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Crystal structure of (μ-hydrogen disulfato)-μ-oxido-bis[(4,4′-di-*tert*-butyl-2,2′-bipyridine)oxidovanadium(IV/V)] acetonitrile monosolvate

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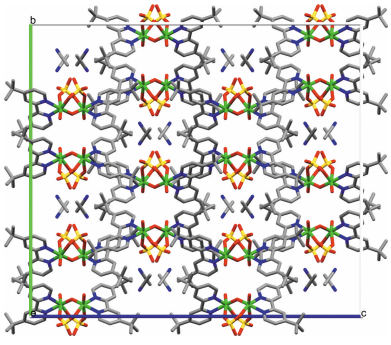
The dinuclear oxidovanadium(IV/V) complex, $[V_2(HS_2O_8)O_3(C_{18}H_{24}N_2)_2]\cdot CH_3CN$ or $[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]\cdot CH_3CN$ (4,4′-^{t}Bubpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), has crystallographic C_2 symmetry and exhibits a distorted octahedral geometry around the vanadium center, where the two 4,4′-^{t}Bubpy ligands are nearly orthogonal to each other. The two vanadium ions are linked by an oxo anion and a unique protonated sulfate anion $[H(SO_4)_2^{3-}]$. In the crystal, intermolecular C—H$\cdots\pi$ and π–π interactions between the 4,4′-^{t}Bubpy ligands are present, leading to a three-dimensional network.

1. Chemical context

The sulfate anion (SO_4^{2-}) plays an important role as a ligand for transition-metal compounds, including polyoxometalates (Walsh *et al.*, 2016), metal sulfates (Natarajan & Mandal, 2008), and polynuclear complexes with organic ligands (Papatriantafyllopoulou *et al.*, 2009). Based on these compounds, a variety of catalysts (Wang *et al.*, 2021), magnetic materials (Gómez-García *et al.*, 2016), and metal–organic frameworks (Mi *et al.*, 2022) have been developed in recent years. A hydrogensulfate anion (HSO_4^-) is also found in transition-metal compounds, and HSO_4^- more often acts as a counter-anion than as a ligand (Díaz-Torres & Alvarez, 2011). Thus, transition-metal complexes having an HSO_4^- ligand are still limited in number. In sulfated metal oxide catalysts (*e.g.*, V_2O_5-based catalysts), however, a surface-protonated sulfate group is often proposed as a Brønsted acid site and affects the catalytic activity (Xie *et al.*, 2021). Hence, a transition-metal complex having a protonated sulfate anion as the ligand is expected to be an appropriate model compound to understand the active site of sulfated solid catalysts at the molecular level. Herein, we report the crystal structure of a dinuclear oxidovanadium(IV/V) complex with 4,4′-di-*tert*-butyl-2,2′-bipyridine (4,4′-^{t}Bubpy) ligands, the two vanadium ions of which are linked by an oxo anion and a unique protonated sulfate anion $[H(SO_4)_2^{3-}]$.



2. Structural commentary

A single-crystal X-ray structure analysis revealed a novel dinuclear oxidovanadium(IV/V) complex $[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]$ (**V_2**) with crystallographic C_2 symmetry (Fig. 1). Complex **V_2** exhibits a distorted octahedral geometry around the vanadium centre, where the two 4,4′-^{t}Bubpy ligands are nearly orthogonal to each other [the

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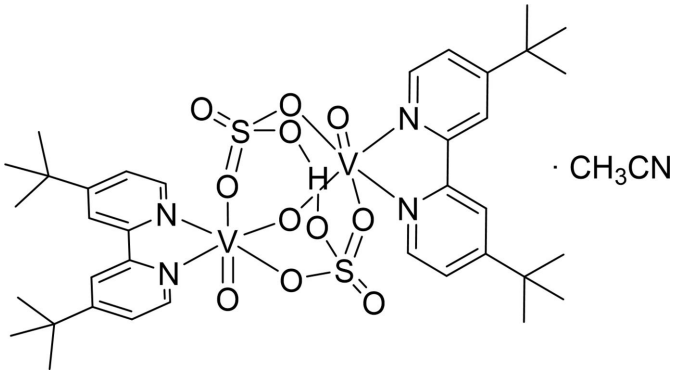
Table 1
BVS calculations for vanadium atoms of $[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]$ (**V_2**).

BVS calculations were conducted using X-ray data of $[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]$. Bond-valence parameters: V^{IV}—O (1.784 Å), V^{V}—O (1.803 Å), and V—N (1.86 Å) (Brese & O'Keeffe, 1991).

