metal-organic compounds

cis-Dioxido[N′-(2-oxidobenzylidene)pyridinium-4-carbohydrazidato-$\kappa^3 O,N',O'$]-vanadium(V)

Gholam Hossein Shahverdizadeh,[a]‡ Seik Weng Ng,[b,c] Edward R. T. Tiekink[b]* and Babak Mirtamizdoust[d]

[a]Department of Chemistry, Faculty of Science, Tabriz Branch, Islamic Azad University, PO Box 1655, Tabriz, Iran, [b]Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia, [c]Chemistry Department, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah, Saudi Arabia, and [d]Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, PO Box 5166616471, Tabriz, Iran

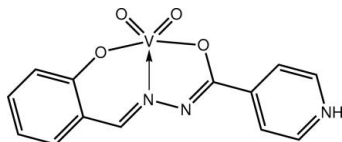Correspondence e-mail: edward.tiekink@gmail.com

The title Schiff base complex, [V(C$_{13}$H$_{10}$N$_3$O$_2$)O$_2$], features a square-pyramidal coordination geometry defined by the O,N',O'-donors of the tridentate Schiff base ligand and two oxide O atoms; one oxide O atom occupies the apical position. In the crystal, pyridinium–oxide N—H⋯O hydrogen bonds lead to zigzag supramolecular chains with a flattened topology along [101]. The investigated crystal was twinned by nonmerohedry; the minor component refined to 18.5 (5)%.

Related literature

For a related Schiff base vanadyl complex containing a protonated pyridyl residue, see: Yu *et al.* (2007). For the crystallization procedure, see: Harrowfield *et al.* (1996). For a related structure, see: Shahverdizadeh *et al.* (2012). For additional structural analysis, see: Spek (2009); Addison *et al.* (1984).

Experimental

Crystal data

[V(C$_{13}$H$_{10}$N$_3$O$_2$)O$_2$]
M_r = 323.18
Monoclinic, $P2_1/n$
a = 7.1215 (3) Å
b = 14.5243 (6) Å
c = 11.9233 (5) Å
β = 94.081 (3)°
V = 1230.16 (9) Å^3
Z = 4
Cu $K\alpha$ radiation

μ = 6.96 mm^{-1}
T = 100 K
0.25 × 0.25 × 0.25 mm

Data collection

Agilent SuperNova Dual diffractometer with Atlas detector
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010) T_{min} = 0.275, T_{max} = 0.275

2559 measured reflections
2559 independent reflections
2467 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.171
S = 1.26
2559 reflections

191 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Table 1
Selected bond lengths (Å).

V—O1	1.904 (3)	V—O4	1.654 (3)
V—O2	2.006 (3)	V—N1	2.140 (4)
V—O3	1.610 (4)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N3—H1⋯O4^i	0.88	1.75	2.610 (5)	164

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

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT5805).

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
Agilent (2010). *CrysAlis PRO*. Agilent Technologies, Yarnton, Oxfordshire, England.
Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Harrowfield, J. M., Miyamae, H., Skelton, B. W., Soudi, A. A. & White, A. H. (1996). *Aust. J. Chem.* **49**, 1165–1169.
Shahverdizadeh, G. H., Ng, S. W., Tiekink, E. R. T. & Mirtamizdoust, B. (2012). *Acta Cryst.* E**68**, m221-m222.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yu, Q., Li, C.-Y., Bian, H.-D., Liang, H., Song, H.-S. & Wang, H.-G. (2007). *Chin. J. Struct. Chem.* **26**, 37–40.

‡ Additional correspondence author, e-mail: shahverdizadeh@iaut.ac.ir.

supplementary materials

cis-Dioxido[*N′*-(2-oxidobenzylidene)pyridinium-4-carbohydrazidato-*κ³O,N′,O′*]vanadium(V)

Gholam Hossein Shahverdizadeh, Seik Weng Ng, Edward R. T. Tiekink and Babak Mirtamizdoust

Comment

In continuation of structural studies of vanadyl Schiff base complexes (Shahverdizadeh *et al.*, 2012), the title complex, (I), was characterized.

