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Redetermination of diammonium trivanadate, $(NH_4)_2V_3O_8$

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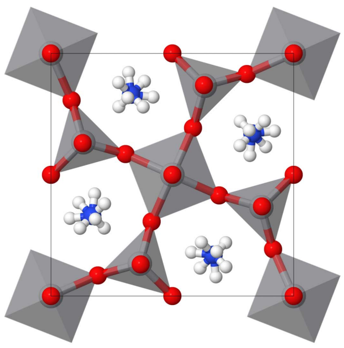
The crystal structure of $(NH_4)_2V_3O_8$ has been reported twice using single-crystal X-ray data [Theobald *et al.* (1984). *J. Phys. Chem. Solids*, **45**, 581–587; Range *et al.* (1988). *Z. Naturforsch. Teil B*, **43**, 309–317]. In both cases, the orientation of the ammonium cation in the asymmetric unit was poorly defined: in Theobald's study, the shape and dimensions were constrained for NH_4^+, while in Range's study, H atoms were not included. In the present study, we collected a highly redundant data set for this ternary oxide, at 0.61 Å resolution, using Ag *Kα* radiation. These accurate data reveal that the NH_4^+ cation is disordered by rotation around a non-crystallographic axis. The rotation axis coincides with one N—H bond lying in the mirror *m* symmetry element of space-group type *P*4*bm*, and the remaining H sites were modelled over two disordered positions, with equal occupancy. It therefore follows that the NH_4^+ cations filling the space available in the (001) layered structure formed by $(V_3O_8)^{2-}$ ions do not form strong N—H···O hydrogen bonds with the mixed-valent oxidovanadate(IV,V) anions. This feature could have consequences for the Li-ion intercalation properties of this material, which is used as a cathode for supercapacitors.

3D view



Structure description

Diammonium trivanadate, $(NH_4)_2V_3O_8$, is a well-studied mixed-valent ternary vanadium(IV,V) oxide, in particular for the building of cathodes for supercapacitors, including lithium-ion batteries. Of particular interest is its very high specific capacity, which could theoretically reach 442 mA h/g, with a Coulombic efficiency close to 100% (Xu *et al.*, 2016). Moreover, it can be obtained cheaply and simply, for example by hydrothermal reduction of NH_4VO_3 (Ren *et al.*, 2007), by electroreduction of NH_4VO_3 (Andrukaitis *et*

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al., 1990), or by solid-state reaction between NH_4VO_3 and V_2O_3 at low pressure (Liu & Greedan, 1995).

This mixed-valence oxide belongs to an isotypic series of $A_2V_3O_8$ compounds (A = K, Rb, Cs, NH_4; Yeon *et al.*, 2013) adopting the crystal structure of fresnoite, a pyrosilicate mineral with formula $Ba_2TiSi_2O_8$. Anions $(V_3O_8)^{2-}$ form a layered structure extending parallel to (001), based on $[V^{V}O_4]$ and $[V^{IV}O_5]$ polyhedra sharing oxygen atoms, while NH_4^+ cations are sandwiched by the anionic layers (The Materials Project, 2019). The crystal structure in space group *P*4*bm* has been determined at least twice by single-crystal X-ray diffraction. The first report (Theobald *et al.*, 1984) is based on X-ray data collected on a PW-1100 diffractometer, up to 0.62 Å resolution, with a rather large crystal, with dimensions $0.45 \times 0.30 \times 0.03$ mm^3. The refinement seems to be of very good quality. However, the authors mention that H-atom positions for the cation NH_4^+ retrieved from a difference map did not result in a satisfactory refinement, so the shape and dimensions were constrained for the cation. The second independent report (Range *et al.*, 1988) is based on X-ray data at even higher resolution, measured on a CAD-4 diffractometer. However, H-atom positions were not included for this refinement. For both refinements, only one octant of the reciprocal space was collected $[0 \leq h \leq h_{\max}, 0 \leq k \leq k_{\max}$ and $0 \leq l \leq l_{\max}]$, a common practice in the 1980s. This, however, precludes an accurate correction of data for absorption and other crystal-shape-related effects. A third article published in 2007 mentioned a single-crystal X-ray study for $(NH_4)_2V_3O_8$, using a very small plate-shaped crystal with dimensions $0.04 \times 0.03 \times 0.004$ mm^3, collected on an IPDS diffractometer equipped with a rotating anode (Ren *et al.*, 2007). Apparently, H atoms were included, but details about the structure were not provided in this article.