$[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]$	V1
V(IV)	4.41
V(V)	4.59

dihedral angle between the coordination planes of N1–V1–N2 and $N1^i$–$V1^i$–$N2^i$ is 86.48 (8)°]. The two vanadium ions are linked by bridging O^{2-} and $H(SO_4)_2^{3-}$ ions. The lengths of the V═$O_{terminal}$ [V1—O1; 1.5932 (14) Å], V—$O_{bridging}$ [1.8268 (7)–2.2827 (12) Å], and V—N [2.1077 (14)–2.1399 (14) Å] bonds are within the expected values reported in the literature (Triantafillou *et al.*, 2004; Inoue *et al.*, 2018). For the S—O distances in the $H(SO_4)_2^{3-}$ ion, the distances between S1 and O atoms (O3 and O5) attached to V atom are in the range of 1.4654 (13) to 1.5098 (12) Å, whereas the S═$O_{terminal}$ [S1—O4; 1.4391 (13) Å] bond is substantially shorter. Although, like the O4 atom, the O6 atom is not attached to the V atom, the S1—O6 distance [1.5066 (13) Å] is comparable in length to the S1—O3 distance. Therefore, the S1—O6 distance can be attributed to the S—OH bond (Leszczyński *et al.*, 2012). The hydrogen atom of the $H(SO_4)_2^{3-}$ ligand is located with 0.5 occupancy at two positions (H6 and $H6^i$) (Schindler & Wickleder, 2017) related by the C_2 axis passing through the midpoint of O6···$O6^i$ and the O2 atom. In addition, the O6···$O6^i$ distance (2.48 Å) reflects the strong intramolecular hydrogen-bond interaction in the $H(SO_4)_2^{3-}$ ligand (Cleland *et al.*, 1998).



Bond-valence-sum calculations of complex **V_2** (Table 1) suggest that the two V atoms (V1 and $V1^i$) are in a mixed-valence state of V^{4+} and V^{5+}. In addition, the UV-vis spectrum of **V_2** in CH_3CN shows two weak absorption bands at 553 nm (ε = 82 M^{-1} cm^{-1}) and 669 nm (ε = 29 M^{-1} cm^{-1}), which are considered to be the *d*–*d* bands of V^{4+} (Ballhausen & Gray, 1962; Waidmann *et al.*, 2009). To the best of our knowledge, the dinuclear structure of **V_2** bearing the bridging $H(SO_4)_2^{3-}$ ligand is unprecedented, although there are a few examples of vanadium complexes having the protonated sulfate anion (*e.g.*, HSO_4^-) as the ligand (Nilsson *et al.* 2009; Datta *et al.* 2015).

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

*Cg*2 is the centroid of the N2/C6–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···*Cg*2^i	0.98	2.78	3.431 (2)	124

Symmetry code: (i) $-x+1, -y+1, -z+1$.

3. Supramolecular features

In the crystal of **V_2**, intermolecular C—H···π interactions (Karle *et al.*, 2007) between the H14*A* atom and the pyridine ring of the 4,4′-^{t}Bubpy ligand (Table 2), along with intermolecular π–π interactions (Janiak, 2000) between the pyridine rings of the 4,4′-^{t}Bubpy ligands [*Cg*1···$Cg1^i$ = 3.7222 (13) Å, interplanar distance = 3.6034 (16) Å, slippage = 0.933 Å. *Cg*1 is the centroid of the N1/C1–C5 ring; symmetry code: (i) $-x+\frac{5}{4}, -y+\frac{5}{4}, z$], are present (Fig. 2), forming a three-dimensional network (Fig. 3).

4. Synthesis and crystallization

To a solution of 4,4′-di-*tert*-butyl-2,2′-bipyridyl (4,4′-^{t}Bubpy) (269.0 mg, 1.0 mmol) in EtOH (10 mL) was added a solution