The V atom in (I) is coordinated by the *O,N,O*-tridentate Schiff base ligand and two oxido-O atoms. The resulting NO₄ donor set is based on a square pyramid with oxido-O3 atom in the axial position. The coordination geometry is quantified by the calculation of $\tau = 0.05$ which compares with $\tau = 0.0$ for an ideal square pyramidal geometry and $\tau = 1.0$ for an ideal trigonal bipyramid (Addison *et al.*, 1984). The V═O3 bond length is significantly shorter than the V═O4 bond length, Table 1, an observation ascribed to the influence exerted by the *trans*-N1 atom and the participation of the oxido O4 atom in hydrogen bonding, Table 2. The pyridinium-NH···O(oxido) hydrogen bonding leads to a zigzag chain along [101] with a flattened topology.

The Schiff base ligand in (I) is present as a pyridinium cation. A precedent exists in the literature in a closely related V complex (Yu *et al.*, 2007).

Experimental

A solution of salicylaldehyde (10 mmol) in EtOH (25 ml) was added drop-wise to the solution of 4-pyridinecarboxylic acid hydrazide (10 mmol) in EtOH (15 ml). The mixture was refluxed for 8 h. The yellow precipitate was removed by filtration and recrystallized from MeOH solution. The product (0.5 mmol) was placed in one arm of a branched tube (Harrowfield *et al.*, 1996) and vanadium(IV) oxide acetylacetonate (0.5 mmol) in the other. Methanol was then added to fill both arms, the tube sealed and the ligand-containing arm immersed in a bath at 333 K, while the other was left at ambient temperature. After 8 d, crystals had deposited in the arm held at ambient temperature. These filtered off, washed with acetone and ether, and air-dried. Yield: 72%. M.pt. 566 K.

Refinement

The crystal was a non-merohedral twin. The twin components were separated by the *TwinRotMat* routine in *PLATON* (Spek, 2009); the minor component refined to 18.5 (5)%. Carbon-bound H-atoms were placed in calculated positions [C—H 0.95 Å, U_{iso}(H) $1.2U_{eq}$(C)] and were included in the refinement in the riding model approximation. The pyridinium H-atom was located in a difference Fourier map and was refined with a distance restraint of N—H 0.88±0.01 Å with U_{iso}(H) $1.2U_{eq}$(N). The maximum and minimum residual electron density peaks of 1.36 and 0.84 e Å⁻³, respectively, were located 0.91 Å and 0.65 Å from the V atom, respectively. Owing to poor agreement, the reflection (4 8 11) was omitted from the final refinement.

Computing details

Data collection: *CrysAlis PRO* (Agilent, 2010); cell refinement: *CrysAlis PRO* (Agilent, 2010); data reduction: *CrysAlis PRO* (Agilent, 2010); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).
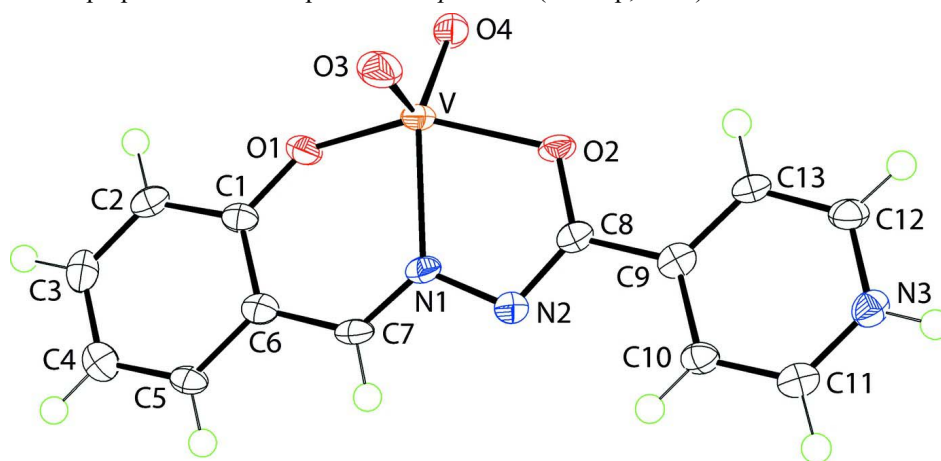
Figure 1