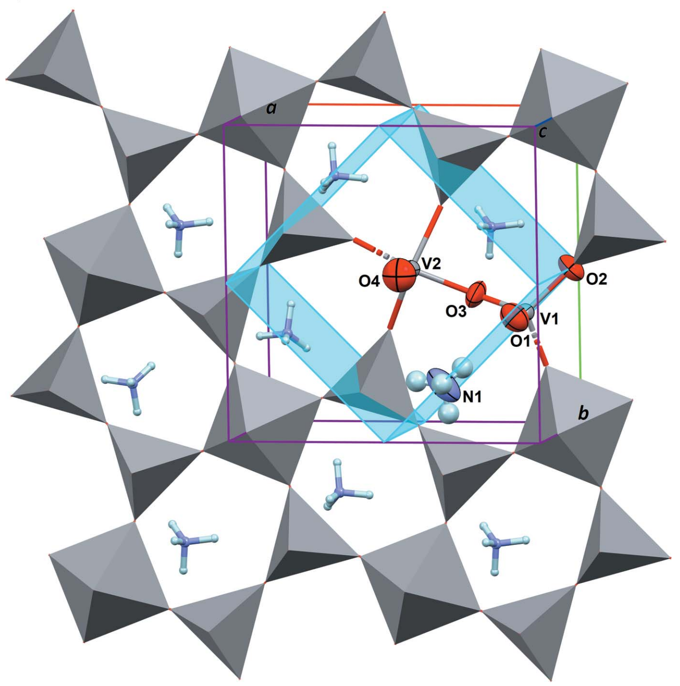

Figure 1
Crystal structure of $(NH_4)_2V_3O_8$ viewed approximately down the *c* axis. The asymmetric unit is represented with displacement ellipsoids drawn at the 90% probability level, and other vanadate groups are drawn with a polyhedral representation. Only one $(V_3O_8)^{2-}$ layer normal to [001] is represented, and a single position for the disordered NH_4^+ cation has been accentuated. Blue planes are the mirror *m* elements of space-group type *P*4*bm*.

Table 1
Bond lengths (Å) and angles (°) in $(NH_4)_2V_3O_8$ for vanadium sites determined in this work, compared to those reported in previous studies.

Labelling scheme for atomic sites is that used in the present work.

Parameter	1984 study [a]	1988 study [b]	This work
Bond lengths (Å)			
V1—O1	1.660 (5)	1.618	1.6353 (18)
V1—O2	1.793 (2)	1.803	1.7958 (9)
V1—O3 (×2)	1.709 (3)	1.720	1.7123 (12)
V2—O3 (×4)	1.962 (3)	1.972	1.9647 (12)
V2—O4	1.650 (8)	1.576	1.592 (3)
Bond angles (°)			
O1—V1—O2	109.2 (3)	110.1	109.20 (10)
O1—V1—O3 (×2)	111.3 (3)	112.2	111.16 (6)
O3—V1—O2 (×2)	107.9 (3)	106.9	107.89 (7)
O3—V1—O3	109.2 (3)	108.1	109.42 (8)
O3—V2—O3 (×2)	146.1 (2)	143.9	145.99 (10)
O3—V2—O3 (×4)	85.1 (1)	84.5	85.09 (3)
O4—V2—O3 (×4)	107.0 (1)	108.0	107.01 (5)

Notes: (*a*) Theobald *et al.* (1984); (*b*) Range *et al.* (1988); parameters for this refinement were calculated from the published unit-cell parameters and atom coordinates.

We have now redetermined the crystal structure of $(NH_4)_2V_3O_8$ (Fig. 1), after collecting a highly redundant data set at 295 K: redundancy was 33 for a resolution of 0.61 Å. The dimensions of the vanadium oxide layers are remarkably close to those determined by Theobald *et al.* (1984), apart for the axial bond lengths V1=O1 and V2=O4, which were overestimated by *ca* 0.02–0.06 Å (see comparison in Table 1). This difference could be a consequence of the wrong positions of some H atoms in Theobald's model.