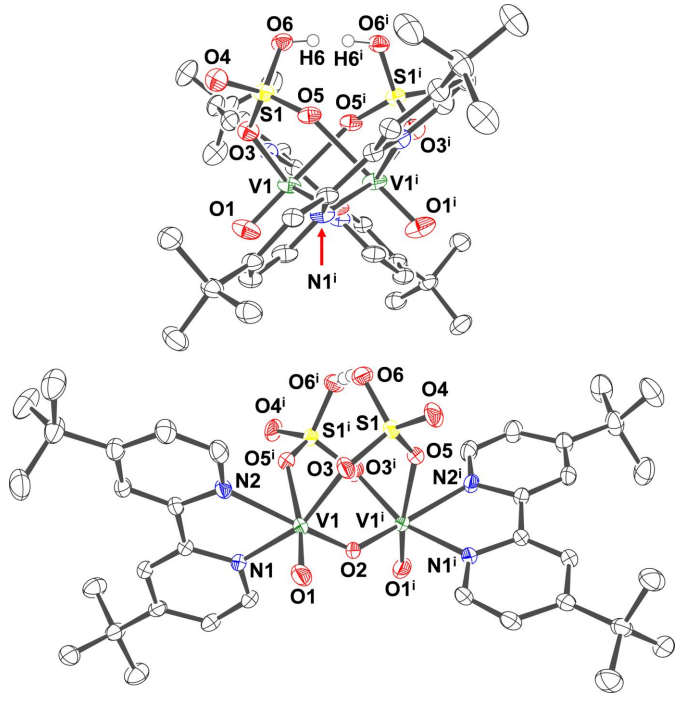


Figure 1
Crystal structure of $[V_2O_2(\mu\text{-}O)(\mu\text{-}H(SO_4)_2)(4,4'\text{-}^t\text{Bubpy})_2]$ (**V_2**) with numbered atoms. Ellipsoids are shown at the 50% probability level. Side view (top) and front view (bottom). The hydrogen atoms of 4,4′-^{t}Bubpy ligands are omitted for clarity. Symmetry code: (i) $-x+\frac{5}{4}$, y, $-z+\frac{5}{4}$. The hydrogen atom of $H(SO_4)_2^{3-}$ ligand is located at two positions (H6 and $H6^i$) with 0.5 occupancy. Selected interatomic distances (Å): V1—O1 1.5932 (14), V1—O2 1.8268 (7), V1—O3 1.9692 (12), V1—$O5^i$ 2.2827 (12), V1—N1 2.1077 (14), V1—N2 2.1399 (14), S1—O3 1.5098 (12), S1—O4 1.4391 (13), S1—O5 1.4654 (13), S1—O6 1.5066 (13), O6···$O6^i$ 2.480 (2).

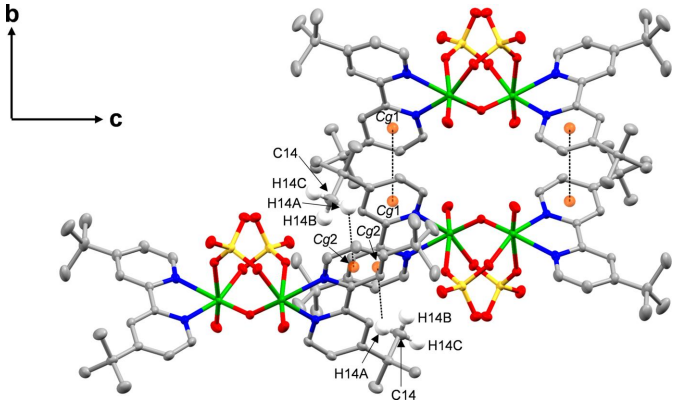


Figure 2
Details of the C—H···π interactions and the π–π interactions between the 4,4′-^{t}Bubpy ligands of **V$_2$**. *Cg*1 and *Cg*2 are the centroids of the N1/C1–C5 ring and the N2/C6–C10 ring, respectively. The hydrogen atoms of 4,4′-^{t}Bubpy ligands except for H14*A*, H14*B*, and H14*C* are omitted for clarity.

of $VOSO_4{\cdot}5H_2O$ (126.8 mg, 0.5 mmol) in EtOH (5.5 mL). After stirring for 2.5 h at 313 K, the solution was concentrated under reduced pressure, and the green precipitate was filtered using Et_2O and dried to afford a green powder. Then, the powder was suspended in water, and an aqueous solution of sodium lauryl sulfate was added. After the mixture had been stirred overnight at ambient temperature, the supernatant liquid was separated from a dark-green oily precipitate by decantation, and the precipitate was washed with water. The precipitate was dissolved in an EtOH–Et_2O mixed solvent. After the color of the solution turned from green to orange, it was evaporated, and the precipitate was filtered using Et_2O and dried to afford a yellowish brown solid, which was recrystallized from CH_3CN and Et_2O to give **V$_2$** (30.8 mg, 13% based on V) as dark-brown crystals. Analysis calculated for $C_{36}H_{49}N_4O_{11}S_2V_2{\cdot}3H_2O$: C, 46.30; H, 5.94; N, 6.00. Found: C, 45.95; H, 5.82; N, 6.05.

