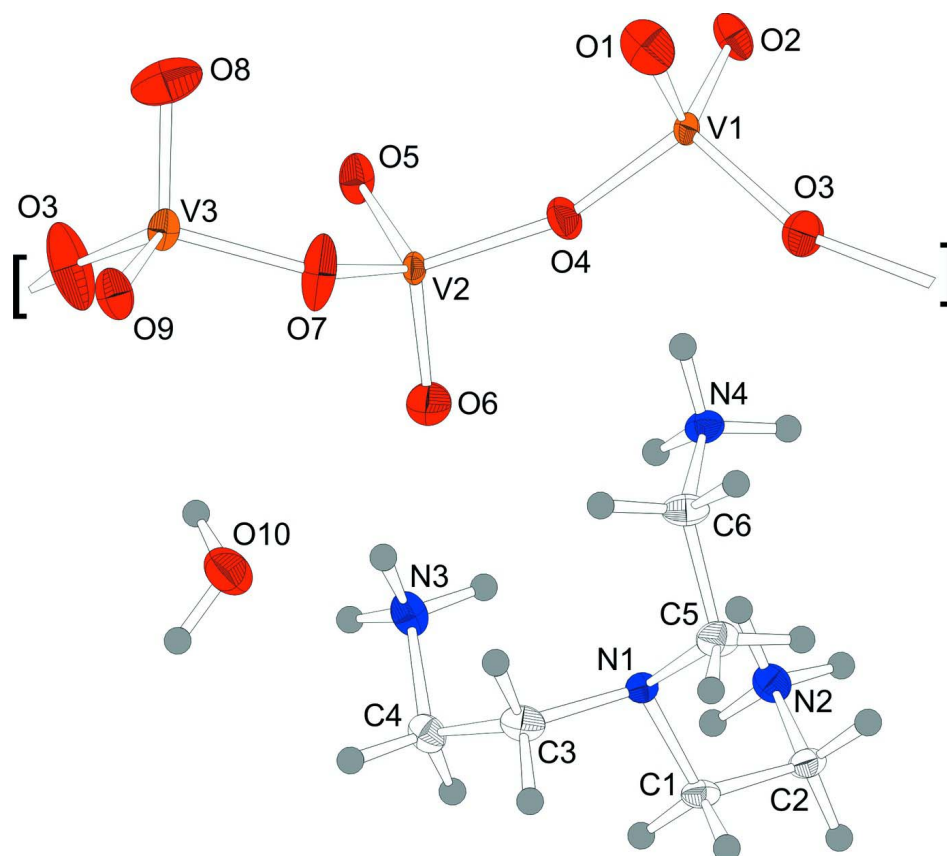
Organically templated metal oxides have been the subject of sustained interest for many years, owing to their structural diversity and potential to exhibit technologically desirable physical properties (Cheetham *et al.*, 1999). Amine-templated metavanadate chain compounds are no exception, with a number of different topologies for chains with identical connectivity having been reported. The synthesis and crystal structure of the title compound, $[\text{trenH}_3][\text{VO}_3]_3 \cdot \text{H}_2\text{O}$, is described here. The three-dimensional packing of the title compound is shown in Fig. 2. The $\{[\text{V}^{\text{VO}_3}]_n\}$ chains are composed of vertex-sharing $[\text{VO}_4]$ tetrahedra and have a repeat unit of six tetrahedra. Each tetrahedron in the chain contains two terminal and two μ^2 -bridging oxide ligands. The $\text{V} - \text{O}_{\text{terminal}}$ and $\text{V} - \text{O}_{\text{bridging}}$ bond lengths range from 1.613 (4) to 1.653 (3) Å and 1.770 (4) to 1.794 (4) Å, respectively. Several compounds containing amine templated metavanadate chains have been previously reported, see: Riou *et al.* (1996), Roman *et al.* (1991), Smith *et al.* (2012), Lin *et al.* (2003) and Tyrselová *et al.* (1995). However, the chain topology of the inorganic anion in the title compound is novel. The $[\text{trenH}_3]^{3+}$ cations, $\{[\text{V}^{\text{VO}_3}]_n\}$ anions and occluded water molecules participate in an extensive three-dimensional hydrogen-bonding network. The three terminal ammonium sites of the $[\text{trenH}_3]^{3+}$ cations each form strong $\text{N} \cdots \text{H} \cdots \text{O}$ hydrogen bonds to terminal oxide atoms on the $\{[\text{V}^{\text{VO}_3}]_n\}$ chain, with $\text{N} \cdots \text{O}$ distances ranging from 2.796 (5) to 3.013 (5) Å. Each occluded water molecule also donates two $\text{O} - \text{H} \cdots \text{O}$ hydrogen bonds to the terminal oxide atoms, with $\text{O} \cdots \text{O}$ distances ranging from 2.738 (4) to 2.996 (5) Å.

