research communications

Synthesis and structural study of tris(2,6-diamino-pyridinium) bis(oxalato)dioxidovanadate(V) 2.5-hydrate

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Crystals of the title compound, $(C_5H_8N_3)_3[VO_2(C_2O_4)_2] \cdot 2.5H_2O$, a mononuclear V^V complex, were obtained by slow evaporation at room temperature of an aqueous solution containing vanadium pentoxide, oxalic acid and 2,6-diamino-pyridine. The asymmetric unit contains one bis(oxalato)dioxovanadate(V) anionic complex, three 2,6-diaminopyridinium cations and two and a half uncoordinated water molecules. The mononuclear vanadium(V) anions are connected to the organic cations and water molecules through a strong N—H⋯O and O—H⋯O hydrogen-bond network, consolidated by π–π stacking interactions, to form a three-dimensional structure.

1. Chemical context

The coordination chemistry of vanadium has received great attention during the last few decades. Many vanadium complexes of the oxalate dianion have been reported having biological (Kordowiak et al., 2000; León et al., 2013) and catalysis applications (Mishra et al., 2002; Maurya et al., 2003). Many non-polymeric structural architectures of vanadium oxalate compounds have been reported, among which the synthesis of mononuclear bis(oxalato)dioxovanadate(V) complexes is limited to the easy formation of aquabis-(oxalato)oxidovanadate(IV) (Lin et al., 2004, Aghabozorg et al., 2007, Sehimi et al., 2016). Dioxovanadate(V) compounds have been studied less often; reported structures include triammonium bis(oxalato)dioxovanadate(V) dihydrate, $(NH_4)[VO_2(C_2O_4)_2] \cdot 2H_2O$ (Hoard et al., 1971; Atovmyan et al., 1972) and tripotassium bis(oxalato)dioxovanadate(V) trihydrate, $K_3[VO_2(C_2O_4)] \cdot 3H_2O$ (Drew et al., 1974; Stomberg, 1986). We report here the crystal structure of a novel dioxo-vanadate(V) complex, (I).
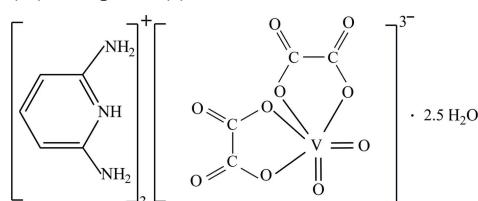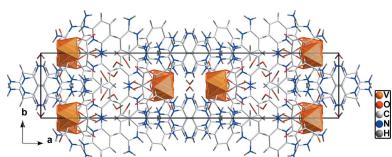

2. Structural commentary

The asymmetric unit of (I) is composed of a complex $[VO_2(C_2O_4)_2]^{3-}$ ion, three protonated 2,6-diaminopyridinium
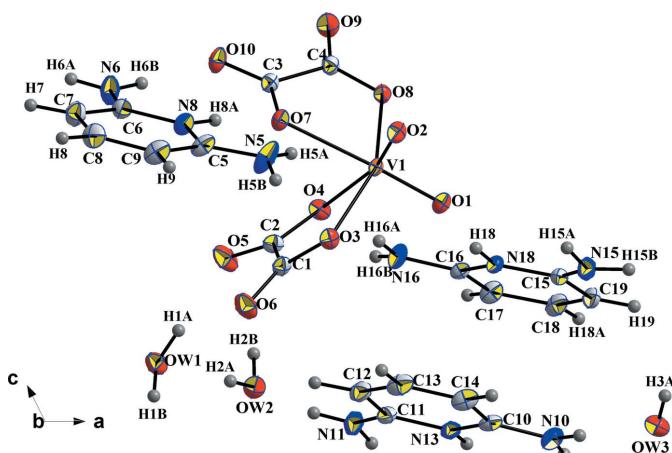
Figure 1
The asymmetric unit of (I) showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms.

cations $(C_5H_8N_3)^+$ and two and a half uncoordinated water molecules (Fig. 1). The anionic complex has an overall charge of -3, requiring a vanadium atom with an oxidation state $+5$. This formal value is in good agreement with the bond-valence-sum calculation (Brown & Altermatt, 1985), which gives a value of 4.99 valence units.
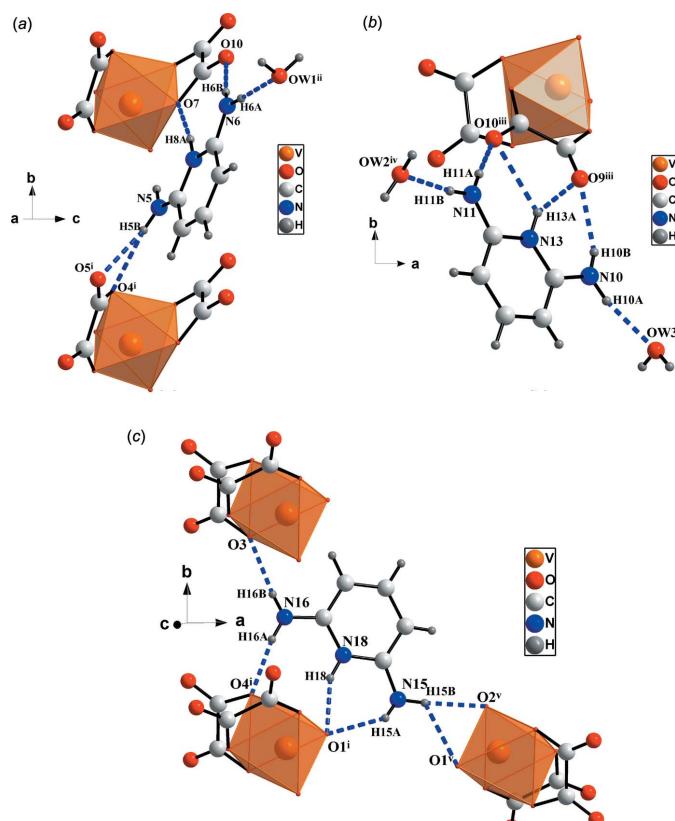
Figure 2
View of N—H···O hydrogen bonds (blue dashed line) formed by (a) the first, (b) the second and (c) the third 2,6-diaminopyridinium cation. [Symmetry codes: (i) $x, y - 1, z$; (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (iii) $x, -y + 2, z - \frac{1}{2}$; (iv) $x, y + 1, z$; (v) $-x + 1, -y, -z + 1$]