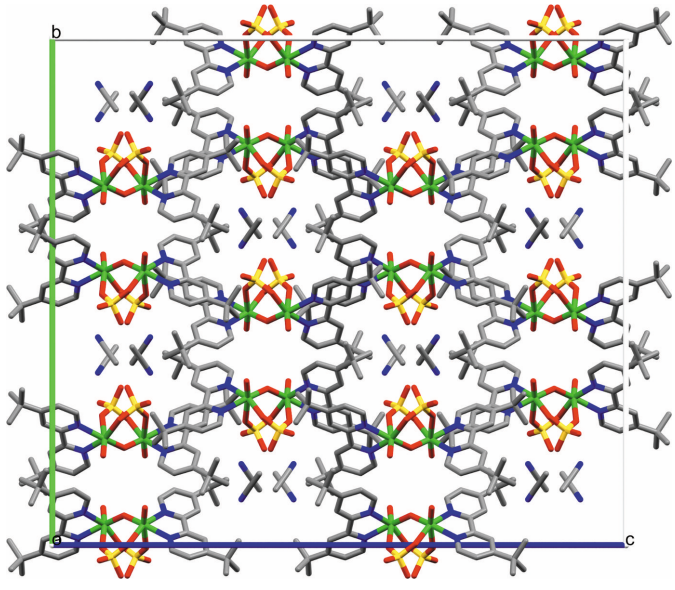


Figure 3
Crystal packing view of **V$_2$**·CH_3CN along the *a* axis.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[V_2(HS_2O_8)O_3(C_{18}H_{24}N_2)_2]{\cdot}C_2H_3N$
M_r	920.84
Crystal system, space group	Orthorhombic, *Fddd*
Temperature (K)	110
a, *b*, *c* (Å)	13.0134 (2), 34.9495 (5), 39.4864 (6)
V (Å^3)	17958.9 (5)
Z	16
Radiation type	Mo *K*α
μ (mm^{-1})	0.57
Crystal size (mm)	0.16 × 0.11 × 0.06
Data collection	
Diffractometer	Rigaku Saturn724+ (2×2 bin mode)
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2020)
T_{min}, T_{max}	0.815, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51528, 6582, 5675
R_{int}	0.049
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.714
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.043, 0.110, 1.12
No. of reflections	6582
No. of parameters	287
No. of restraints	27
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.34

Computer programs: *CrystalClear-SM Expert* (Rigaku, 2011), *OLEX2.solve* (Bourhis *et al.*, 2015), *SHELXL2018/3* (Sheldrick, 2015), and *OLEX2* (Dolomanov *et al.*, 2009).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms were positioned geometrically (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C_{methyl})$.

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supporting information

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Crystal structure of (*μ*-hydrogen disulfato)-*μ*-oxido-bis[(4,4′-di-*tert*-butyl-2,2′-bipyridine)oxidovanadium(IV/V)] acetonitrile monosolvate

Shintaro Kodama, Terushi Hashiguchi and Akihiro Nomoto

Computing details

Data collection: *CrystalClear*-SM Expert 2.0 r7 (Rigaku, 2011); cell refinement: *CrystalClear*-SM Expert 2.0 r7 (Rigaku, 2011); data reduction: *CrystalClear*-SM Expert 2.0 r7 (Rigaku, 2011); program(s) used to solve structure: *olex2.solve* 1.5 (Bourhis *et al.*, 2015); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015); molecular graphics: Olex2 1.5 (Dolomanov *et al.*, 2009); software used to prepare material for publication: Olex2 1.5 (Dolomanov *et al.*, 2009).

(*μ*-Hydrogen disulfato)-*μ*-oxido-bis[(4,4′-di-*tert*-butyl-2,2′-bipyridine)oxidovanadium(IV/V)] acetonitrile monosolvate

Crystal data

$[V_2(HS_2O_8)O_3(C_{18}H_{24}N_2)_2]\cdot C_2H_3N$
M_r = 920.84
Orthorhombic, *Fddd*
a = 13.0134 (2) Å
b = 34.9495 (5) Å
c = 39.4864 (6) Å
V = 17958.9 (5) Å^3
Z = 16
F(000) = 7696
D_x = 1.362 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 30626 reflections
θ = 1.9–30.6°
μ = 0.57 mm^{-1}
T = 110 K
Block, clear dark brown
0.16 × 0.11 × 0.06 mm

Data collection

Rigaku Saturn724+ (2x2 bin mode) diffractometer
Radiation source: Rotating Anode
Detector resolution: 28.5714 pixels mm^{-1}
profile data from *ω*–scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2020)
T_{min} = 0.815, T_{max} = 1.000
51528 measured reflections
6582 independent reflections
5675 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 30.5°, θ_{min} = 2.1°
h = −18→18
k = −49→50
l = −55→54