We identified that the NH_4^+ cation is disordered by rotation around a non-crystallographic axis. The N atom lies in the mirror plane *m* of space group *P*4*bm* (Wyckoff position 4*c*), and after refining positions and displacement parameters for all non-H atoms, the highest positive residual electron density is found in the same plane and can be refined as an H atom (H1). The subsequent difference map suggests that the three missing H atoms are continuously disordered along a ring normal to the *m* plane (Fig. 2). The best model was eventually reached with the second ammonium H atom equally disordered over two 4*c* positions (H2*A* and H2*B*), and the last H atom placed in a general position (8*d*), also disordered over two sites, H3*A* and H3*B*, with occupancies of 0.5 (Fig. 2). Both NH_4^+ parts were refined with soft restraints (see *Refinement details*). The correctness of the model is validated through the refinement of isotropic displacement parameters for all H atoms. Any ordered model for H2 and H3 converged towards too high $U_{\rm iso}$ parameters, in the range 0.12 to 0.18 Å^2, while $U_{\rm iso}(H1) \simeq 0.05$ Å^2. Moreover, N—H bond lengths refined around 0.74 Å, whereas a bond length close to 0.80 Å is expected. In contrast, the proposed model has refined $U_{\rm iso}$(H)

Table 2
Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$N1—H1\cdots O1$	0.78 (3)	2.07 (3)	2.842 (3)	168 (3)
$N1—H2A\cdots O3^{i}$	0.81 (3)	2.41 (4)	2.980 (3)	129 (4)
$N1—H3A\cdots O1^{ii}$	0.83 (3)	2.24 (3)	3.006 (2)	153 (4)
$N1—H2B\cdots O1^{iii}$	0.81 (3)	2.37 (2)	3.006 (3)	136 (1)
$N1—H3B\cdots O3^{iv}$	0.81 (3)	2.49 (3)	3.274 (3)	162 (4)
$N1—H3B\cdots O3^{v}$	0.81 (3)	2.39 (4)	2.980 (3)	130 (4)

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

parameters in the range 0.051 (12) to 0.10 (4) Å^2 and N—H bond lengths between 0.78 (3) and 0.83 (3) Å.

As a consequence, only one significant $N—H\cdots O$ hydrogen bond of medium strength is formed in the crystal structure, involving the N1—H1 bond, which is also the non-crystallographic rotation axis for the disordered cation (Table 2, first entry). All other $N—H\cdots O$ contacts are weaker, with $H\cdots O$ separations in the range 2.24 (3)–2.49 (3) Å (Table 2, entries 2–6; Fig. 3). This makes a difference, for instance, with the structure of ammonium metavanadate, NH_4VO_3, for which the ammonium cation is ordered and which forms at least two strong hydrogen bonds with the vanadium oxide matrix (Pérez-Benítez & Bernès, 2018). The rather poor interaction of the ammonium cation with the $(V_3O_8)^{2-}$ layers in the crystal structure of $(NH_4)_2V_3O_8$ could be of interest for its application as a cathode material for supercapacitors, since the replacement of NH_4^+ cations by Li^+ should be a process with a low free enthalpy, compared to that of other fresnoite-type vanadates. From the structural point of view, however, the matter is more complex: although no definitive data are available so far, it seems that $Li_2V_3O_8$ does not belong to the fresnoite structural type. Theoretical (Koval'chuk *et al.*, 2002) and experimental (de Picciotto *et al.*, 1993; Jouanneau *et al.*, 2005) data for $Li_{1+x}V_3O_8$ show that these vanadates crystallize in the hewettite structural type, in space-group type $P2_1/m$, as does $Na_2V_3O_8$ (Bachmann & Barnes, 1962). On the other hand, to the best of our knowledge, no studies have been made hitherto on the pseudo-binary system $Li_2V_3O_8$–$(NH_4)_2V_3O_8$.