S2. Experimental

All chemicals (reagent grade) were commercially available and were used as received. Deionized water was used in this synthesis. The title compound was prepared under mild hydrothermal conditions in a 23 mL Teflon-lined stainless-steel autoclave. V_2O_5 (0.1449 g, 0.7967 mmol), Na_2TeO_3 (0.0889 g, 0.4012 mmol), tren (0.0620 g, 0.4240 mmol), ethanol (4 ml, 0.069 mol), and H_2O (4 ml, 0.22 mol) were mixed to give a reaction mixture with a molar composition ratio of 2:1:1:170:550. The role of Na_2TeO_3 in this reaction is not understood. Reactions were placed in a 110 °C oven for 5 d. The reactions were then cooled to room temperature at a rate of 6 °C h⁻¹ to promote the growth of large single crystals. Reaction vessels were opened in air, and the title compound was recovered as clear colorless needles in the presence of an unidentified tan powder *via* vacuum filtration.

S3. Refinement

While the H atoms were all located in a difference map, they were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H to 0.95, and O—H = 0.95 Å) and $U_{\text{iso}}(\text{H})$ (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints (Cooper *et al.*, 2010).

**Figure 1**

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

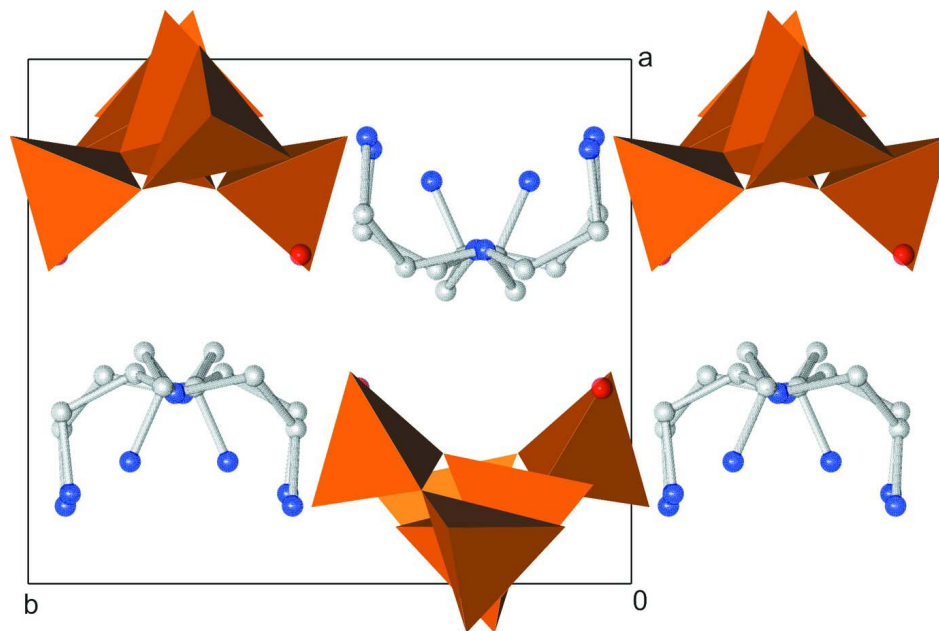


Figure 2

A packing diagram of the title compound, viewed down the c axis. Orange tetrahedra represent $[\text{VO}_4]$, while red, blue and white spheres represent oxygen, nitrogen, carbon and hydrogen atoms, respectively.

catena-Poly[2,2',2''-nitrilotris(ethanaminium) [tri- μ -oxido-tris[dioxidovanadate(V)] monohydrate]

Crystal data

$(\text{C}_6\text{H}_{21}\text{N}_4)[\text{V}_3\text{O}_9]\cdot\text{H}_2\text{O}$

$M_r = 464.09$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 9.6624\ (14)\ \text{\AA}$