The molecular structure of (I) showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.
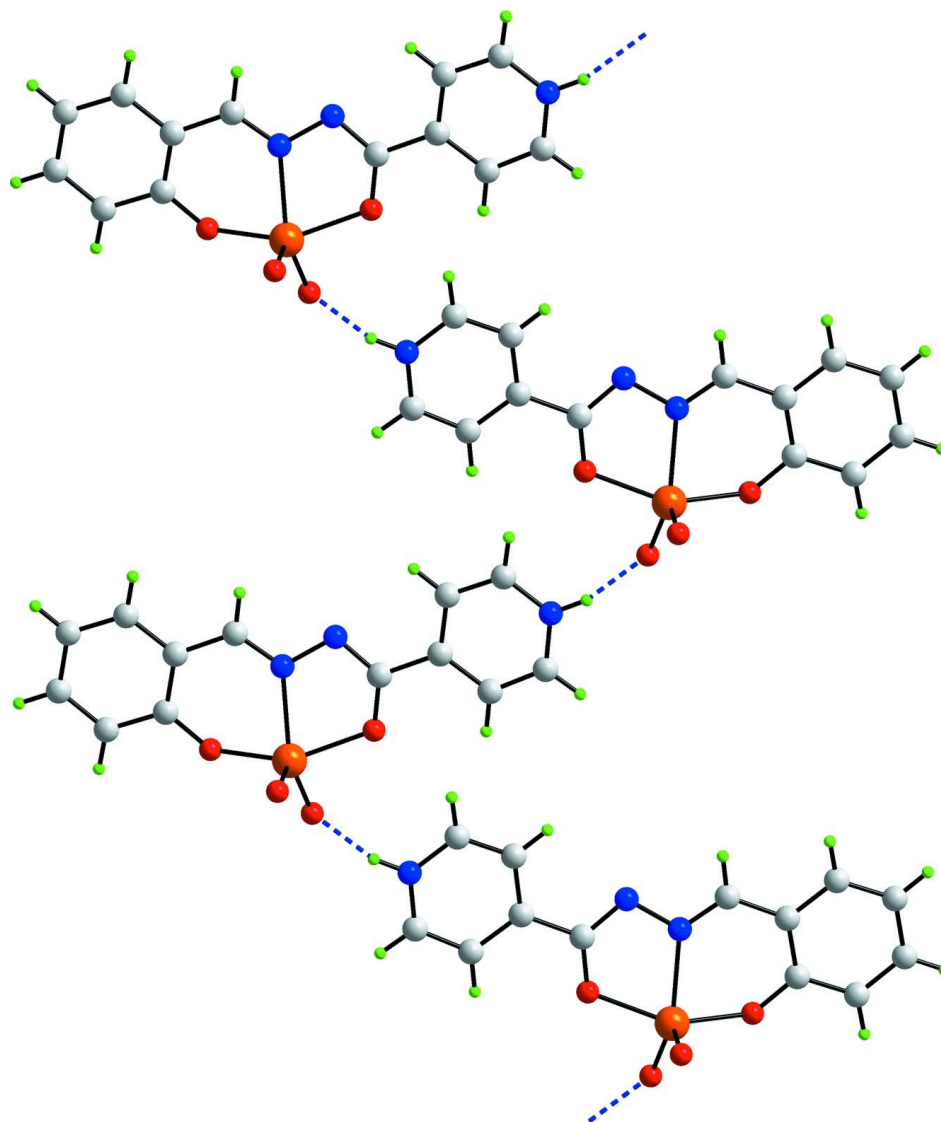
Figure 2

A view of the zigzag supramolecular chain along [101] in (I). The N—H···O hydrogen bonds are shown as blue dashed lines.

***cis*-Dioxido[*N′*-(2-oxidobenzylidene)pyridinium-4-carbohydrazidato- *κ³O,N′,O′*]vanadium(V)**

Crystal data

$[V(C_{13}H_{10}N_3O_2)O_2]$	$F(000) = 656$
$M_r = 323.18$	$D_x = 1.745$ Mg m^{-3}
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Hall symbol: -P 2yn	Cell parameters from 5747 reflections
$a = 7.1215$ (3) Å	$\theta = 3.0–76.6°$
$b = 14.5243$ (6) Å	$\mu = 6.96$ mm^{-1}
$c = 11.9233$ (5) Å	$T = 100$ K
$\beta = 94.081$ (3)°	Polyhedron, brown
$V = 1230.16$ (9) Å^3	$0.25 \times 0.25 \times 0.25$ mm
$Z = 4$	