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.110
S = 1.12
6582 reflections
287 parameters
27 restraints
Primary atom site location: iterative
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2 + 46.648P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.50 e Å^{-3}
$\Delta\rho_{min}$ = −0.33 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	0.70713 (2)	0.54069 (2)	0.59096 (2)	0.02335 (8)	
S1	0.75306 (3)	0.47690 (2)	0.64590 (2)	0.02120 (10)	
O5	0.66572 (10)	0.49435 (3)	0.66352 (3)	0.0235 (2)	
O3	0.78535 (10)	0.50242 (4)	0.61695 (3)	0.0255 (3)	
O6	0.71873 (10)	0.43950 (3)	0.63066 (3)	0.0258 (3)	
O4	0.84010 (10)	0.46966 (4)	0.66746 (3)	0.0299 (3)	
O1	0.79258 (12)	0.57322 (4)	0.58859 (3)	0.0369 (3)	
O2	0.625000	0.55852 (5)	0.625000	0.0394 (5)	
N2	0.75091 (11)	0.51363 (4)	0.54454 (3)	0.0216 (3)	
N1	0.60817 (12)	0.56465 (4)	0.55441 (3)	0.0224 (3)	
C3	0.48418 (13)	0.59696 (5)	0.50377 (4)	0.0225 (3)	
C6	0.69971 (13)	0.52426 (5)	0.51604 (4)	0.0202 (3)	
C7	0.72724 (13)	0.51037 (5)	0.48439 (4)	0.0223 (3)	
H7	0.688735	0.517593	0.464972	0.027*	
C8	0.81169 (13)	0.48568 (5)	0.48092 (4)	0.0252 (3)	
C11	0.41640 (14)	0.61383 (5)	0.47598 (5)	0.0260 (3)	
C4	0.55602 (13)	0.56814 (4)	0.49641 (4)	0.0210 (3)	
H4	0.562535	0.558953	0.473872	0.025*	
C5	0.61741 (13)	0.55301 (4)	0.52172 (4)	0.0200 (3)	
C2	0.47668 (14)	0.60821 (5)	0.53749 (5)	0.0265 (3)	
H2	0.428897	0.627475	0.543821	0.032*	
C10	0.83025 (13)	0.48947 (5)	0.54148 (4)	0.0259 (3)	
H10	0.865230	0.481514	0.561393	0.031*	
C9	0.86340 (14)	0.47561 (5)	0.51049 (5)	0.0283 (4)	
H9	0.921500	0.459194	0.509397	0.034*	
C1	0.53844 (15)	0.59148 (5)	0.56180 (4)	0.0266 (3)	
H1	0.531067	0.599365	0.584695	0.032*	
C15	0.84388 (15)	0.47210 (6)	0.44572 (5)	0.0329 (4)	
C12	0.48286 (15)	0.62876 (5)	0.44658 (5)	0.0310 (4)	
H12A	0.524627	0.607783	0.437528	0.047*	
H12B	0.527993	0.649180	0.454815	0.047*	
H12C	0.438268	0.638807	0.428664	0.047*	
C13	0.34999 (16)	0.64692 (6)	0.48896 (6)	0.0375 (5)	
H13A	0.394311	0.666815	0.498583	0.056*	
H13B	0.302988	0.637465	0.506451	0.056*	
H13C	0.310203	0.657649	0.470150	0.056*	
C14	0.34585 (16)	0.58193 (6)	0.46305 (5)	0.0346 (4)	
H14A	0.299790	0.573763	0.481303	0.052*	
H14B	0.387562	0.560154	0.455598	0.052*	

