Crystal structure of diethylammonium dioxido-{Z}-N-[(pyridin-2-yl)carbonylazanidyl]pyridine-2-carboximidato}vanadate(1−) monohydrate

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The title compound, $(C_4H_{12}N)[V(C_{12}H_8N_4O_2)O_2]\cdot H_2O$, was synthesized *via* aerial oxidation on refluxing picolinohydrazide with ethyl picolinate followed by addition of $V^{IV}O(acac)_2$ and diethylamine in methanol. It crystallizes in the triclinic crystal system in space group $P\bar{1}$. In the complex anion, the dioxido-vanadium(V) moiety exhibits a distorted square-pyramidal geometry. In the crystal, extensive hydrogen bonding links the water molecule to two complex anions and one diethylammonium ion. One of the CH_2 groups in the diethyl-amine is disordered over two sets of sites in a 0.7:0.3 ratio.

1. Chemical context

Vanadium, a biologically important trace element with the +V oxidation state, has received considerable attention among the three (*viz.*, +III, +IV and +V) physiologically important oxidation states. In this oxidation state, vanadium exists in three different motifs, *viz.*, VO^{3+}, $V_2O_3^{4+}$ and VO_2^+. The formation and stability of these three motifs depends upon the nature of the solvent, the pH of the reaction medium and basicity of the donor atoms of the ligand(s), with a preference for N, O-donor ligands because of the hard acidic nature of V^V. It is evident from the literature (Mondal *et al.*, 2010, 2008) that the vanadium complexes containing VO_2^+ motifs are formed in basic media. Vanadium compounds show the catalytic cycle of haloperoxidase activity has been suggested to proceed through hydrogen-bonding interactions (Colpas *et al.*, 1996; Messerschimdt & Wever, 1996; Weyand *et al.*, 1999; Isupov *et al.*, 2000). In the presence of appropriate hydrogen-bond donors, hydrogen bonding is a general feature of vanadium(IV) and vanadium(V) complexes (Mondal *et al.*, 2010; Plass, 1997, 1998; Plass & Yozgatli, 2003; Pohlmann & Plass, 2001; Pohlmann *et al.*, 2005; Vergopoulos *et al.*, 1993; Sutradhar *et al.*, 2006). In general, these examples lead to the formation of hydrogen-bonded molecular assemblies ranging from simple dimers to three-dimensional networks.
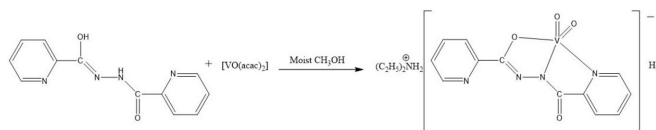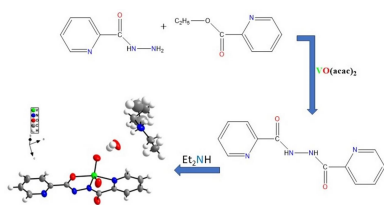
In this work, an ionic compound of dioxidovanadium(V) containing a symmetric *N*-(pyridine-2-ylcarbamoyl)picolina-mide (Shao *et al.*, 1999) ligand (H_2L) bound to vanadium through NNO in an asymmetric fashion, was synthesized in the presence of diethylamine in good yield and characterized

Table 1
Selected bond lengths (Å).

V1—O2	1.6107 (15)	V1—N2	2.0385 (15)
V1—O3	1.9461 (14)	V1—N1	2.1170 (15)
V1—O1	1.6310 (16)		

by X-ray crystallography. The title compound may be used for antidiabetic drug development (Jia *et al.*, 2017).