$b = 10.9179\ (15)\ \text{\AA}$

$c = 15.768\ (2)\ \text{\AA}$

$\beta = 100.565\ (2)^\circ$

$V = 1635.2\ (4)\ \text{\AA}^3$

$Z = 4$

$F(000) = 944$

$D_x = 1.885\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2067 reflections

$\theta = 2.6\text{--}29.5^\circ$

$\mu = 1.73\ \text{mm}^{-1}$

$T = 100\ \text{K}$

Block, colorless

$0.26 \times 0.20 \times 0.16\ \text{mm}$

Data collection

Bruker SMART APEX CCD area-detector
diffractometer

Radiation source: fine focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2008)

$T_{\min} = 0.623$, $T_{\max} = 0.746$

14279 measured reflections

4719 independent reflections

3195 reflections with $I > 2.0\sigma(I)$

$R_{\text{int}} = 0.061$

$\theta_{\max} = 30.1^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -13 \rightarrow 13$

$k = -15 \rightarrow 15$

$l = -20 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.094$

$S = 1.00$

2860 reflections

208 parameters

0 restraints

Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters not refined

Method = Modified Shelldrick $w = 1/[\sigma^2(F^2) + (0.03P)^2 + 7.47P]$,
 where $P = (\max(F_o^2, 0) + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.0003744$
 $\Delta\rho_{\max} = 1.44 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$

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

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|-------------|----------------------------------|
| V1 | 0.92597 (7) | 0.75226 (7) | 0.71937 (5) | 0.0135 |
| V2 | 0.87185 (7) | 0.80317 (7) | 0.49412 (4) | 0.0120 |
| V3 | 0.75379 (8) | 0.58481 (7) | 0.35925 (5) | 0.0152 |
| O1 | 0.8914 (4) | 0.6089 (3) | 0.7288 (2) | 0.0320 |
| O2 | 1.0944 (3) | 0.7734 (3) | 0.7595 (2) | 0.0217 |
| O3 | 0.8219 (5) | 0.8480 (4) | 0.7734 (2) | 0.0498 |
| O4 | 0.8935 (3) | 0.8036 (3) | 0.6095 (2) | 0.0244 |
| O5 | 1.0270 (3) | 0.7839 (3) | 0.4659 (2) | 0.0220 |
| O6 | 0.8112 (4) | 0.9374 (3) | 0.4625 (2) | 0.0379 |
| O7 | 0.7512 (4) | 0.6883 (4) | 0.4472 (2) | 0.0354 |
| O8 | 0.8542 (4) | 0.4695 (4) | 0.4011 (3) | 0.0429 |
| O9 | 0.5943 (3) | 0.5335 (3) | 0.3264 (2) | 0.0233 |
| O10 | 0.6272 (4) | 0.9517 (3) | 0.2942 (2) | 0.0326 |
| N1 | 0.3633 (3) | 0.7571 (3) | 0.4750 (2) | 0.0124 |
| N2 | 0.1483 (4) | 0.5617 (3) | 0.4189 (2) | 0.0186 |
| N3 | 0.2327 (4) | 0.8310 (4) | 0.6220 (2) | 0.0199 |
| N4 | 0.1714 (4) | 0.9305 (3) | 0.3650 (2) | 0.0173 |
| C1 | 0.3965 (4) | 0.6257 (4) | 0.4704 (3) | 0.0144 |
| C2 | 0.2953 (4) | 0.5559 (4) | 0.4031 (3) | 0.0161 |
| C3 | 0.4414 (4) | 0.8077 (4) | 0.5560 (3) | 0.0180 |
| C4 | 0.3751 (4) | 0.7766 (4) | 0.6334 (3) | 0.0178 |
| C5 | 0.4008 (5) | 0.8229 (4) | 0.4007 (3) | 0.0195 |
| C6 | 0.3272 (4) | 0.9449 (4) | 0.3853 (3) | 0.0186 |
| H1 | 0.7169 | 0.9334 | 0.2807 | 0.0389* |
| H2 | 0.5660 | 0.9794 | 0.2437 | 0.0389* |
| H3 | 0.4912 | 0.6178 | 0.4588 | 0.0191* |
| H4 | 0.3936 | 0.5894 | 0.5259 | 0.0187* |
| H5 | 0.2977 | 0.5904 | 0.3470 | 0.0191* |
| H6 | 0.3247 | 0.4713 | 0.4050 | 0.0189* |
| H7 | 0.1445 | 0.5268 | 0.4736 | 0.0240* |
| H8 | 0.0880 | 0.5172 | 0.3752 | 0.0240* |
| H9 | 0.1185 | 0.6447 | 0.4180 | 0.0240* |
| H10 | 0.5379 | 0.7765 | 0.5656 | 0.0209* |
| H11 | 0.4435 | 0.8963 | 0.5511 | 0.0211* |
| H12 | 0.4324 | 0.8092 | 0.6858 | 0.0219* |
| H13 | 0.3682 | 0.6886 | 0.6390 | 0.0222* |
| H14 | 0.1764 | 0.7994 | 0.5709 | 0.0245* |
| H15 | 0.1904 | 0.8116 | 0.6701 | 0.0245* |
| H16 | 0.2399 | 0.9174 | 0.6173 | 0.0245* |