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5B···O4^i	0.87 (2)	2.47 (2)	3.2515 (14)	150.0 (19)
N5—H5B···O5^i	0.87 (2)	2.31 (2)	3.1196 (16)	154.7 (19)
N8—H8A···O7	0.95 (2)	1.87 (2)	2.8118 (13)	174.1 (18)
N6—H6A···OW1^{ii}	0.86 (2)	2.00 (2)	2.8559 (15)	171.0 (19)
N6—H6B···O10	0.84 (2)	2.07 (2)	2.9018 (15)	176.4 (19)
N10—H10A···OW3	0.88 (2)	2.08 (2)	2.9463 (15)	169 (2)
N10—H10B···O9^{iii}	0.82 (2)	2.17 (2)	2.8863 (15)	146.8 (18)
N13—H13A···O9^{iii}	0.90 (2)	2.01 (2)	2.8309 (15)	150.3 (17)
N13—H13A···O10^{iii}	0.90 (2)	2.615 (19)	3.3149 (14)	135.2 (16)
N11—H11A···O10^{iii}	0.84 (2)	2.02 (2)	2.8401 (14)	165 (2)
N11—H11B···OW2^{iv}	0.861 (19)	2.00 (2)	2.8522 (14)	173.1 (19)
N15—H15A···O1^i	0.85 (2)	2.252 (19)	2.9914 (14)	145.5 (17)
N15—H15B···O1^v	0.882 (19)	2.570 (19)	3.0641 (13)	116.2 (15)
N15—H15B···O2^v	0.882 (19)	2.01 (2)	2.8926 (14)	175.9 (19)
N16—H16A···O4^i	0.887 (18)	1.990 (18)	2.8695 (13)	170.5 (16)
N16—H16B···O3	0.843 (19)	2.085 (19)	2.9156 (12)	168.5 (17)
N18—H18···O1^i	0.917 (19)	1.993 (19)	2.8541 (12)	155.7 (16)
OW1—H1A···O5	0.92 (2)	1.79 (2)	2.6550 (13)	155.8 (19)
OW1—H1B···OW2^{vi}	0.90 (2)	1.84 (2)	2.7270 (13)	169 (2)
OW2—H2A···OW1^i	0.87 (2)	1.87 (3)	2.7384 (14)	173 (2)
OW2—H2B···O6	0.90 (3)	1.93 (3)	2.7896 (13)	160 (2)
OW3—H3A···O8^{vii}	0.79 (2)	2.10 (2)	2.8621 (10)	161 (2)

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

In the coordination polyhedron of V^V, the central vanadium has distorted octahedral geometry with two terminal oxygen atoms and four oxygen atoms from two oxalate groups. The two terminal oxygen atoms O1 and O2 are located at shortened V—O distances of 1.6433 (8) and 1.6317 (8) Å, respectively, which is typical for a double-bonded vanadyl group, and form a *cis*-vanadyl grouping in the usual monodentate fashion. Substantially elongated complexing bonds [2.1644 (8) and 2.2248 (8) Å] extend from the vanadium to the two carboxylate oxygen atoms O4 and O7, while two other carboxylate oxygen atoms O3 and O8 are at 2.0020 (8) and 2.0026 (8) Å respectively.

The geometric parameters for the 2,6-diaminopyridinium cations do not show any unusual features and are in agreement with those previously reported for bis(2,6-diaminopyridinium) oxalate dihydrate, $2C_5H_8N_3^+ \cdot C_2O_2^{2-} \cdot 2H_2O$ (Odabaşoğlu *et al.*, 2006).

3. Supramolecular features

The charged components are connected by an extensive hydrogen-bonding network. The amine and pyridine nitrogen atoms of the 2,6- diaminopyridinuim cations act as hydrogen-bond donors and coordinate the complex ions $[VO_2(C_2O_4)_2]^{3-}$ to each other or to water molecules *via* N—H···O hydrogen bonds as shown in Fig. 2, with bond lengths between 1.87 (2) and 2.61 (2) Å (Table 1).