2. Structural commentary

The solid-state molecular structure was confirmed by single-crystal X-ray characterization. The title compound crystallizes in the triclinic crystal system, space group $P\bar{1}$. The asymmetric unit (Fig. 1*a*) comprises a diethylammonium cation, a complex dioxidovanadium(V) and a water molecule, which is inter-linked between the two ionic parts of the compound through hydrogen bonding (Fig. 1*b*). The anionic part of the compound consists of one crystallographically independent V^{5+} ion, two oxido ligands and one NNO donor ligand with coordination sphere of the VO_3N_2 type (Fig. 1*a*). The V^{5+} ion is coordinated by two oxygen (O1 and O2) atoms (oxido ligands), one nitrogen (N1) atom of the pyridine ring, one deprotonated
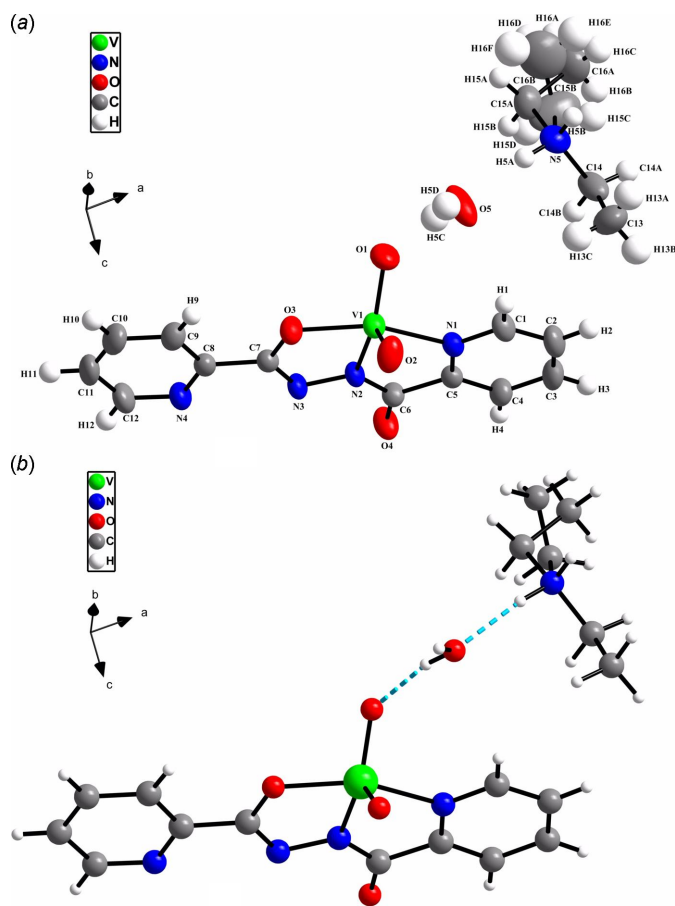

(a)

(b)

Figure 1
(*a*) The molecular structure with the atom-numbering scheme and ellipsoids drawn at the 50% probability level and (*b*) the intramolecular hydrogen bond.

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N5—H5A$\cdots$O5	0.95 (3)	1.92 (3)	2.848 (3)	165 (3)
N5—H5B$\cdots$N3[i]	0.85 (3)	2.08 (3)	2.918 (3)	171 (3)
O5—H5C$\cdots$O1	0.85	1.94	2.776 (3)	169
O5—H5D$\cdots$O4[ii]	0.85	1.99	2.838 (2)	178
C2—H2$\cdots$O2[iii]	0.93	2.48	3.277 (3)	143
C14—H14A$\cdots$O4[i]	0.97	2.57	3.172 (3)	121
C15A—H15A$\cdots$N4[i]	0.97	2.59	3.233 (5)	124

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

amide nitrogen (N2) atom and a deprotonated amide-oxygen (O3) through enolization (Fig. 2) of the ligand. The five-coordinate V^{5+} ion has a distorted square-pyramidal geometry with one of the two oxido oxygen atoms (O1) at the apex. The extent of distortion from a perfect square-pyramidal geometry can be quantified by the structural index parameter ($\tau = 0.35$), as determined from the equation $\tau = (\beta - \alpha)/60$ (where β and α are the two largest $L—M—L$ angles), which is 0 for an idealized square pyramid and 1 for a trigonal bipyramid (Nair *et al.*, 2018; Ghosh *et al.*, 2022). The square plane consists of one nitrogen atom from the pyridine ring (N1), one depro-tonated amide nitrogen (N2), one enolate oxygen (O3) and one oxido oxygen (O2) atom of the ligands. The vanadium atom is located 0.555 (4) Å above the equatorial plane and displaced towards the axial O1 atom. Selected bonds involving the V atom are given in Table 1. The V—O1 bond is longer than V—O2, probably due to the involvement of O1 in a hydrogen bond with the water hydrogen atom H5C (Table 2). Among the three V—O bonds, the longest is the V—O3 bond length due to the absence of a V—O π-bond (Mondal *et al.*, 2010; Jia *et al.*, 2017). In the absence of diethylamine, the formation of neutral dioxido complex has been reported in which the uncoordinated pyridine atom N4 is protonated (Jia *et al.*, 2017), but in this case the protonation of the diethyl-amine moiety (pK_a = 10.98) is probably due to its higher basicity than pyridine (pK_a = 5.23).