| | | | | |
|-----|--------|--------|--------|---------|
| H17 | 0.3702 | 0.7723 | 0.3497 | 0.0240* |
| H18 | 0.5027 | 0.8342 | 0.4091 | 0.0241* |
| H19 | 0.3508 | 0.9958 | 0.4366 | 0.0226* |
| H20 | 0.3573 | 0.9845 | 0.3373 | 0.0229* |
| H21 | 0.1284 | 1.0088 | 0.3561 | 0.0223* |
| H22 | 0.1465 | 0.8828 | 0.3140 | 0.0223* |
| H23 | 0.1400 | 0.8905 | 0.4115 | 0.0223* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| V1 | 0.0147 (3) | 0.0181 (4) | 0.0087 (3) | 0.0034 (3) | 0.0046 (3) | -0.0010 (3) |
| V2 | 0.0124 (3) | 0.0158 (4) | 0.0081 (3) | 0.0005 (3) | 0.0028 (3) | -0.0025 (3) |
| V3 | 0.0125 (3) | 0.0188 (4) | 0.0157 (4) | -0.0053 (3) | 0.0062 (3) | -0.0037 (3) |
| O1 | 0.032 (2) | 0.025 (2) | 0.036 (2) | -0.0146 (15) | -0.0010 (17) | 0.0016 (16) |
| O2 | 0.0239 (17) | 0.0250 (18) | 0.0149 (16) | -0.0088 (13) | 0.0000 (13) | 0.0037 (13) |
| O3 | 0.058 (3) | 0.074 (3) | 0.019 (2) | 0.042 (2) | 0.0113 (19) | -0.001 (2) |
| O4 | 0.0225 (16) | 0.039 (2) | 0.0122 (15) | 0.0070 (15) | 0.0038 (13) | 0.0007 (15) |
| O5 | 0.0161 (15) | 0.034 (2) | 0.0177 (16) | -0.0063 (13) | 0.0081 (13) | -0.0052 (14) |
| O6 | 0.056 (3) | 0.031 (2) | 0.025 (2) | 0.0182 (19) | 0.0041 (18) | 0.0015 (16) |
| O7 | 0.032 (2) | 0.049 (2) | 0.031 (2) | -0.0281 (18) | 0.0210 (17) | -0.0238 (18) |
| O8 | 0.028 (2) | 0.032 (2) | 0.071 (3) | 0.0053 (17) | 0.014 (2) | 0.003 (2) |
| O9 | 0.0206 (16) | 0.0303 (19) | 0.0184 (17) | -0.0104 (14) | 0.0023 (13) | -0.0028 (14) |
| O10 | 0.0283 (19) | 0.047 (2) | 0.0227 (19) | 0.0063 (17) | 0.0044 (15) | 0.0061 (17) |
| N1 | 0.0124 (16) | 0.0120 (16) | 0.0136 (17) | 0.0000 (14) | 0.0043 (13) | 0.0019 (14) |
| N2 | 0.0161 (18) | 0.0198 (19) | 0.0188 (19) | -0.0023 (15) | 0.0007 (15) | -0.0005 (16) |
| N3 | 0.0159 (18) | 0.028 (2) | 0.0158 (19) | -0.0045 (16) | 0.0041 (15) | 0.0007 (16) |
| N4 | 0.0143 (17) | 0.0140 (18) | 0.022 (2) | 0.0004 (14) | 0.0004 (15) | -0.0020 (16) |
| C1 | 0.0109 (19) | 0.015 (2) | 0.018 (2) | 0.0030 (16) | 0.0043 (16) | 0.0040 (17) |
| C2 | 0.015 (2) | 0.015 (2) | 0.019 (2) | 0.0045 (16) | 0.0043 (17) | 0.0012 (17) |
| C3 | 0.0107 (19) | 0.019 (2) | 0.024 (2) | -0.0026 (17) | 0.0016 (17) | 0.0026 (19) |
| C4 | 0.016 (2) | 0.017 (2) | 0.018 (2) | -0.0043 (16) | -0.0014 (17) | -0.0005 (17) |
| C5 | 0.015 (2) | 0.024 (2) | 0.021 (2) | 0.0039 (18) | 0.0090 (18) | 0.0054 (19) |
| C6 | 0.015 (2) | 0.014 (2) | 0.027 (2) | 0.0009 (17) | 0.0046 (18) | 0.0065 (19) |