H14C	0.305067	0.591466	0.443967	0.052*	
C18	0.93513 (18)	0.44437 (7)	0.44714 (6)	0.0434 (5)	
H18A	0.915526	0.421472	0.459928	0.065*	
H18B	0.993353	0.456879	0.458329	0.065*	
H18C	0.954806	0.437044	0.424081	0.065*	
C17	0.87660 (19)	0.50771 (7)	0.42503 (5)	0.0437 (5)	
H17A	0.929138	0.521948	0.437572	0.065*	
H17B	0.816724	0.524171	0.421258	0.065*	
H17C	0.904661	0.499545	0.403158	0.065*	
C16	0.75339 (19)	0.45218 (7)	0.42815 (6)	0.0467 (6)	
H16A	0.695186	0.469893	0.426686	0.070*	
H16B	0.733200	0.429568	0.441237	0.070*	
H16C	0.773966	0.444343	0.405306	0.070*	
N3	0.6842 (6)	0.5900 (2)	0.3294 (2)	0.102 (2)	0.5
C19	0.5721 (5)	0.64049 (17)	0.36076 (15)	0.0605 (14)	0.5
H19A	0.549690	0.660308	0.344825	0.091*	0.5
H19B	0.611988	0.652277	0.379037	0.091*	0.5
H19C	0.511740	0.627648	0.370330	0.091*	0.5
C20	0.6367 (5)	0.61212 (17)	0.34275 (17)	0.0616 (15)	0.5
H6	0.659 (3)	0.4376 (11)	0.6263 (12)	0.022 (11)*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.03845 (17)	0.01764 (13)	0.01395 (13)	−0.00275 (11)	−0.00195 (11)	0.00237 (10)
S1	0.0276 (2)	0.01950 (18)	0.01648 (18)	−0.00117 (15)	−0.00710 (15)	0.00280 (14)
O5	0.0351 (6)	0.0179 (5)	0.0175 (5)	0.0015 (5)	−0.0031 (5)	0.0012 (4)
O3	0.0312 (6)	0.0263 (6)	0.0188 (6)	−0.0014 (5)	−0.0056 (5)	0.0055 (5)
O6	0.0299 (7)	0.0197 (5)	0.0278 (6)	0.0026 (5)	−0.0082 (5)	−0.0035 (5)
O4	0.0337 (7)	0.0335 (7)	0.0225 (6)	−0.0012 (5)	−0.0126 (5)	0.0061 (5)
O1	0.0574 (9)	0.0273 (6)	0.0260 (7)	−0.0137 (6)	−0.0164 (6)	0.0075 (5)
O2	0.0866 (16)	0.0163 (8)	0.0154 (8)	0.000	−0.0162 (9)	0.000
N2	0.0258 (7)	0.0224 (6)	0.0165 (6)	−0.0021 (5)	−0.0045 (5)	0.0027 (5)
N1	0.0361 (8)	0.0169 (6)	0.0142 (6)	−0.0020 (5)	0.0000 (5)	−0.0007 (5)
C3	0.0267 (8)	0.0173 (7)	0.0236 (8)	−0.0009 (6)	−0.0029 (6)	−0.0032 (6)
C6	0.0248 (7)	0.0199 (7)	0.0160 (7)	−0.0009 (6)	−0.0030 (6)	0.0017 (6)
C7	0.0259 (8)	0.0238 (7)	0.0171 (7)	0.0025 (6)	−0.0047 (6)	−0.0001 (6)
C8	0.0259 (8)	0.0288 (8)	0.0207 (8)	0.0024 (7)	−0.0022 (6)	−0.0010 (6)
C11	0.0290 (8)	0.0202 (7)	0.0289 (8)	0.0042 (6)	−0.0069 (7)	−0.0053 (6)
C4	0.0267 (8)	0.0196 (7)	0.0167 (7)	0.0002 (6)	−0.0016 (6)	−0.0022 (6)
C5	0.0280 (8)	0.0163 (6)	0.0157 (7)	−0.0014 (6)	−0.0010 (6)	−0.0007 (5)
C2	0.0331 (9)	0.0202 (7)	0.0260 (8)	0.0017 (6)	0.0018 (7)	−0.0064 (6)
C10	0.0255 (8)	0.0306 (8)	0.0216 (8)	0.0004 (7)	−0.0069 (6)	0.0034 (7)
C9	0.0252 (8)	0.0342 (9)	0.0257 (8)	0.0061 (7)	−0.0041 (7)	0.0014 (7)
C1	0.0418 (10)	0.0195 (7)	0.0185 (7)	−0.0011 (7)	0.0019 (7)	−0.0046 (6)
C15	0.0333 (9)	0.0419 (10)	0.0234 (8)	0.0141 (8)	−0.0034 (7)	−0.0064 (8)
C12	0.0378 (10)	0.0261 (8)	0.0292 (9)	0.0026 (7)	−0.0079 (7)	0.0021 (7)
C13	0.0373 (10)	0.0317 (10)	0.0436 (11)	0.0128 (8)	−0.0062 (9)	−0.0083 (8)

C14	0.0348 (10)	0.0284 (9)	0.0407 (11)	−0.0005 (7)	−0.0120 (8)	−0.0066 (8)
C18	0.0416 (11)	0.0547 (13)	0.0337 (11)	0.0206 (10)	−0.0025 (9)	−0.0081 (10)
C17	0.0523 (13)	0.0544 (13)	0.0243 (9)	0.0141 (11)	0.0077 (9)	0.0033 (9)
C16	0.0444 (12)	0.0551 (14)	0.0404 (12)	0.0158 (10)	−0.0109 (10)	−0.0243 (11)
N3	0.088 (4)	0.100 (4)	0.117 (5)	−0.037 (3)	0.042 (4)	−0.029 (4)
C19	0.073 (3)	0.063 (3)	0.045 (3)	−0.037 (3)	0.003 (3)	−0.007 (2)
C20	0.053 (3)	0.065 (3)	0.067 (3)	−0.022 (3)	0.008 (3)	0.001 (2)

Geometric parameters (Å, º)