The three nitrogen atoms N5, N6 and N8 of the first 2,6-diaminopyridinium cation act as donors of five hydrogen bonds, N5—H5B···O4^i, N5—H5B···O5^i, N8—H8A···O7, N6—H6A···OW1^{ii} and N6—H6B···O10 (Table 1), and link two complex ions to a water molecule.
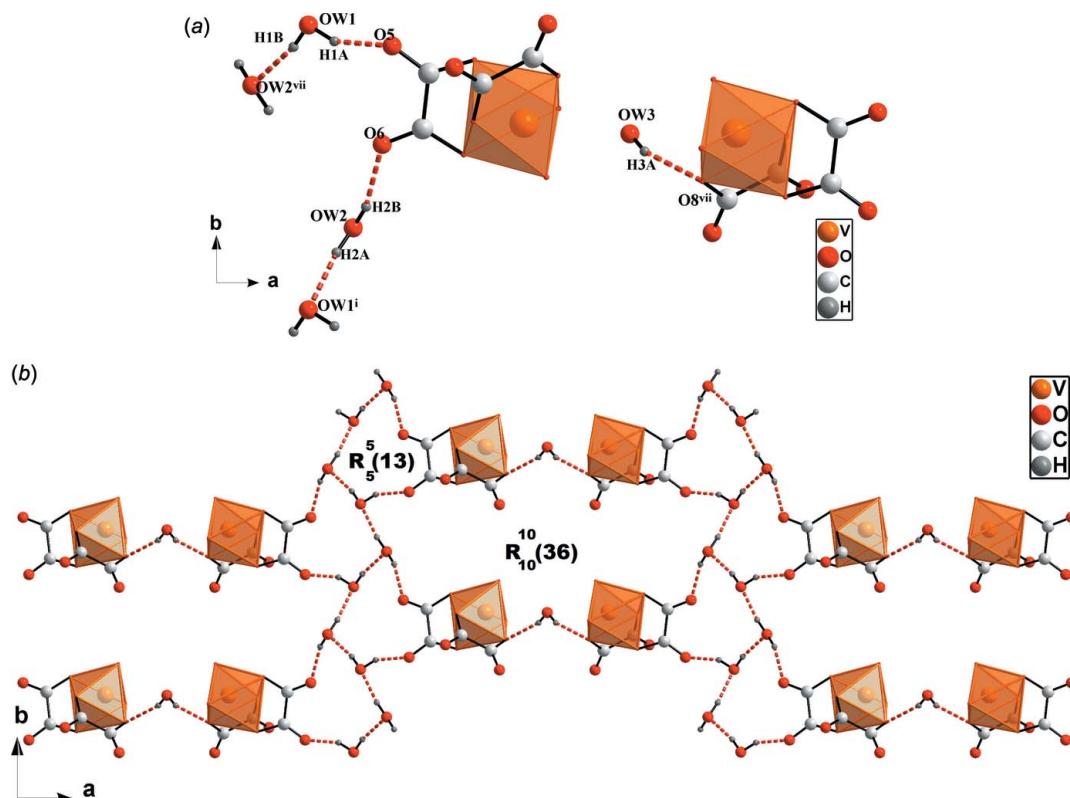
Figure 3
(a) View of O—H···O hydrogen bonds (red dashed line) formed by the two-and-half water molecules. [Symmetry codes: (i) $x, y - 1, z$; (vi) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (vii) $-x + 1, -y + 1, -z + 1$]. (b) $R_5^5(13)$ and $R_{10}^{10}(36)$ motifs.

In the same way, the three nitrogen atoms N10, N11 and N13 of the second 2,6-diaminopyridinium cation act as donors of six hydrogen bonds, N10—H10A···OW3, N10—H10B···O9^{iii}, N13—H13A···O9^{iii}, N13—H13A···O10^{iii}, N11—H11A···O10^{iii} and N11—H11B···OW2^{iv} (Table 1), coordinating a complex ion to two water molecules.

The third 2,6-diaminopyridinium cation links three complex ions *via* the six hydrogen bonds N15—H15A···O1^i, N15—H15B···O1^v, N15—H15B···O2^v, N16—H16A···O4^i, N16—H16B···O3 and N18—H18···O1^i (Table 1), established by their three nitrogen atoms N15, N16 and N18.

The water molecules act as hydrogen-bond donors *via* five O—H···O hydrogen bonds involving their oxygen atoms, OW1—H1A···O5, OW1—H1B···OW2^{vi}, OW2—H2A···OW1^i, OW2—H2B···O6 and OW3—H3A···O8^{vii} (Table 2) and coordinate the complex ions to the water molecules, generating $R_5^5(13)$ and $R_{10}^{10}(36)$ hydrogen-bonded rings, as shown in Fig. 3.

The 2,6-diaminopyridinium cations in the supramolecular structure of (I) are paired *via* π–π stacking with intercentroid distances of 3.6652 (1) and 3.8155 (2)Å, as illustrated in Fig. 4, consolidating the three-dimensional network (Fig. 5).

4. Synthesis and crystallization

All reagents and solvents were commercially available and used without further purification. Elemental analyses for carbon, nitrogen and hydrogen were performed on a