3. Supramolecular features

The oxygen (O5) atom of water acts as a hydrogen-bond donor with an acceptor oxido group (O1) of the dioxidovan-adium(V) complex in the same asymmetric unit (O5—H5C$\cdots$O1) and a symmetry-related amide oxygen (O4) atom in a neighbouring asymmetric unit (O5—H5D$\cdots$O4) (Table 2). The O5 atom also acts as a hydrogen-bond acceptor for the amine H5A atom (N5—H5A$\cdots$O5). Another amine hydrogen (H5B) is hydrogen bonded with the N3 atom
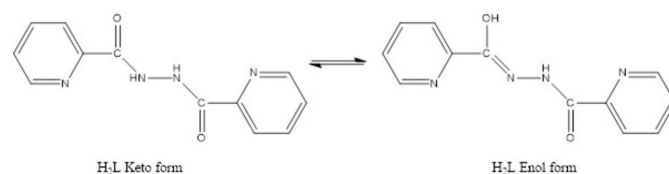

Figure 2
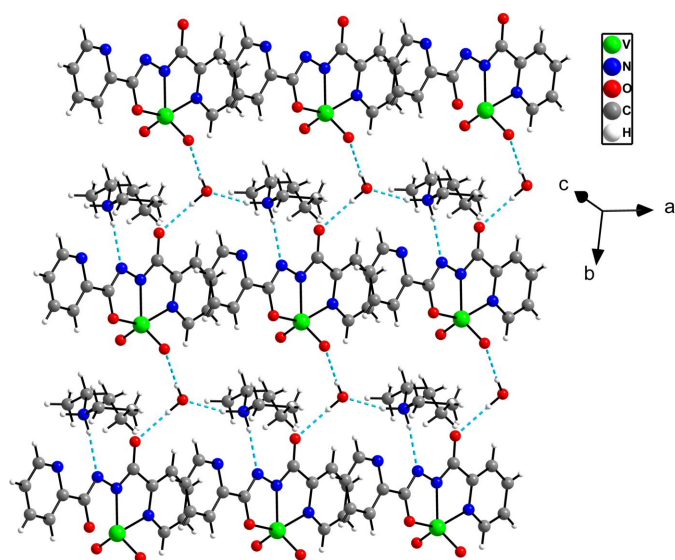The keto–enol tautomeric forms of the ligand.

Figure 3
The hydrogen bonding in adjacent asymmetric units.

(N5—H5B···N3) of an adjacent complex. Two C—H···O and one C—H···N interactions are also observed. These hydrogen bonds within the same and different asymmetric units enhance
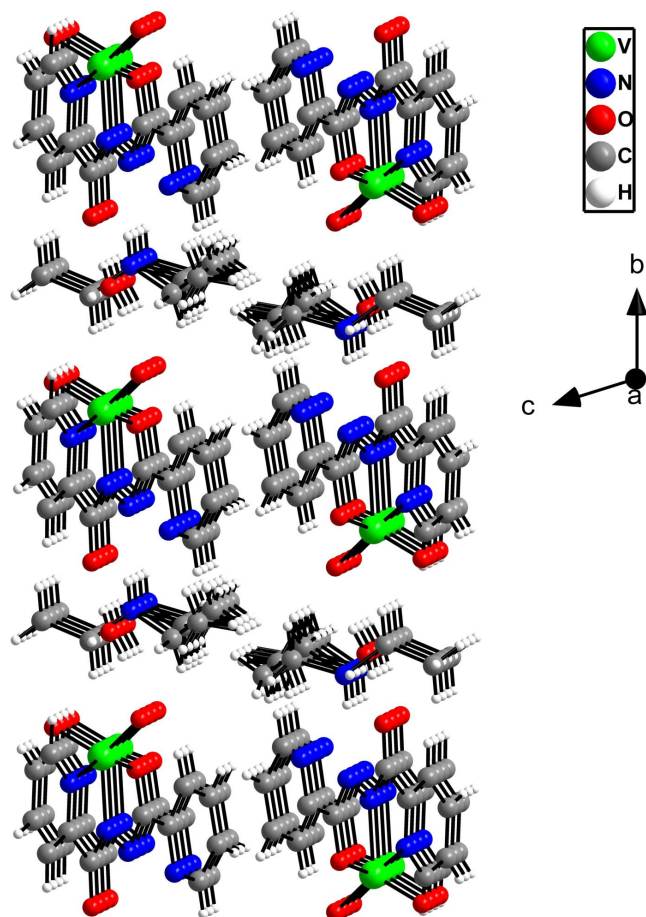
Table 3
Experimental details.