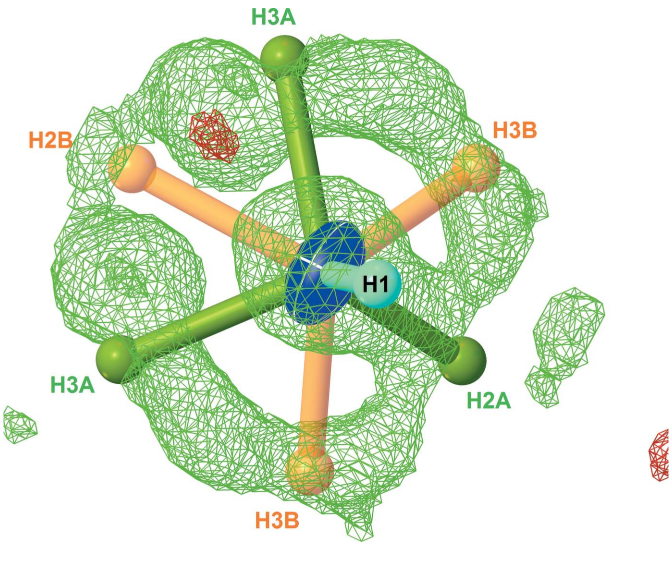

Figure 2
Difference electron-density map in the vicinity of the N-atom site calculated on the basis of a model including N1 and H1 atoms (R_1 = 0.0183, wR_2 = 0.0420). The difference map is plotted at the 0.18 e$^-$ Å^{-3} level with a resolution of 0.05 Å (Dolomanov *et al.*, 2009). At this level, only positive residuals are observed (green wire), corresponding essentially to the N—H σ bond and missing H atoms. Positions for all H atoms in the final refinement (R_1 = 0.0163, wR_2 = 0.0296) are superimposed on the calculated difference map, showing the fit between the experimental data and the proposed model.

Synthesis and crystallization

Good-quality single crystals of $(NH_4)_2V_3O_8$ were obtained as a by product during the reaction between ammonium metavanadate (NH_4VO_3, 0.5 g, 4.27 mmol), and metformin hydrochloride ($HMetf^+Cl^-$, 0.425 g, 2.56 mmol) in 75 ml of distilled water and 1 ml of acetic acid 5% *v*/*v*. Ammonium metavanadate and metformin hydrochloride were dissolved in water by gently heating the mixture. Given that our main purpose was to synthesize decavanadate salts $(HMetf)_6(V_{10}O_{28})\cdot n(H_2O)$, a small amount of acetic acid was added to the mixture, to achieve a pH of *ca* 6.5. In fact, under these conditions, a mixture of two different hydrates of the desired compound were obtained, $(HMetf)_6(V_{10}O_{28})\cdot 6(H_2O)$ (orange needles) and $(HMetf)_6(V_{10}O_{28})\cdot 4(H_2O)$ (orange plates). Other crystallized products were the double salt $(NH_4)_2(H_2Metf)_2(V_{10}O_{28})\cdot 10(H_2O)$ (orange needles), the unreacted colourless $HMetf^+Cl^-$, and a tiny amount of dark-blue single-crystals of $(NH_4)_2V_3O_8$, the structure of which is discussed here.

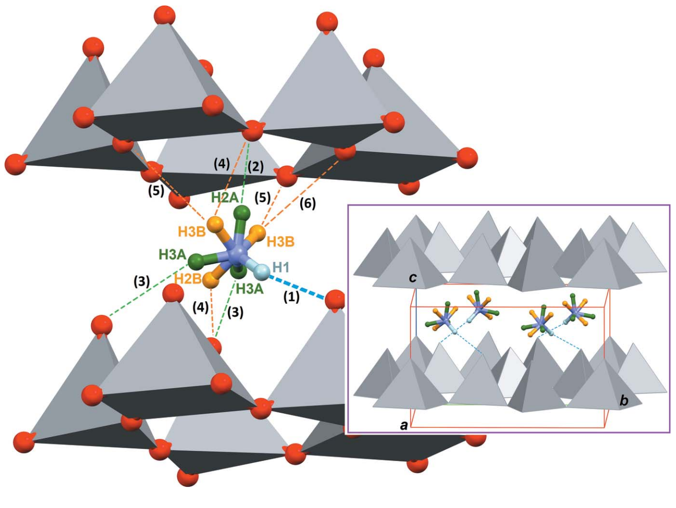

Figure 3
Part of the crystal structure of $(NH_4)_2V_3O_8$ showing the $N—H\cdots O$ hydrogen bonds. The NH_4^+ cation is disordered over two positions, N1/H1/H2*A*/H3*A* (green) and N1/H1/H2*B*/H3*B* (orange). Hydrogen bonds are represented as dashed lines, with a label referring to entries in Table 2. The inset shows how the cations interact with the vanadium oxide matrix. Only the strongest $N1—H1\cdots O1$ hydrogen bond is represented.

Table 3
Experimental details.