Data collection

Agilent SuperNova Dual diffractometer with Atlas detector	$T_{min} = 0.275$, $T_{max} = 0.275$
Radiation source: SuperNova (Cu) X-ray Source	2559 measured reflections
	2559 independent reflections
Mirror monochromator	2467 reflections with $I > 2\sigma(I)$
Detector resolution: 10.4041 pixels mm^{-1}	$R_{int} = 0.000$
ω scans	$\theta_{max} = 76.8°$, $\theta_{min} = 4.8°$
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2010)	$h = -8 \rightarrow 8$
	$k = -18 \rightarrow 18$
	$l = -1 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.064$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.171$	
$S = 1.26$	H-atom parameters constrained
2559 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 7.6276P]$
191 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 1.36$ e Å^{-3}
	$\Delta\rho_{min} = -0.84$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
V	0.65274 (12)	0.54174 (6)	0.30415 (6)	0.0148 (2)
O1	0.5622 (5)	0.6639 (2)	0.3213 (3)	0.0182 (7)
O2	0.6790 (5)	0.4125 (2)	0.3624 (3)	0.0153 (7)
O3	0.8525 (5)	0.5579 (3)	0.2519 (3)	0.0236 (8)
O4	0.4995 (5)	0.5080 (2)	0.2016 (3)	0.0203 (8)
N2	0.7647 (6)	0.4717 (3)	0.5387 (3)	0.0153 (8)
N1	0.7142 (6)	0.5531 (3)	0.4819 (3)	0.0131 (8)
N3	0.9037 (6)	0.1409 (3)	0.5891 (3)	0.0160 (8)
H1	0.9366	0.0860	0.6149	0.019*
C1	0.6069 (7)	0.7323 (3)	0.3920 (4)	0.0135 (9)
C2	0.5699 (7)	0.8232 (3)	0.3575 (4)	0.0162 (9)
H2	0.5206	0.8347	0.2827	0.019*
C3	0.6035 (7)	0.8964 (3)	0.4303 (4)	0.0186 (10)
H3	0.5744	0.9573	0.4055	0.022*
C4	0.6804 (7)	0.8817 (3)	0.5407 (4)	0.0180 (10)
H4	0.7032	0.9319	0.5907	0.022*