Crystal data	
Chemical formula	(C$_4$H$_{12}$N)[V(C$_{12}$H$_8$N$_4$O$_2$)O$_2$]·H$_2$O
M_r	415.32
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	298
a, b, c (Å)	7.6850 (4), 9.4135 (4), 13.9147 (7)
α, β, γ (°)	105.609 (2), 101.103 (2), 96.253 (2)
V (Å^3)	937.50 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.57
Crystal size (mm)	0.32 × 0.18 × 0.03
Data collection	
Diffractometer	Bruker D8 Quest with Photon II area detector
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.670, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	61285, 5048, 3852
R_{int}	0.081
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.685
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.110, 1.06
No. of reflections	5048
No. of parameters	274
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

the crystal packing of the compounds (Figs. 1*b* and 3). The mono-periodic constructs are packed perpendicular to the *bc* plane, giving rise to an overall three-dimensional packing arrangement (Fig. 4).

4. Database survey

Mondal *et al.* (2010) reported numerous ionic dioxidovanadium(V) compounds with *O*,*N*,*O* donor ligands in presence of different types of bases. Jia *et al.* (2017) also reported a neutral dioxidovanadium(V) compound with the same ligand.

5. Synthesis and crystallization

To a solution of picolinohydrazide (0.137 g, 1 mmol) in methanol (25 ml) was added ethyl picolinate (0.151 g, 1 mmol). The solution was heated under reflux for 3 h. The reaction mixture was cooled to room temperature and a methanolic solution (20 ml) of [V^{IV}O(acac)$_2$] (0.265 g, 1 mmol) was added with stirring. After stirring for 2 h, a methanolic solution (10 ml) of diethylamine (1 ml) was added with continuous stirring. The solution immediately turned yellow and the reaction mixture was then refluxed for 1 h. The reaction mixture was then kept for slow evaporation at room temperature. A yellow X-ray quality crystalline compound was obtained, which was filtered, washed with methanol and dried over silica gel (fused). Yield: 0.34 g (82%). Crystals of the

Figure 4
The three-dimensional packing arrangement of the components of the title compound.

complex were obtained after 4-days on slow evaporation at room temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. N-bound H atoms were refined with $U_{iso}(H) = 1.2U_{eq}(N)$. C-bound H atoms and water H atoms were placed at calculated positions (C—H = 0.93–0.97 Å, O—H = 0.85 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(C-methyl,O). Initially, residual electron density ws noted near to C15. The part command was used to locate the two positions of C15 (*i.e.*, C15*A*, in PART 1; and C15*B*, in PART 2). The site occupancie are 0.7 and 0.3, respectively. Subsequently, an isotropic refinement was done and finally, an anisotropic refinement is performed.

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supporting information

Crystal structure of diethylammonium dioxido{*Z*)-*N*-[(pyridin-2-yl)carbonylaza-nidyl]pyridine-2-carboximidato}vanadate(1−) monohydrate

Bipul Mondal

Computing details

Diethylammonium dioxido{*Z*)-*N*-[(pyridin-2-yl)carbonylazanidyl]pyridine-2-carboximidato}vanadate(1-) monohydrate

Crystal data

$(C_4H_{12}N)[V(C_{12}H_8N_4O_2)O_2]\cdot H_2O$	$Z = 2$
$M_r = 415.32$	$F(000) = 432$
Triclinic, $P\overline{1}$	$D_x = 1.471$ Mg m^{-3}
$a = 7.6850$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.4135$ (4) Å	Cell parameters from 9990 reflections
$c = 13.9147$ (7) Å	$\theta = 2.3$–30.2°
$\alpha = 105.609$ (2)°	$\mu = 0.57$ mm^{-1}
$\beta = 101.103$ (2)°	$T = 298$ K
$\gamma = 96.253$ (2)°	BLOCK, yellow
$V = 937.50$ (8) Å^3	$0.32 \times 0.18 \times 0.03$ mm