Crystal data	
Chemical formula	$(NH_4)_2V_3O_8$
M_r	316.90
Crystal system, space group	Tetragonal, *P*4*bm*
Temperature (K)	295
a, *c* (Å)	8.9062 (4), 5.5784 (3)
V (Å^3)	442.48 (5)
Z	2
Radiation type	Ag *K*α, λ = 0.56083 Å
μ (mm^{-1})	1.60
Crystal size (mm)	0.06 × 0.06 × 0.03
Data collection	
Diffractometer	Stoe Stadivari
Absorption correction	Multi-scan (*X-RED32*; Stoe & Cie, 2019)
T_{min}, T_{max}	0.410, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26907, 1106, 930
R_{int}	0.061
(sin θ/λ)$_{max}$ (Å^{-1})	0.823
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.016, 0.030, 0.87
No. of reflections	1106
No. of parameters	57
No. of restraints	18
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.44, −0.23
Absolute structure	Refined as an inversion twin.
Absolute structure parameter	0.36 (4)

Computer programs: *X-AREA* (Stoe & Cie, 2019), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The five H atoms modelling the disordered NH_4^+ cation were refined with free coordinates and free isotropic displacement parameters. While H1 fully occupies its site, H2 and H3 are equally disordered over two sites, H2*A*/H2*B* and H3*A*/H3*B*, respectively. All N—H bond lengths were restrained to a common free variable *d*, with a standard deviation of 0.02 Å (5 restraints), and the tetrahedral shape of each disordered part was upheld by restricting H···H separations to $(8/3)^{1/2}\times d$, within a standard deviation of 0.03 Å (12 restraints). The free variable *d* converged to 0.81 (2) Å (Sheldrick, 2015*b*). The crystal was considered as a racemic twin, and the batch scale factor refined to $x = 0.36$ (4).

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full crystallographic data

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Redetermination of diammonium trivanadate, $(NH_4)_2V_3O_8$

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Diammonium trivanadate

Crystal data

$(NH_4)_2V_3O_8$
$M_r = 316.90$
Tetragonal, *P*4*bm*
$a = 8.9062$ (4) Å
$c = 5.5784$ (3) Å
$V = 442.48$ (5) Å^3
$Z = 2$
$F(000) = 310$
$D_x = 2.379$ Mg m^{-3}
Ag *Kα* radiation, $\lambda = 0.56083$ Å
Cell parameters from 21170 reflections
$\theta = 2.9$–32.5°
$\mu = 1.60$ mm^{-1}
$T = 295$ K
Prism, blue
0.06 × 0.06 × 0.03 mm

Data collection

Stoe Stadivari diffractometer
Radiation source: Sealed X-ray tube, Axo Astix-f Microfocus source
Graded multilayer mirror monochromator
Detector resolution: 5.81 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (X-RED32; Stoe & Cie, 2019)
$T_{\min} = 0.410$, $T_{\max} = 1.000$
26907 measured reflections
1106 independent reflections
930 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.061$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 2.6°$
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.030$
$S = 0.87$
1106 reflections
57 parameters
18 restraints
0 constraints
Primary atom site location: dual
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0141P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.44$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Absolute structure: Refined as an inversion twin.
Absolute structure parameter: 0.36 (4)

Special details

Refinement. Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
V1	0.13352 (2)	0.63352 (2)	0.29279 (12)	0.01254 (6)	
V2	0.500000	0.500000	0.28825 (18)	0.01385 (9)	
O1	0.13050 (15)	0.63050 (15)	0.5859 (3)	0.0251 (4)	
O2	0.000000	0.500000	0.1799 (4)	0.0208 (5)	
O3	0.30693 (14)	0.58500 (14)	0.1852 (3)	0.0237 (2)	
O4	0.500000	0.500000	0.5737 (5)	0.0326 (6)	
N1	0.33009 (19)	0.83009 (19)	0.8234 (6)	0.0309 (6)	
H1	0.280 (2)	0.780 (2)	0.740 (5)	0.051 (12)*	
H2A	0.317 (5)	0.817 (5)	0.965 (6)	0.10 (4)*	0.5
H3A	0.320 (3)	0.921 (3)	0.794 (9)	0.08 (2)*	0.5
H2B	0.385 (3)	0.885 (3)	0.749 (11)	0.06 (3)*	0.5
H3B	0.279 (4)	0.880 (4)	0.914 (6)	0.09 (2)*	0.5