V1—O5^{i}	2.2827 (12)	C10—H10	0.9500
V1—O3	1.9692 (12)	C10—C9	1.385 (3)
V1—O1	1.5932 (14)	C9—H9	0.9500
V1—O2	1.8268 (7)	C1—H1	0.9500
V1—N2	2.1399 (14)	C15—C18	1.534 (3)
V1—N1	2.1077 (14)	C15—C17	1.549 (3)
S1—O5	1.4654 (13)	C15—C16	1.534 (3)
S1—O3	1.5098 (12)	C12—H12A	0.9800
S1—O6	1.5066 (13)	C12—H12B	0.9800
S1—O4	1.4391 (13)	C12—H12C	0.9800
O6—H6	0.80 (4)	C13—H13A	0.9800
N2—C6	1.360 (2)	C13—H13B	0.9800
N2—C10	1.339 (2)	C13—H13C	0.9800
N1—C5	1.359 (2)	C14—H14A	0.9800
N1—C1	1.337 (2)	C14—H14B	0.9800
C3—C11	1.526 (2)	C14—H14C	0.9800
C3—C4	1.405 (2)	C18—H18A	0.9800
C3—C2	1.392 (2)	C18—H18B	0.9800
C6—C7	1.388 (2)	C18—H18C	0.9800
C6—C5	1.486 (2)	C17—H17A	0.9800
C7—H7	0.9500	C17—H17B	0.9800
C7—C8	1.404 (2)	C17—H17C	0.9800
C8—C9	1.393 (2)	C16—H16A	0.9800
C8—C15	1.527 (2)	C16—H16B	0.9800
C11—C12	1.539 (3)	C16—H16C	0.9800
C11—C13	1.532 (2)	N3—C20	1.120 (9)
C11—C14	1.532 (2)	C19—H19A	0.9800
C4—H4	0.9500	C19—H19B	0.9800
C4—C5	1.384 (2)	C19—H19C	0.9800
C2—H2	0.9500	C19—C20	1.482 (8)
C2—C1	1.382 (3)		
O3—V1—O5^{i}	85.44 (5)	N2—C10—H10	118.7
O3—V1—N2	90.49 (5)	N2—C10—C9	122.69 (15)
O3—V1—N1	160.47 (5)	C9—C10—H10	118.7
O1—V1—O5^{i}	172.18 (6)	C8—C9—H9	119.9
O1—V1—O3	98.89 (7)	C10—C9—C8	120.11 (16)
O1—V1—O2	102.02 (7)	C10—C9—H9	119.9

O1—V1—N2	94.54 (7)	N1—C1—C2	122.68 (16)
O1—V1—N1	95.89 (6)	N1—C1—H1	118.7
O2—V1—O5^{i}	83.64 (5)	C2—C1—H1	118.7
O2—V1—O3	98.66 (5)	C8—C15—C18	112.05 (16)
O2—V1—N2	159.52 (5)	C8—C15—C17	107.79 (16)
O2—V1—N1	90.62 (5)	C8—C15—C16	110.01 (17)
N2—V1—O5^{i}	78.84 (5)	C18—C15—C17	108.31 (18)
N1—V1—O5^{i}	78.52 (5)	C18—C15—C16	108.92 (18)
N1—V1—N2	75.63 (5)	C16—C15—C17	109.72 (18)
O5—S1—O3	109.23 (7)	C11—C12—H12A	109.5
O5—S1—O6	108.70 (8)	C11—C12—H12B	109.5
O6—S1—O3	107.02 (7)	C11—C12—H12C	109.5
O4—S1—O5	113.76 (8)	H12A—C12—H12B	109.5
O4—S1—O3	109.43 (8)	H12A—C12—H12C	109.5
O4—S1—O6	108.49 (8)	H12B—C12—H12C	109.5
S1—O5—V1^{i}	143.30 (7)	C11—C13—H13A	109.5
S1—O3—V1	130.69 (8)	C11—C13—H13B	109.5
S1—O6—H6	117 (3)	C11—C13—H13C	109.5
V1—O2—V1^{i}	140.11 (10)	H13A—C13—H13B	109.5
C6—N2—V1	117.24 (11)	H13A—C13—H13C	109.5
C10—N2—V1	124.13 (11)	H13B—C13—H13C	109.5
C10—N2—C6	118.41 (14)	C11—C14—H14A	109.5
C5—N1—V1	118.52 (11)	C11—C14—H14B	109.5
C1—N1—V1	122.95 (11)	C11—C14—H14C	109.5
C1—N1—C5	118.51 (15)	H14A—C14—H14B	109.5
C4—C3—C11	120.86 (15)	H14A—C14—H14C	109.5
C2—C3—C11	122.56 (15)	H14B—C14—H14C	109.5
C2—C3—C4	116.56 (15)	C15—C18—H18A	109.5
N2—C6—C7	121.55 (15)	C15—C18—H18B	109.5
N2—C6—C5	114.41 (14)	C15—C18—H18C	109.5
C7—C6—C5	123.97 (14)	H18A—C18—H18B	109.5
C6—C7—H7	119.8	H18A—C18—H18C	109.5
C6—C7—C8	120.33 (15)	H18B—C18—H18C	109.5
C8—C7—H7	119.8	C15—C17—H17A	109.5
C7—C8—C15	119.64 (15)	C15—C17—H17B	109.5
C9—C8—C7	116.86 (16)	C15—C17—H17C	109.5
C9—C8—C15	123.49 (16)	H17A—C17—H17B	109.5
C3—C11—C12	110.40 (15)	H17A—C17—H17C	109.5
C3—C11—C13	112.15 (15)	H17B—C17—H17C	109.5
C3—C11—C14	107.75 (14)	C15—C16—H16A	109.5
C13—C11—C12	108.28 (16)	C15—C16—H16B	109.5
C14—C11—C12	109.39 (15)	C15—C16—H16C	109.5
C14—C11—C13	108.84 (16)	H16A—C16—H16B	109.5
C3—C4—H4	119.7	H16A—C16—H16C	109.5
C5—C4—C3	120.58 (15)	H16B—C16—H16C	109.5
C5—C4—H4	119.7	H19A—C19—H19B	109.5
N1—C5—C6	114.19 (14)	H19A—C19—H19C	109.5
N1—C5—C4	121.35 (15)	H19B—C19—H19C	109.5