C5	0.7221 (7)	0.7929 (3)	0.5749 (4)	0.0146 (9)
H5	0.7756	0.7825	0.6491	0.018*
C6	0.6874 (6)	0.7174 (3)	0.5027 (4)	0.0135 (9)
C7	0.7303 (7)	0.6258 (3)	0.5432 (4)	0.0146 (9)
H7	0.7731	0.6187	0.6201	0.018*
C8	0.7437 (7)	0.4041 (3)	0.4673 (4)	0.0140 (9)
C9	0.7986 (6)	0.3110 (3)	0.5094 (4)	0.0135 (9)
C10	0.8734 (6)	0.2998 (3)	0.6209 (4)	0.0144 (9)
H10	0.8878	0.3512	0.6700	0.017*
C11	0.9251 (7)	0.2134 (3)	0.6575 (4)	0.0158 (9)
H11	0.9768	0.2051	0.7325	0.019*
C12	0.8337 (7)	0.1491 (3)	0.4826 (4)	0.0165 (10)
H12	0.8204	0.0959	0.4363	0.020*
C13	0.7805 (7)	0.2341 (3)	0.4394 (4)	0.0147 (9)
H13	0.7326	0.2402	0.3633	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V	0.0189 (4)	0.0164 (4)	0.0089 (4)	−0.0021 (3)	0.0006 (3)	−0.0011 (3)
O1	0.0264 (19)	0.0157 (16)	0.0122 (16)	0.0027 (14)	−0.0009 (14)	−0.0033 (13)
O2	0.0190 (17)	0.0179 (16)	0.0084 (14)	0.0027 (14)	−0.0028 (12)	0.0011 (12)
O3	0.028 (2)	0.0260 (19)	0.0183 (17)	−0.0065 (16)	0.0091 (15)	−0.0051 (14)
O4	0.028 (2)	0.0172 (16)	0.0151 (17)	−0.0034 (15)	−0.0057 (14)	0.0013 (13)
N2	0.018 (2)	0.0150 (19)	0.0125 (18)	−0.0010 (16)	−0.0001 (15)	0.0001 (15)
N1	0.0134 (19)	0.0172 (19)	0.0090 (17)	−0.0012 (15)	0.0024 (14)	0.0010 (14)
N3	0.016 (2)	0.0169 (19)	0.0153 (19)	0.0043 (16)	0.0030 (15)	0.0024 (15)
C1	0.011 (2)	0.018 (2)	0.012 (2)	0.0004 (17)	0.0019 (17)	−0.0018 (17)
C2	0.015 (2)	0.022 (2)	0.012 (2)	0.0002 (19)	0.0031 (17)	0.0031 (18)
C3	0.018 (2)	0.014 (2)	0.025 (3)	0.0009 (19)	0.007 (2)	0.0022 (19)
C4	0.014 (2)	0.018 (2)	0.022 (2)	−0.0007 (19)	0.0019 (19)	−0.0026 (19)
C5	0.015 (2)	0.018 (2)	0.011 (2)	0.0007 (18)	0.0040 (17)	−0.0035 (17)
C6	0.009 (2)	0.019 (2)	0.013 (2)	−0.0009 (17)	0.0049 (17)	−0.0017 (17)
C7	0.015 (2)	0.021 (2)	0.008 (2)	−0.0014 (19)	0.0021 (17)	−0.0007 (17)
C8	0.013 (2)	0.018 (2)	0.012 (2)	−0.0003 (18)	0.0014 (17)	0.0021 (17)
C9	0.007 (2)	0.019 (2)	0.015 (2)	0.0000 (17)	0.0023 (16)	0.0018 (18)
C10	0.012 (2)	0.018 (2)	0.012 (2)	−0.0026 (18)	−0.0020 (17)	0.0000 (17)
C11	0.013 (2)	0.021 (2)	0.013 (2)	0.0009 (18)	0.0011 (17)	0.0012 (18)
C12	0.019 (2)	0.020 (2)	0.011 (2)	0.0035 (19)	0.0031 (18)	−0.0005 (18)
C13	0.016 (2)	0.019 (2)	0.009 (2)	−0.0001 (18)	0.0025 (17)	0.0017 (17)

Geometric parameters (Å, º)

V—O1	1.904 (3)	C3—C4	1.405 (7)
V—O2	2.006 (3)	C3—H3	0.9500
V—O3	1.610 (4)	C4—C5	1.379 (7)
V—O4	1.654 (3)	C4—H4	0.9500
V—N1	2.140 (4)	C5—C6	1.405 (6)
O1—C1	1.327 (6)	C5—H5	0.9500
O2—C8	1.307 (5)	C6—C7	1.441 (7)