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.00932 (8)	0.00932 (8)	0.01900 (14)	−0.00001 (10)	0.00065 (19)	0.00065 (19)
V2	0.00970 (11)	0.00970 (11)	0.0222 (2)	0.000	0.000	0.000
O1	0.0275 (6)	0.0275 (6)	0.0202 (8)	−0.0048 (7)	−0.0022 (5)	−0.0022 (5)
O2	0.0208 (7)	0.0208 (7)	0.0208 (12)	−0.0085 (9)	0.000	0.000
O3	0.0126 (5)	0.0218 (6)	0.0365 (6)	0.0056 (5)	0.0016 (5)	0.0049 (5)
O4	0.0356 (10)	0.0356 (10)	0.0266 (15)	0.000	0.000	0.000
N1	0.0352 (8)	0.0352 (8)	0.0225 (17)	−0.0173 (9)	0.0000 (7)	0.0000 (7)

Geometric parameters (Å, º)

V1—O1	1.6353 (18)	V2—O4	1.592 (3)
V1—O2	1.7958 (9)	N1—H1	0.78 (3)
V1—O3	1.7123 (12)	N1—H2A	0.81 (3)
V1—O3^{i}	1.7123 (12)	N1—H3A	0.83 (3)
V2—O3	1.9647 (12)	N1—H3A^{i}	0.83 (3)
V2—O3^{ii}	1.9647 (12)	N1—H2B	0.81 (3)
V2—O3^{iii}	1.9647 (12)	N1—H3B	0.81 (3)
V2—O3^{iv}	1.9647 (12)	N1—H3B^{i}	0.81 (3)
O1—V1—O2	109.20 (10)	O4—V2—O3	107.01 (5)
O1—V1—O3	111.16 (6)	V1—O2—V1^{v}	138.94 (15)
O1—V1—O3^{i}	111.16 (6)	V1—O3—V2	141.64 (9)
O3—V1—O2	107.89 (7)	H1—N1—H2A	115 (5)
O3^{i}—V1—O2	107.89 (7)	H1—N1—H3A	112 (3)
O3—V1—O3^{i}	109.42 (8)	H2A—N1—H3A	109 (3)
O3^{ii}—V2—O3^{iii}	145.99 (10)	H1—N1—H3A^{i}	112 (3)
O3^{ii}—V2—O3^{iv}	85.09 (3)	H2A—N1—H3A^{i}	109 (3)
O3^{iii}—V2—O3^{iv}	85.09 (3)	H3A—N1—H3A^{i}	99 (4)
O3^{ii}—V2—O3	85.09 (3)	H1—N1—H2B	113 (5)

O3^{iii}—V2—O3	85.09 (3)	H1—N1—H3B	111 (3)
O3^{iv}—V2—O3	145.99 (10)	H2B—N1—H3B	109 (3)
O4—V2—O3^{ii}	107.01 (5)	H1—N1—H3B^{i}	111 (3)
O4—V2—O3^{iii}	107.01 (5)	H2B—N1—H3B^{i}	109 (3)
O4—V2—O3^{iv}	107.01 (5)	H3B—N1—H3B^{i}	103 (5)
O1—V1—O2—V1^{v}	0.000 (1)	O1—V1—O3—V2	11.34 (15)
O3—V1—O2—V1^{v}	120.94 (6)	O3^{i}—V1—O3—V2	134.50 (8)
O3^{i}—V1—O2—V1^{v}	−120.94 (6)	O2—V1—O3—V2	−108.36 (14)

Symmetry codes: (i) *y*−1/2, *x*+1/2, *z*; (ii) −*y*+1, *x*, *z*; (iii) *y*, −*x*+1, *z*; (iv) −*x*+1, −*y*+1, *z*; (v) −*x*, −*y*+1, *z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.78 (3)	2.07 (3)	2.842 (3)	168 (3)
N1—H2*A*···O3^{vi}	0.81 (3)	2.41 (4)	2.980 (3)	129 (4)
N1—H3*A*···O1^{vii}	0.83 (3)	2.24 (3)	3.006 (2)	153 (4)
N1—H2*B*···O1^{iii}	0.81 (3)	2.37 (2)	3.006 (3)	136 (1)
N1—H3*B*···O3^{viii}	0.81 (3)	2.49 (3)	3.274 (3)	162 (4)
N1—H3*B*···O3^{ix}	0.81 (3)	2.39 (4)	2.980 (3)	130 (4)

Symmetry codes: (iii) *y*, −*x*+1, *z*; (vi) *x*, *y*, *z*+1; (vii) −*y*+1, *x*+1, *z*; (viii) −*x*+1/2, *y*+1/2, *z*+1; (ix) *y*−1/2, *x*+1/2, *z*+1.