Data collection

Bruker D8 Quest with Photon II area detector diffractometer	5048 independent reflections
	3852 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.081$
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)	$\theta_{max} = 29.1°$, $\theta_{min} = 2.3°$
	$h = -10\rightarrow10$
$T_{min} = 0.670$, $T_{max} = 0.747$	$k = -12\rightarrow12$
61285 measured reflections	$l = -19\rightarrow19$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.038$	and constrained refinement
$wR(F^2) = 0.110$	$w = 1/[\sigma^2(F_o^2) + (0.045P)^2 + 0.4439P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
5048 reflections	$(\Delta/\sigma)_{max} = 0.001$
274 parameters	$\Delta\rho_{max} = 0.43$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.39$ e Å^{-3}

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
V1	0.58085 (4)	0.29537 (3)	0.78356 (3)	0.03307 (10)	
N4	0.0021 (2)	−0.1100 (2)	0.63830 (14)	0.0431 (4)	
O2	0.5724 (2)	0.42364 (17)	0.88516 (12)	0.0518 (4)	
O3	0.32784 (18)	0.22542 (14)	0.71551 (11)	0.0394 (3)	
N3	0.36076 (19)	−0.00629 (16)	0.73136 (13)	0.0332 (3)	
C1	0.9836 (3)	0.3489 (2)	0.88556 (17)	0.0419 (5)	
H1	0.979921	0.446045	0.882458	0.050*	
O1	0.6564 (2)	0.36927 (18)	0.70301 (13)	0.0528 (4)	
C2	1.1439 (3)	0.3148 (3)	0.92898 (18)	0.0487 (5)	
H2	1.246761	0.387685	0.955215	0.058*	
O5	0.8727 (2)	0.6487 (2)	0.7639 (2)	0.0755 (6)	
H5C	0.799539	0.566441	0.738019	0.113*	
H5D	0.806183	0.714430	0.777364	0.113*	
N2	0.53498 (19)	0.07461 (16)	0.77552 (12)	0.0316 (3)	
C4	0.9945 (3)	0.0640 (2)	0.89249 (17)	0.0415 (4)	
H4	0.996177	−0.034329	0.893312	0.050*	
N5	1.2242 (3)	0.6901 (2)	0.72745 (16)	0.0484 (5)	
H5A	1.107 (4)	0.694 (3)	0.740 (2)	0.058*	
H5B	1.276 (4)	0.777 (3)	0.732 (2)	0.058*	
C3	1.1493 (3)	0.1707 (3)	0.93290 (18)	0.0493 (5)	
H3	1.256060	0.145211	0.962437	0.059*	
O4	0.64803 (19)	−0.13258 (15)	0.80366 (14)	0.0497 (4)	
N1	0.8323 (2)	0.24697 (17)	0.84751 (12)	0.0325 (3)	
C5	0.8380 (2)	0.1063 (2)	0.85105 (14)	0.0313 (4)	
C7	0.2627 (2)	0.08519 (19)	0.70259 (14)	0.0311 (4)	
C6	0.6610 (2)	0.00098 (19)	0.80739 (15)	0.0330 (4)	
C14	1.3191 (3)	0.6392 (3)	0.8113 (2)	0.0598 (7)	
H14A	1.442548	0.635076	0.805965	0.072*	
H14B	1.261482	0.539255	0.805202	0.072*	
C13	1.3170 (4)	0.7421 (4)	0.9123 (2)	0.0828 (10)	
H13A	1.371411	0.841452	0.917594	0.124*	
H13B	1.383288	0.709304	0.965860	0.124*	
H13C	1.194956	0.742057	0.918946	0.124*	
C15A	1.1933 (5)	0.5973 (5)	0.6175 (4)	0.0527 (10)	0.7
H15A	1.112883	0.639100	0.573984	0.063*	0.7
H15B	1.137207	0.496051	0.609451	0.063*	0.7
C16A	1.3721 (7)	0.5944 (7)	0.5852 (5)	0.0695 (13)	0.7
H16A	1.349650	0.557036	0.511873	0.104*	0.7
H16B	1.438875	0.530498	0.615382	0.104*	0.7