N2—C8	1.301 (6)	C7—H7	0.9500
N2—N1	1.396 (5)	C8—C9	1.485 (6)
N1—C7	1.285 (6)	C9—C13	1.394 (7)
N3—C11	1.335 (6)	C9—C10	1.406 (6)
N3—C12	1.336 (6)	C10—C11	1.370 (7)
N3—H1	0.8800	C10—H10	0.9500
C1—C2	1.402 (7)	C11—H11	0.9500
C1—C6	1.418 (6)	C12—C13	1.382 (7)
C2—C3	1.383 (7)	C12—H12	0.9500
C2—H2	0.9500	C13—H13	0.9500
O3—V—O4	108.16 (19)	C5—C4—H4	120.6
O3—V—O1	102.77 (18)	C3—C4—H4	120.6
O4—V—O1	98.34 (16)	C4—C5—C6	121.5 (4)
O3—V—O2	101.95 (17)	C4—C5—H5	119.2
O4—V—O2	91.08 (15)	C6—C5—H5	119.2
O1—V—O2	149.21 (14)	C5—C6—C1	119.6 (4)
O3—V—N1	104.35 (17)	C5—C6—C7	119.4 (4)
O4—V—N1	146.37 (17)	C1—C6—C7	121.0 (4)
O1—V—N1	82.48 (15)	N1—C7—C6	124.0 (4)
O2—V—N1	73.82 (14)	N1—C7—H7	118.0
C1—O1—V	134.3 (3)	C6—C7—H7	118.0
C8—O2—V	115.9 (3)	N2—C8—O2	124.9 (4)
C8—N2—N1	108.0 (4)	N2—C8—C9	116.8 (4)
C7—N1—N2	114.2 (4)	O2—C8—C9	118.3 (4)
C7—N1—V	129.1 (3)	C13—C9—C10	119.1 (4)
N2—N1—V	116.3 (3)	C13—C9—C8	121.0 (4)
C11—N3—C12	122.0 (4)	C10—C9—C8	119.9 (4)
C11—N3—H1	119.0	C11—C10—C9	118.8 (4)
C12—N3—H1	119.0	C11—C10—H10	120.6
O1—C1—C2	119.1 (4)	C9—C10—H10	120.6
O1—C1—C6	122.7 (4)	N3—C11—C10	120.8 (4)
C2—C1—C6	118.2 (4)	N3—C11—H11	119.6
C3—C2—C1	121.3 (4)	C10—C11—H11	119.6
C3—C2—H2	119.3	N3—C12—C13	120.5 (4)
C1—C2—H2	119.3	N3—C12—H12	119.7
C2—C3—C4	120.6 (5)	C13—C12—H12	119.7
C2—C3—H3	119.7	C12—C13—C9	118.8 (4)
C4—C3—H3	119.7	C12—C13—H13	120.6
C5—C4—C3	118.8 (4)	C9—C13—H13	120.6
O3—V—O1—C1	−73.7 (4)	C4—C5—C6—C7	−178.8 (5)
O4—V—O1—C1	175.5 (4)	O1—C1—C6—C5	−176.7 (4)
O2—V—O1—C1	69.0 (6)	C2—C1—C6—C5	1.9 (7)
N1—V—O1—C1	29.4 (4)	O1—C1—C6—C7	1.9 (7)
O3—V—O2—C8	92.1 (3)	C2—C1—C6—C7	−179.6 (4)
O4—V—O2—C8	−159.1 (3)	N2—N1—C7—C6	179.6 (4)
O1—V—O2—C8	−50.7 (5)	V—N1—C7—C6	7.4 (7)
N1—V—O2—C8	−9.6 (3)	C5—C6—C7—N1	−175.7 (5)

C8—N2—N1—C7	−179.4 (4)	C1—C6—C7—N1	5.7 (7)
C8—N2—N1—V	−6.2 (5)	N1—N2—C8—O2	−2.6 (6)
O3—V—N1—C7	82.3 (4)	N1—N2—C8—C9	177.3 (4)
O4—V—N1—C7	−112.8 (5)	V—O2—C8—N2	10.6 (6)
O1—V—N1—C7	−19.1 (4)	V—O2—C8—C9	−169.3 (3)
O2—V—N1—C7	−179.2 (4)	N2—C8—C9—C13	179.7 (4)
O3—V—N1—N2	−89.8 (3)	O2—C8—C9—C13	−0.4 (7)
O4—V—N1—N2	75.1 (4)	N2—C8—C9—C10	−1.5 (7)
O1—V—N1—N2	168.9 (3)	O2—C8—C9—C10	178.3 (4)
O2—V—N1—N2	8.7 (3)	C13—C9—C10—C11	−0.5 (7)
V—O1—C1—C2	154.5 (4)	C8—C9—C10—C11	−179.2 (4)
V—O1—C1—C6	−27.0 (7)	C12—N3—C11—C10	0.8 (7)
O1—C1—C2—C3	176.1 (4)	C9—C10—C11—N3	−0.5 (7)
C6—C1—C2—C3	−2.5 (7)	C11—N3—C12—C13	0.0 (7)
C1—C2—C3—C4	1.5 (7)	N3—C12—C13—C9	−1.0 (7)
C2—C3—C4—C5	0.2 (7)	C10—C9—C13—C12	1.2 (7)
C3—C4—C5—C6	−0.8 (7)	C8—C9—C13—C12	179.9 (4)
C4—C5—C6—C1	−0.3 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H1···O4[i]	0.88	1.75	2.610 (5)	164

Symmetry code: (i) *x*+1/2, −*y*+1/2, *z*+1/2.