Flash2000 Organic Elemental Analyser, CHNS-O analyser by Thermo Scientific (Centre of Scientific Instrumentation of the University of Granada). An ICP-OES Perkin-Elmer Optima 8300 Spectrometer (Centre of Scientific Instrumentation of the University of Granada) was used to determine the metal content in the complex.
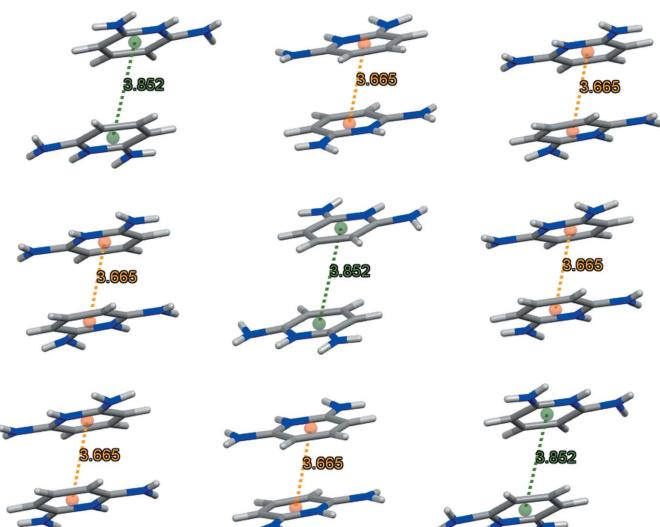
Figure 4
π–π stacking interactions (orange and green dashed lines) between adjacent 2,6-diaminopyridinium organic cations.
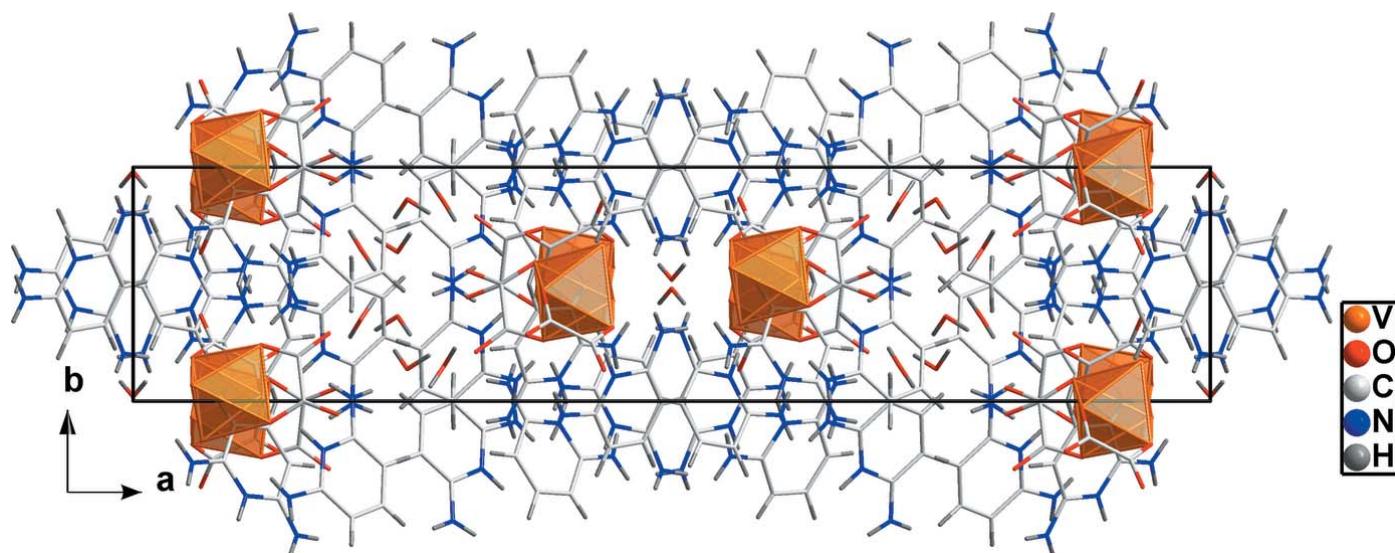
Figure 5
View of the packing of the title compound.

A mixture of vanadium pentoxide (V_2O_5/Merck, 99%), 2,6-diaminopyridine ($C_5H_7N_3$/Sigma Aldrich, 98%) and oxalic acid dihydrate ($C_2H_2O_4 \cdot 2H_2O$/Prolabo, 99,5%) were used as starting materials.

Under continuous stirring at 373 K, a solution of oxalic acid dihydrate (0.126 g, 1 mmol) dissolved in 10 cm³ of distilled water was added dropwise to a stirring solution of vanadium pentoxide (0.181 g, 1 mmol) dissolved in 20 cm³ of distilled water. After 15 minutes of mixture stirring, 2,6-diaminopyridine (0.218 g, 2 mmol) was added to the mixture without prior dissolution. The final solution was kept under continuous stirring and heated for a further hour. After filtration, the filtrate was placed in a petri dish and kept at room temperature. After a week to ten days, orange–brown crystals, stable at room temperature and of suitable size for a structural study, appeared.

The elemental analytical results for carbon, hydrogen and nitrogen are close to the calculated values. Calculated: C: 35.97%, H: 4.61%, N: 19.87%; V: 8.03%, Found C: 35.53%, H: 5.15%, N: 19.74%, V: 10.85%.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_5H_8N_3)_3[VO_2(C_2O_4)_2]\cdot 2.5H_2O$
M_r	1268.90
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	38.972 (2), 7.5746 (4), 20.8208 (12)
β (°)	116.551 (2)
V (Å³)	5498.0 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.44
Crystal size (mm)	$0.54 \times 0.31 \times 0.28$
Data collection	
Diffractometer	Bruker Venture
Absorption correction	Numerical (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.877, 0.929
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	32414, 8409, 7884
R_{int}	0.017
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.716
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.087, 1.10
No. of reflections	8409
No. of parameters	491
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.44, −0.66

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2006) and *publCIF* (Westrip, 2010).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms of the 2,6-diaminopyridinium cations and water molecules were located in difference-Fourier maps and refined freely with isotropic displacement parameters.

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References

Aghabozorg, H., Motyeian, E., Aghajani, Z., Ghadermazi, M. & Attar Gharamaleki, J. (2007). *Acta Cryst.* E**63**, m1754–m1755.

Atovmyan, B. O. & Sokolova, Yu. A. (1972). *Zh. Strukt. Khim.* **12**, 984–985.

Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bruker (2012). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Drew, R. E., Einstein, F. W. B. & Gransden, S. E. (1974). *Can. J. Chem.* **52**, 2184–2189.

Hoard, J. L., Scheidt, W. R. & Tsai, C. (1971). *J. Am. Chem. Soc.* **93**, 3867–3872.

Kordowiak, A. M., Dudek, B. & Gyrboś, R. (2000). *Comp. Biochem. & Phys.* C**125**, 11–16.

León, E. I., Etcheverry, S. B., Parajón-Costa, B. S. & Baran, E. J. (2013). *Biol. Trace Elem. Res.* **155**, 295–300.

Lin, L., Wu, S.-F., Huang, C.-C., Zhang, H.-H., Huang, X.-H. & Lian, Z.-X. (2004). *Acta Cryst.* E**60**, m631–m633.

Maurya, M. R., Kumar, M., Titinchi, S. J. J., Abbo, H. S. & Chand, S. (2003). *Catal. Lett.* **86**, 97–105.

Mishra, G. S. & Kumar, A. (2002). *Catal. Lett.* **81**, 113–117.

Odabaşoğlu, M. & Büyükgüngör, O. (2006). *Acta Cryst.* E**62**, o4543–o4544.