H16C	1.440214	0.693958	0.608190	0.104*	0.7
C8	0.0699 (2)	0.0330 (2)	0.65164 (14)	0.0326 (4)	
C9	−0.0329 (3)	0.1301 (2)	0.61863 (16)	0.0421 (5)	
H9	0.017119	0.229460	0.630326	0.050*	
C10	−0.2108 (3)	0.0772 (3)	0.56808 (19)	0.0534 (6)	
H10	−0.282243	0.140321	0.544890	0.064*	
C11	−0.2801 (3)	−0.0687 (3)	0.55262 (19)	0.0554 (6)	
H11	−0.398965	−0.107782	0.517707	0.067*	
C12	−0.1699 (3)	−0.1567 (3)	0.58996 (19)	0.0526 (6)	
H12	−0.219043	−0.255526	0.580788	0.063*	
C15B	1.279 (3)	0.5710 (13)	0.6404 (12)	0.102 (6)	0.3
H15C	1.399256	0.553432	0.665826	0.123*	0.3
H15D	1.196845	0.477106	0.621828	0.123*	0.3
C16B	1.276 (3)	0.6182 (19)	0.5559 (13)	0.116 (6)	0.3
H16D	1.270778	0.533969	0.497547	0.173*	0.3
H16E	1.383543	0.688974	0.567037	0.173*	0.3
H16F	1.172786	0.664919	0.543386	0.173*	0.3

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.03157 (16)	0.02325 (15)	0.04138 (19)	0.00202 (11)	0.00358 (13)	0.00908 (12)
N4	0.0319 (8)	0.0415 (9)	0.0525 (11)	−0.0027 (7)	0.0019 (7)	0.0175 (8)
O2	0.0457 (8)	0.0400 (8)	0.0543 (9)	0.0124 (7)	−0.0010 (7)	−0.0046 (7)
O3	0.0345 (7)	0.0278 (6)	0.0520 (8)	0.0024 (5)	−0.0009 (6)	0.0141 (6)
N3	0.0249 (7)	0.0277 (7)	0.0438 (9)	−0.0003 (6)	0.0023 (6)	0.0111 (6)
C1	0.0354 (10)	0.0326 (9)	0.0495 (12)	−0.0043 (8)	0.0055 (9)	0.0056 (9)
O1	0.0511 (9)	0.0474 (9)	0.0672 (11)	0.0019 (7)	0.0118 (8)	0.0329 (8)
C2	0.0319 (10)	0.0489 (12)	0.0526 (13)	−0.0062 (9)	0.0018 (9)	0.0049 (10)
O5	0.0432 (9)	0.0467 (10)	0.146 (2)	0.0060 (8)	0.0276 (11)	0.0400 (12)
N2	0.0239 (7)	0.0261 (7)	0.0422 (9)	0.0002 (5)	0.0031 (6)	0.0106 (6)
C4	0.0325 (9)	0.0428 (11)	0.0485 (12)	0.0072 (8)	0.0035 (8)	0.0163 (9)
N5	0.0555 (12)	0.0325 (9)	0.0583 (12)	0.0029 (8)	0.0163 (10)	0.0151 (9)
C3	0.0294 (10)	0.0594 (14)	0.0536 (13)	0.0053 (9)	−0.0009 (9)	0.0162 (11)
O4	0.0362 (7)	0.0312 (7)	0.0835 (12)	0.0050 (6)	0.0057 (7)	0.0260 (7)
N1	0.0288 (7)	0.0288 (7)	0.0371 (8)	0.0010 (6)	0.0065 (6)	0.0076 (6)
C5	0.0283 (8)	0.0318 (9)	0.0339 (9)	0.0043 (7)	0.0067 (7)	0.0108 (7)
C7	0.0306 (8)	0.0289 (8)	0.0324 (9)	0.0018 (7)	0.0058 (7)	0.0090 (7)
C6	0.0320 (9)	0.0262 (8)	0.0399 (10)	0.0035 (7)	0.0040 (7)	0.0119 (7)
C14	0.0450 (12)	0.0587 (15)	0.098 (2)	0.0169 (11)	0.0232 (13)	0.0522 (15)
C13	0.072 (2)	0.124 (3)	0.0664 (19)	0.0195 (19)	0.0103 (15)	0.054 (2)
C15A	0.049 (2)	0.041 (2)	0.059 (3)	0.0063 (15)	0.0060 (18)	0.0045 (17)
C16A	0.066 (3)	0.077 (3)	0.065 (3)	0.019 (2)	0.023 (2)	0.011 (2)
C8	0.0296 (8)	0.0355 (9)	0.0317 (9)	0.0034 (7)	0.0066 (7)	0.0095 (7)
C9	0.0372 (10)	0.0438 (11)	0.0438 (11)	0.0103 (8)	0.0046 (8)	0.0127 (9)
C10	0.0353 (11)	0.0700 (16)	0.0564 (14)	0.0171 (11)	0.0032 (10)	0.0232 (12)
C11	0.0260 (9)	0.0803 (17)	0.0554 (14)	0.0011 (10)	0.0004 (9)	0.0221 (13)
C12	0.0344 (11)	0.0547 (13)	0.0609 (15)	−0.0099 (9)	0.0015 (10)	0.0178 (11)