C4—C5—C6	124.43 (14)	C20—C19—H19A	109.5
C3—C2—H2	119.9	C20—C19—H19B	109.5
C1—C2—C3	120.28 (16)	C20—C19—H19C	109.5
C1—C2—H2	119.9	N3—C20—C19	178.4 (7)
V1—N2—C6—C7	175.43 (12)	C7—C6—C5—N1	−175.49 (16)
V1—N2—C6—C5	−1.51 (18)	C7—C6—C5—C4	2.7 (3)
V1—N2—C10—C9	−172.91 (14)	C7—C8—C9—C10	0.7 (3)
V1—N1—C5—C6	−0.61 (18)	C7—C8—C15—C18	−178.11 (18)
V1—N1—C5—C4	−178.82 (12)	C7—C8—C15—C17	62.8 (2)
V1—N1—C1—C2	177.27 (13)	C7—C8—C15—C16	−56.8 (2)
O5^{i}—V1—O2—V1^{i}	36.88 (3)	C11—C3—C4—C5	179.87 (15)
O5—S1—O3—V1	−24.59 (12)	C11—C3—C2—C1	178.68 (16)
O3—V1—O2—V1^{i}	−47.50 (4)	C4—C3—C11—C12	−54.6 (2)
O3—S1—O5—V1^{i}	14.21 (15)	C4—C3—C11—C13	−175.46 (16)
O6—S1—O5—V1^{i}	−102.23 (13)	C4—C3—C11—C14	64.8 (2)
O6—S1—O3—V1	92.92 (11)	C4—C3—C2—C1	0.4 (3)
O4—S1—O5—V1^{i}	136.79 (12)	C5—N1—C1—C2	−1.0 (3)
O4—S1—O3—V1	−149.72 (10)	C5—C6—C7—C8	174.54 (16)
O1—V1—O2—V1^{i}	−148.59 (5)	C2—C3—C11—C12	127.22 (18)
N2—V1—O2—V1^{i}	68.14 (17)	C2—C3—C11—C13	6.4 (2)
N2—C6—C7—C8	−2.1 (3)	C2—C3—C11—C14	−113.38 (19)
N2—C6—C5—N1	1.4 (2)	C2—C3—C4—C5	−1.9 (2)
N2—C6—C5—C4	179.52 (15)	C10—N2—C6—C7	0.7 (2)
N2—C10—C9—C8	−2.1 (3)	C10—N2—C6—C5	−176.23 (15)
N1—V1—O2—V1^{i}	115.25 (4)	C9—C8—C15—C18	3.4 (3)
C3—C4—C5—N1	1.9 (2)	C9—C8—C15—C17	−115.7 (2)
C3—C4—C5—C6	−176.08 (15)	C9—C8—C15—C16	124.7 (2)
C3—C2—C1—N1	1.0 (3)	C1—N1—C5—C6	177.74 (15)
C6—N2—C10—C9	1.4 (3)	C1—N1—C5—C4	−0.5 (2)
C6—C7—C8—C9	1.3 (3)	C15—C8—C9—C10	179.22 (18)
C6—C7—C8—C15	−177.25 (17)		

Symmetry code: (i) −*x*+5/4, *y*, −*z*+5/4.

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the N2/C6–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14*A*···*Cg*2^{ii}	0.98	2.78	3.431 (2)	124

Symmetry code: (ii) −*x*+1, −*y*+1, −*z*+1.