Sehimi, H., Chérif, I. & Zid, M. F. (2016). *Acta Cryst.* E**72**, 724–729.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

Stomberg, R. (1986). *Acta Chem. Scand.* A**40**, 168–176.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

Synthesis and structural study of tris(2,6-diaminopyridinium) bis-(oxalato)dioxidovanadate(V) 2.5-hydrate

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Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Tris(2,6-diaminopyridinium) bis(oxalato)dioxidovanadate(V) 2.5-hydrate

Crystal data
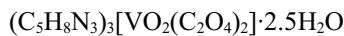
$(C_5H_8N_3)_3[VO_2(C_2O_4)_2]\cdot 2.5H_2O$	$F(000) = 2632$
$M_r = 1268.90$	$D_x = 1.533$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 38.972$ (2) Å	Cell parameters from 33946 reflections
$b = 7.5746$ (4) Å	$\theta = 2.2$–30.6°
$c = 20.8208$ (12) Å	$\mu = 0.44$ mm^{-1}
$\beta = 116.551$ (2)°	$T = 100$ K
$V = 5498.0$ (5) Å^3	Prism, orange-brown
$Z = 4$	$0.54 \times 0.31 \times 0.28$ mm

Data collection

Bruker Venture diffractometer	8409 independent reflections
Radiation source: fine-focus sealed tube	7884 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.017$
Absorption correction: numerical (SADABS; Sheldrick, 1996)	$\theta_{max} = 30.6°$, $\theta_{min} = 2.2°$
$T_{min} = 0.877$, $T_{max} = 0.929$	$h = -55 \rightarrow 54$
32414 measured reflections	$k = -8 \rightarrow 10$
	$l = -29 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.032$	All H-atom parameters refined
$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2 + 5.9089P]$
$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
8409 reflections	$(\Delta/\sigma)_{max} = 0.001$
491 parameters	$\Delta\rho_{max} = 0.44$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.66$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

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}
V1	0.41895 (2)	0.51731 (2)	0.53978 (2)	0.01188 (5)
O1	0.44546 (2)	0.56998 (11)	0.49956 (4)	0.01743 (15)
O2	0.43619 (2)	0.32872 (11)	0.57872 (4)	0.01834 (16)
O3	0.37302 (2)	0.40795 (10)	0.45955 (4)	0.01608 (15)
O4	0.38117 (2)	0.73971 (10)	0.49208 (4)	0.01663 (15)
C1	0.34163 (3)	0.49862 (15)	0.42904 (6)	0.01604 (19)
C2	0.34638 (3)	0.69347 (15)	0.45406 (6)	0.01666 (19)
O5	0.31838 (3)	0.78943 (13)	0.43753 (5)	0.0290 (2)
O6	0.31082 (3)	0.44355 (13)	0.38420 (5)	0.0270 (2)
O7	0.38034 (2)	0.52494 (10)	0.59251 (4)	0.01578 (15)
O8	0.44487 (2)	0.68508 (11)	0.62182 (4)	0.01635 (15)
C3	0.38693 (3)	0.65717 (14)	0.63407 (6)	0.01499 (18)
C4	0.42578 (3)	0.74855 (15)	0.65372 (6)	0.01634 (19)
O9	0.43714 (3)	0.86623 (13)	0.69874 (5)	0.02635 (19)
O10	0.36600 (3)	0.71404 (12)	0.65962 (5)	0.02217 (17)
C5	0.32523 (4)	0.12402 (15)	0.56396 (6)	0.0204 (2)
N5	0.35544 (4)	0.08838 (15)	0.55082 (8)	0.0301 (3)
H5A	0.3711 (6)	0.166 (3)	0.5552 (11)	0.040 (5)*
H5B	0.3527 (6)	−0.006 (3)	0.5255 (12)	0.042 (6)*
N8	0.32350 (3)	0.28965 (13)	0.58800 (5)	0.01779 (18)
H8A	0.3427 (6)	0.372 (3)	0.5924 (10)	0.037 (5)*
C6	0.29533 (3)	0.34407 (16)	0.60538 (6)	0.0195 (2)
N6	0.29672 (3)	0.51242 (15)	0.62589 (7)	0.0259 (2)
H6A	0.2794 (6)	0.543 (3)	0.6385 (11)	0.038 (5)*
H6B	0.3165 (6)	0.570 (3)	0.6337 (10)	0.035 (5)*
C7	0.26704 (4)	0.22302 (18)	0.59948 (7)	0.0242 (2)
H7	0.2459 (5)	0.258 (3)	0.6093 (10)	0.035 (5)*
C8	0.26825 (4)	0.05496 (18)	0.57483 (7)	0.0251 (2)
H8	0.2490 (6)	−0.027 (3)	0.5720 (10)	0.033 (5)*
C9	0.29675 (4)	0.00273 (16)	0.55638 (7)	0.0239 (2)
H9	0.2974 (6)	−0.114 (3)	0.5399 (10)	0.038 (5)*
C10	0.41609 (3)	0.75481 (16)	0.25317 (6)	0.0181 (2)
N10	0.44513 (3)	0.76369 (16)	0.23561 (6)	0.0228 (2)
H10A	0.4591 (6)	0.670 (3)	0.2394 (11)	0.044 (6)*
H10B	0.4489 (5)	0.854 (3)	0.2183 (10)	0.033 (5)*
N13	0.39527 (3)	0.90492 (14)	0.24518 (5)	0.01700 (18)
H13A	0.4021 (5)	1.004 (3)	0.2302 (10)	0.032 (5)*
C11	0.36515 (3)	0.91707 (16)	0.26207 (6)	0.0181 (2)
N11	0.34804 (3)	1.07389 (16)	0.25299 (6)	0.0241 (2)