Geometric parameters (Å, °)

| | | | |
|--------------------|-------------|--------|-----------|
| V1—O1 | 1.613 (3) | N3—H14 | 0.950 |
| V1—O2 | 1.651 (3) | N3—H15 | 0.950 |
| V1—O3 | 1.773 (4) | N3—H16 | 0.950 |
| V1—O4 | 1.793 (3) | N4—C6 | 1.489 (5) |
| V2—V3 | 3.2585 (11) | N4—H21 | 0.950 |
| V2—O4 | 1.793 (3) | N4—H22 | 0.950 |
| V2—O5 | 1.654 (3) | N4—H23 | 0.950 |
| V2—O6 | 1.623 (4) | C1—C2 | 1.510 (6) |
| V2—O7 | 1.778 (3) | C1—H3 | 0.969 |
| V3—O3 ⁱ | 1.769 (4) | C1—H4 | 0.966 |
| V3—O7 | 1.793 (3) | C2—H5 | 0.967 |

| | | | |
|------------------------|-------------|------------|-----------|
| V3—O8 | 1.651 (4) | C2—H6 | 0.966 |
| V3—O9 | 1.632 (3) | C3—C4 | 1.517 (6) |
| O10—H1 | 0.950 | C3—H10 | 0.978 |
| O10—H2 | 0.950 | C3—H11 | 0.970 |
| N1—C1 | 1.475 (5) | C4—H12 | 0.975 |
| N1—C3 | 1.468 (5) | C4—H13 | 0.968 |
| N1—C5 | 1.475 (5) | C5—C6 | 1.508 (6) |
| N2—C2 | 1.488 (5) | C5—H17 | 0.976 |
| N2—H7 | 0.950 | C5—H18 | 0.977 |
| N2—H8 | 0.950 | C6—H19 | 0.974 |
| N2—H9 | 0.950 | C6—H20 | 0.962 |
| N3—C4 | 1.479 (6) | | |
| O1—V1—O2 | 107.86 (17) | H15—N3—H16 | 109.5 |
| O1—V1—O3 | 112.5 (2) | C6—N4—H21 | 109.5 |
| O2—V1—O3 | 109.83 (19) | C6—N4—H22 | 109.2 |
| O1—V1—O4 | 112.94 (18) | H21—N4—H22 | 109.5 |
| O2—V1—O4 | 108.21 (15) | C6—N4—H23 | 109.6 |
| O3—V1—O4 | 105.41 (17) | H21—N4—H23 | 109.5 |
| V3—V2—O4 | 128.76 (12) | H22—N4—H23 | 109.5 |
| V3—V2—O5 | 87.55 (11) | N1—C1—C2 | 114.0 (3) |
| O4—V2—O5 | 109.31 (15) | N1—C1—H3 | 108.5 |
| V3—V2—O6 | 113.39 (14) | C2—C1—H3 | 109.6 |
| O4—V2—O6 | 106.12 (17) | N1—C1—H4 | 108.2 |
| O5—V2—O6 | 109.05 (19) | C2—C1—H4 | 107.9 |
| V3—V2—O7 | 24.27 (11) | H3—C1—H4 | 108.6 |
| O4—V2—O7 | 111.67 (17) | C1—C2—N2 | 112.1 (3) |
| O5—V2—O7 | 110.85 (16) | C1—C2—H5 | 109.0 |
| O6—V2—O7 | 109.7 (2) | N2—C2—H5 | 108.7 |
| V2—V3—O3 ⁱ | 93.50 (13) | C1—C2—H6 | 108.2 |
| V2—V3—O7 | 24.06 (10) | N2—C2—H6 | 108.7 |
| O3 ⁱ —V3—O7 | 112.99 (19) | H5—C2—H6 | 110.2 |
| V2—V3—O8 | 100.80 (15) | N1—C3—C4 | 112.9 (3) |
| O3 ⁱ —V3—O8 | 110.4 (2) | N1—C3—H10 | 109.0 |
| O7—V3—O8 | 105.2 (2) | C4—C3—H10 | 109.2 |
| V2—V3—O9 | 130.93 (12) | N1—C3—H11 | 108.7 |
| O3 ⁱ —V3—O9 | 111.19 (18) | C4—C3—H11 | 107.8 |
| O7—V3—O9 | 108.37 (16) | H10—C3—H11 | 109.1 |
| O8—V3—O9 | 108.46 (19) | C3—C4—N3 | 109.4 (4) |
| V1—O3—V3 ⁱⁱ | 159.3 (2) | C3—C4—H12 | 110.0 |
| V2—O4—V1 | 161.2 (2) | N3—C4—H12 | 109.1 |
| V3—O7—V2 | 131.66 (19) | C3—C4—H13 | 110.0 |
| H1—O10—H2 | 109.5 | N3—C4—H13 | 109.4 |
| C1—N1—C3 | 109.1 (3) | H12—C4—H13 | 108.8 |
| C1—N1—C5 | 110.3 (3) | N1—C5—C6 | 112.4 (3) |
| C3—N1—C5 | 110.2 (3) | N1—C5—H17 | 107.3 |
| C2—N2—H7 | 109.4 | C6—C5—H17 | 107.7 |
| C2—N2—H8 | 109.6 | N1—C5—H18 | 110.0 |