C15B	0.179 (19)	0.039 (5)	0.083 (10)	0.028 (9)	0.019 (12)	0.013 (6)
C16B	0.137 (17)	0.088 (10)	0.111 (14)	0.029 (11)	0.046 (13)	−0.005 (9)

Geometric parameters (Å, º)

V1—O2	1.6107 (15)	C4—C5	1.378 (3)
V1—O3	1.9461 (14)	N5—C14	1.473 (3)
V1—O1	1.6310 (16)	N5—C15A	1.502 (5)
V1—N2	2.0385 (15)	N5—C15B	1.573 (16)
V1—N1	2.1170 (15)	O4—C6	1.237 (2)
N4—C8	1.340 (2)	N1—C5	1.343 (2)
N4—C12	1.329 (3)	C5—C6	1.506 (2)
O3—C7	1.311 (2)	C7—C8	1.480 (2)
N3—N2	1.400 (2)	C14—C13	1.481 (4)
N3—C7	1.296 (2)	C15A—C16A	1.526 (7)
C1—C2	1.375 (3)	C8—C9	1.383 (3)
C1—N1	1.342 (2)	C9—C10	1.380 (3)
C2—C3	1.377 (3)	C10—C11	1.362 (4)
N2—C6	1.327 (2)	C11—C12	1.374 (3)
C4—C3	1.385 (3)	C15B—C16B	1.36 (2)
O2—V1—O3	102.55 (7)	C1—N1—V1	123.69 (13)
O2—V1—O1	110.64 (9)	C1—N1—C5	118.88 (16)
O2—V1—N2	121.01 (8)	C5—N1—V1	117.43 (12)
O2—V1—N1	95.14 (7)	C4—C5—C6	123.33 (17)
O3—V1—N2	74.82 (5)	N1—C5—C4	121.92 (17)
O3—V1—N1	148.99 (6)	N1—C5—C6	114.75 (15)
O1—V1—O3	102.22 (7)	O3—C7—C8	117.03 (15)
O1—V1—N2	127.77 (8)	N3—C7—O3	122.55 (16)
O1—V1—N1	94.92 (7)	N3—C7—C8	120.41 (16)
N2—V1—N1	74.24 (6)	N2—C6—C5	109.38 (15)
C12—N4—C8	116.92 (18)	O4—C6—N2	129.15 (17)
C7—O3—V1	117.29 (11)	O4—C6—C5	121.47 (16)
C7—N3—N2	106.98 (14)	N5—C14—C13	110.7 (2)
N1—C1—C2	122.3 (2)	N5—C15A—C16A	109.9 (3)
C1—C2—C3	118.8 (2)	N4—C8—C7	117.44 (16)
N3—N2—V1	118.33 (10)	N4—C8—C9	122.41 (18)
C6—N2—V1	124.19 (12)	C9—C8—C7	120.14 (17)
C6—N2—N3	117.46 (14)	C10—C9—C8	119.0 (2)
C5—C4—C3	118.71 (19)	C11—C10—C9	119.1 (2)
C14—N5—C15A	120.9 (2)	C10—C11—C12	118.2 (2)
C14—N5—C15B	94.6 (6)	N4—C12—C11	124.4 (2)
C2—C3—C4	119.43 (19)	C16B—C15B—N5	111.2 (11)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···O5	0.95 (3)	1.92 (3)	2.848 (3)	165 (3)

N5—H5*B*···N3[i]	0.85 (3)	2.08 (3)	2.918 (3)	171 (3)
O5—H5*C*···O1	0.85	1.94	2.776 (3)	169
O5—H5*D*···O4[ii]	0.85	1.99	2.838 (2)	178
C2—H2···O2[iii]	0.93	2.48	3.277 (3)	143
C14—H14*A*···O4[i]	0.97	2.57	3.172 (3)	121
C15*A*—H15*A*···N4[i]	0.97	2.59	3.233 (5)	124

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