H11A	0.3536 (6)	1.152 (3)	0.2307 (11)	0.043 (5)*
H11B	0.3295 (5)	1.088 (3)	0.2644 (10)	0.031 (5)*
C12	0.35486 (4)	0.76673 (18)	0.28837 (6)	0.0222 (2)
H12	0.3329 (5)	0.778 (3)	0.2984 (10)	0.031 (5)*
C13	0.37542 (4)	0.61321 (17)	0.29592 (7)	0.0247 (2)
H13	0.3675 (6)	0.501 (3)	0.3123 (10)	0.033 (5)*
C14	0.40600 (4)	0.60402 (17)	0.27926 (7)	0.0230 (2)
H14	0.4198 (6)	0.504 (3)	0.2841 (11)	0.039 (6)*
C15	0.47700 (3)	−0.13176 (15)	0.41695 (6)	0.01577 (19)
N15	0.49100 (3)	−0.29671 (15)	0.42598 (6)	0.0222 (2)
H15A	0.4848 (5)	−0.371 (3)	0.4494 (10)	0.029 (4)*
H15B	0.5133 (6)	−0.312 (3)	0.4253 (10)	0.033 (5)*
N18	0.44624 (3)	−0.10508 (12)	0.43083 (5)	0.01337 (16)
H18A	0.4831 (5)	0.275 (2)	0.3702 (9)	0.028 (4)*
C16	0.42852 (3)	0.05396 (14)	0.42368 (6)	0.01396 (18)
N16	0.39901 (3)	0.06024 (13)	0.43990 (6)	0.01817 (18)
H16A	0.3916 (5)	−0.032 (2)	0.4570 (9)	0.022 (4)*
H16B	0.3889 (5)	0.159 (3)	0.4397 (9)	0.027 (4)*
C17	0.44205 (4)	0.19760 (15)	0.39958 (6)	0.0192 (2)
H17	0.4304 (5)	0.315 (2)	0.3964 (9)	0.026 (4)*
C18	0.47321 (4)	0.17289 (17)	0.38535 (7)	0.0218 (2)
H18	0.4387 (5)	−0.200 (3)	0.4490 (9)	0.028 (4)*
C19	0.49093 (3)	0.01017 (17)	0.39314 (6)	0.0202 (2)
H19	0.5114 (5)	−0.010 (2)	0.3839 (10)	0.026 (4)*
OW1	0.25449 (3)	0.86277 (12)	0.32000 (5)	0.02255 (17)
H1A	0.2743 (6)	0.806 (3)	0.3570 (11)	0.039 (5)*
H1B	0.2432 (7)	0.786 (3)	0.2835 (13)	0.054 (6)*
OW2	0.28869 (3)	0.15066 (13)	0.29340 (5)	0.02227 (17)
H2A	0.2759 (7)	0.064 (3)	0.3002 (12)	0.052 (6)*
H2B	0.2985 (7)	0.225 (3)	0.3309 (13)	0.057 (7)*
OW3	0.500000	0.48083 (18)	0.250000	0.0223 (2)
H3A	0.5113 (6)	0.419 (3)	0.2838 (10)	0.044 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
V1	0.01305 (8)	0.01016 (8)	0.01423 (9)	0.00085 (6)	0.00771 (6)	0.00032 (6)
O1	0.0194 (4)	0.0173 (4)	0.0194 (4)	−0.0009 (3)	0.0121 (3)	0.0003 (3)
O2	0.0219 (4)	0.0154 (4)	0.0212 (4)	0.0052 (3)	0.0126 (3)	0.0044 (3)
O3	0.0171 (3)	0.0111 (3)	0.0201 (4)	−0.0003 (3)	0.0083 (3)	−0.0033 (3)
O4	0.0184 (4)	0.0104 (3)	0.0186 (4)	−0.0001 (3)	0.0060 (3)	0.0006 (3)
C1	0.0170 (5)	0.0147 (5)	0.0177 (5)	−0.0008 (4)	0.0088 (4)	−0.0034 (4)
C2	0.0189 (5)	0.0145 (5)	0.0152 (4)	0.0020 (4)	0.0063 (4)	−0.0009 (4)
O5	0.0224 (4)	0.0239 (4)	0.0311 (5)	0.0097 (4)	0.0034 (4)	−0.0065 (4)
O6	0.0189 (4)	0.0260 (5)	0.0302 (5)	−0.0039 (3)	0.0058 (4)	−0.0105 (4)
O7	0.0175 (3)	0.0138 (3)	0.0197 (4)	−0.0014 (3)	0.0116 (3)	−0.0020 (3)
O8	0.0138 (3)	0.0182 (4)	0.0174 (3)	−0.0010 (3)	0.0073 (3)	−0.0033 (3)
C3	0.0168 (4)	0.0135 (4)	0.0160 (4)	0.0020 (4)	0.0086 (4)	0.0014 (4)