| | | | |
|------------|-------|------------|-----------|
| H7—N2—H8 | 109.5 | C6—C5—H18 | 110.1 |
| C2—N2—H9 | 109.5 | H17—C5—H18 | 109.2 |
| H7—N2—H9 | 109.5 | C5—C6—N4 | 111.7 (3) |
| H8—N2—H9 | 109.5 | C5—C6—H19 | 109.8 |
| C4—N3—H14 | 109.4 | N4—C6—H19 | 108.2 |
| C4—N3—H15 | 109.9 | C5—C6—H20 | 108.8 |
| H14—N3—H15 | 109.5 | N4—C6—H20 | 108.5 |
| C4—N3—H16 | 109.1 | H19—C6—H20 | 109.8 |
| H14—N3—H16 | 109.5 | | |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| O10—H1 \cdots O1 ⁱ | 0.95 | 2.06 | 2.997 (6) | 170 (1) |
| O10—H2 \cdots O9 ⁱⁱⁱ | 0.95 | 1.83 | 2.739 (6) | 160 (1) |
| N2—H7 \cdots O8 ^{iv} | 0.95 | 1.97 | 2.864 (6) | 155 (1) |
| N2—H8 \cdots O1 ^{iv} | 0.95 | 2.18 | 2.951 (6) | 138 (1) |
| N2—H9 \cdots O5 ^v | 0.95 | 1.98 | 2.850 (6) | 152 (1) |
| C4—H13 \cdots O9 ^{iv} | 0.97 | 2.50 | 3.447 (6) | 167 (1) |
| N3—H14 \cdots O5 ^v | 0.95 | 2.00 | 2.912 (6) | 162 (1) |
| N3—H15 \cdots O2 ^v | 0.95 | 1.87 | 2.819 (6) | 176 (1) |
| N3—H16 \cdots O6 ^{vi} | 0.95 | 2.03 | 2.853 (6) | 144 (1) |
| N3—H16 \cdots O10 ^{vi} | 0.95 | 2.23 | 2.925 (6) | 129 (1) |
| C6—H19 \cdots O6 ^{vi} | 0.97 | 2.54 | 3.222 (6) | 127 (1) |
| N4—H21 \cdots O4 ^{vi} | 0.95 | 2.14 | 3.013 (6) | 152 (1) |
| N4—H22 \cdots O2 ^{vii} | 0.95 | 1.94 | 2.796 (6) | 150 (1) |
| N4—H23 \cdots O5 ^v | 0.95 | 1.90 | 2.803 (6) | 157 (1) |

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