C4	0.0153 (4)	0.0162 (5)	0.0168 (5)	0.0012 (4)	0.0066 (4)	−0.0015 (4)
O9	0.0224 (4)	0.0266 (5)	0.0296 (5)	−0.0040 (3)	0.0112 (4)	−0.0147 (4)
O10	0.0234 (4)	0.0207 (4)	0.0292 (4)	0.0016 (3)	0.0178 (4)	−0.0043 (3)
C5	0.0312 (6)	0.0143 (5)	0.0213 (5)	−0.0028 (4)	0.0167 (5)	−0.0010 (4)
N5	0.0476 (7)	0.0148 (5)	0.0475 (7)	−0.0058 (5)	0.0387 (6)	−0.0068 (5)
N8	0.0220 (4)	0.0140 (4)	0.0212 (4)	−0.0025 (3)	0.0131 (4)	−0.0017 (3)
C6	0.0192 (5)	0.0202 (5)	0.0204 (5)	−0.0005 (4)	0.0102 (4)	−0.0010 (4)
N6	0.0229 (5)	0.0215 (5)	0.0385 (6)	−0.0020 (4)	0.0183 (5)	−0.0083 (4)
C7	0.0215 (5)	0.0259 (6)	0.0286 (6)	−0.0036 (5)	0.0142 (5)	−0.0015 (5)
C8	0.0267 (6)	0.0227 (6)	0.0269 (6)	−0.0074 (5)	0.0130 (5)	0.0010 (5)
C9	0.0345 (6)	0.0154 (5)	0.0260 (6)	−0.0060 (5)	0.0173 (5)	−0.0013 (4)
C10	0.0240 (5)	0.0184 (5)	0.0119 (4)	−0.0013 (4)	0.0079 (4)	−0.0021 (4)
N10	0.0303 (5)	0.0211 (5)	0.0233 (5)	0.0042 (4)	0.0174 (4)	0.0028 (4)
N13	0.0196 (4)	0.0180 (4)	0.0147 (4)	−0.0008 (3)	0.0088 (3)	0.0022 (3)
C11	0.0185 (5)	0.0226 (5)	0.0131 (4)	−0.0012 (4)	0.0070 (4)	0.0020 (4)
N11	0.0232 (5)	0.0273 (5)	0.0272 (5)	0.0050 (4)	0.0162 (4)	0.0104 (4)
C12	0.0241 (5)	0.0258 (6)	0.0185 (5)	−0.0054 (5)	0.0114 (4)	0.0017 (4)
C13	0.0335 (6)	0.0207 (5)	0.0211 (5)	−0.0078 (5)	0.0135 (5)	0.0000 (4)
C14	0.0336 (6)	0.0162 (5)	0.0208 (5)	−0.0020 (5)	0.0136 (5)	−0.0013 (4)
C15	0.0134 (4)	0.0206 (5)	0.0124 (4)	0.0015 (4)	0.0050 (4)	−0.0013 (4)
N15	0.0204 (5)	0.0250 (5)	0.0243 (5)	0.0094 (4)	0.0128 (4)	0.0053 (4)
N18	0.0154 (4)	0.0120 (4)	0.0140 (4)	0.0001 (3)	0.0078 (3)	−0.0001 (3)
C16	0.0177 (4)	0.0114 (4)	0.0138 (4)	−0.0009 (4)	0.0080 (4)	−0.0017 (3)
N16	0.0250 (5)	0.0097 (4)	0.0273 (5)	0.0019 (3)	0.0184 (4)	0.0009 (3)
C17	0.0266 (5)	0.0121 (5)	0.0223 (5)	−0.0029 (4)	0.0140 (4)	−0.0002 (4)
C18	0.0263 (6)	0.0202 (5)	0.0225 (5)	−0.0083 (4)	0.0142 (5)	−0.0014 (4)
C19	0.0176 (5)	0.0263 (6)	0.0194 (5)	−0.0042 (4)	0.0108 (4)	−0.0016 (4)
OW1	0.0192 (4)	0.0214 (4)	0.0242 (4)	0.0024 (3)	0.0072 (3)	−0.0005 (3)
OW2	0.0227 (4)	0.0209 (4)	0.0247 (4)	−0.0021 (3)	0.0119 (3)	−0.0030 (3)
OW3	0.0222 (6)	0.0201 (6)	0.0200 (6)	0.000	0.0052 (5)	0.000

Geometric parameters (Å, º)

V1—O2	1.6317 (8)	N10—H10A	0.88 (2)
V1—O1	1.6433 (8)	N10—H10B	0.82 (2)
V1—O3	2.0020 (8)	N13—C11	1.3706 (14)
V1—O8	2.0026 (8)	N13—H13A	0.90 (2)
V1—O4	2.1644 (8)	C11—N11	1.3337 (16)
V1—O7	2.2248 (8)	C11—C12	1.3978 (16)
O3—C1	1.2948 (13)	N11—H11A	0.84 (2)
O4—C2	1.2761 (14)	N11—H11B	0.861 (19)
C1—O6	1.2189 (14)	C12—C13	1.3807 (19)
C1—C2	1.5485 (15)	C12—H12	0.970 (18)
C2—O5	1.2254 (14)	C13—C14	1.3841 (19)
O7—C3	1.2725 (13)	C13—H13	1.012 (19)
O8—C4	1.2914 (13)	C14—H14	0.91 (2)
C3—O10	1.2335 (13)	C15—N15	1.3425 (15)
C3—C4	1.5442 (15)	C15—N18	1.3679 (13)

C4—O9	1.2240 (14)	C15—C19	1.3916 (16)
C5—N5	1.3498 (17)	N15—H15A	0.85 (2)
C5—N8	1.3635 (15)	N15—H15B	0.882 (19)
C5—C9	1.3944 (17)	N18—C16	1.3632 (14)
N5—H5A	0.82 (2)	N18—H18	0.917 (19)
N5—H5B	0.87 (2)	C16—N16	1.3364 (14)
N8—C6	1.3643 (15)	C16—C17	1.3965 (15)
N8—H8A	0.95 (2)	N16—H16A	0.887 (18)
C6—N6	1.3382 (16)	N16—H16B	0.843 (19)
C6—C7	1.3966 (17)	C17—C18	1.3855 (17)
N6—H6A	0.86 (2)	C17—H17	0.987 (18)
N6—H6B	0.84 (2)	C18—C19	1.3863 (18)
C7—C8	1.3811 (19)	C18—H18A	0.979 (18)
C7—H7	0.969 (19)	C19—H19	0.915 (18)
C8—C9	1.3855 (19)	OW1—H1A	0.92 (2)
C8—H8	0.955 (19)	OW1—H1B	0.90 (2)
C9—H9	0.95 (2)	OW2—H2A	0.87 (2)
C10—N10	1.3375 (16)	OW2—H2B	0.90 (3)
C10—N13	1.3632 (15)	OW3—H3A	0.79 (2)
C10—C14	1.3946 (17)	OW3—H3A^i	0.79 (2)
O2—V1—O1	104.64 (4)	C8—C9—H9	121.2 (12)
O2—V1—O3	93.92 (4)	C5—C9—H9	120.3 (12)
O1—V1—O3	101.92 (4)	N10—C10—N13	117.06 (11)
O2—V1—O8	101.13 (4)	N10—C10—C14	124.60 (12)
O1—V1—O8	95.07 (4)	N13—C10—C14	118.33 (11)
O3—V1—O8	153.67 (3)	C10—N10—H10A	120.1 (14)
O2—V1—O4	162.54 (4)	C10—N10—H10B	120.3 (14)
O1—V1—O4	91.77 (4)	H10A—N10—H10B	119.4 (19)
O3—V1—O4	76.58 (3)	C10—N13—C11	123.78 (10)
O8—V1—O4	82.98 (3)	C10—N13—H13A	119.3 (12)
O2—V1—O7	89.80 (4)	C11—N13—H13A	116.9 (12)
O1—V1—O7	164.36 (4)	N11—C11—N13	117.04 (11)
O3—V1—O7	82.69 (3)	N11—C11—C12	124.63 (11)
O8—V1—O7	75.94 (3)	N13—C11—C12	118.32 (11)
O4—V1—O7	74.62 (3)	C11—N11—H11A	118.1 (15)
C1—O3—V1	119.09 (7)	C11—N11—H11B	119.9 (13)
C2—O4—V1	112.79 (7)	H11A—N11—H11B	121.4 (19)
O6—C1—O3	125.84 (11)	C13—C12—C11	118.51 (11)
O6—C1—C2	120.83 (10)	C13—C12—H12	124.7 (11)
O3—C1—C2	113.33 (9)	C11—C12—H12	116.7 (11)
O5—C2—O4	125.27 (11)	C12—C13—C14	122.33 (12)
O5—C2—C1	120.89 (10)	C12—C13—H13	119.6 (11)
O4—C2—C1	113.84 (9)	C14—C13—H13	118.1 (11)
C3—O7—V1	112.38 (7)	C13—C14—C10	118.73 (12)
C4—O8—V1	119.21 (7)	C13—C14—H14	123.3 (13)
O10—C3—O7	126.65 (11)	C10—C14—H14	118.0 (13)
O10—C3—C4	119.21 (10)	N15—C15—N18	116.59 (10)

O7—C3—C4	114.13 (9)	N15—C15—C19	124.76 (11)
O9—C4—O8	124.79 (11)	N18—C15—C19	118.63 (10)
O9—C4—C3	120.37 (10)	C15—N15—H15A	119.9 (13)
O8—C4—C3	114.77 (9)	C15—N15—H15B	117.4 (13)
N5—C5—N8	116.69 (11)	H15A—N15—H15B	117.1 (18)
N5—C5—C9	124.59 (12)	C16—N18—C15	123.82 (10)
N8—C5—C9	118.71 (11)	C16—N18—H18	119.8 (11)
C5—N5—H5A	120.6 (15)	C15—N18—H18	116.3 (11)
C5—N5—H5B	114.1 (14)	N16—C16—N18	117.07 (10)
H5A—N5—H5B	123 (2)	N16—C16—C17	124.67 (10)
C5—N8—C6	123.57 (10)	N18—C16—C17	118.26 (10)
C5—N8—H8A	118.5 (12)	C16—N16—H16A	123.1 (11)
C6—N8—H8A	118.0 (12)	C16—N16—H16B	119.1 (12)
N6—C6—N8	116.75 (11)	H16A—N16—H16B	117.3 (16)
N6—C6—C7	124.85 (12)	C18—C17—C16	118.65 (11)
N8—C6—C7	118.40 (11)	C18—C17—H17	121.8 (10)
C6—N6—H6A	115.6 (14)	C16—C17—H17	119.4 (10)
C6—N6—H6B	117.4 (14)	C17—C18—C19	122.23 (11)
H6A—N6—H6B	125.6 (19)	C17—C18—H18A	118.1 (11)
C8—C7—C6	118.76 (12)	C19—C18—H18A	119.6 (11)
C8—C7—H7	120.2 (12)	C18—C19—C15	118.39 (11)
C6—C7—H7	120.9 (12)	C18—C19—H19	124.3 (11)
C7—C8—C9	122.06 (12)	C15—C19—H19	117.3 (11)
C7—C8—H8	117.8 (12)	H1A—OW1—H1B	108.3 (19)
C9—C8—H8	120.1 (12)	H2A—OW2—H2B	113 (2)
C8—C9—C5	118.48 (12)	H3A—OW3—H3A^i	108 (3)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*B*···O4^{ii}	0.87 (2)	2.47 (2)	3.2515 (14)	150.0 (19)
N5—H5*B*···O5^{ii}	0.87 (2)	2.31 (2)	3.1196 (16)	154.7 (19)
N8—H8*A*···O7	0.95 (2)	1.87 (2)	2.8118 (13)	174.1 (18)
N6—H6*A*···O*W*1^{iii}	0.86 (2)	2.00 (2)	2.8559 (15)	171.0 (19)
N6—H6*B*···O10	0.84 (2)	2.07 (2)	2.9018 (15)	176.4 (19)
N10—H10*A*···O*W*3	0.88 (2)	2.08 (2)	2.9463 (15)	169 (2)
N10—H10*B*···O9^{iv}	0.82 (2)	2.17 (2)	2.8863 (15)	146.8 (18)
N13—H13*A*···O9^{iv}	0.90 (2)	2.01 (2)	2.8309 (13)	150.3 (17)
N13—H13*A*···O10^{iv}	0.90 (2)	2.615 (19)	3.3149 (14)	135.2 (16)
N11—H11*A*···O10^{iv}	0.84 (2)	2.02 (2)	2.8401 (14)	165 (2)
N11—H11*B*···O*W*2^{v}	0.861 (19)	2.00 (2)	2.8522 (14)	173.1 (19)
N15—H15*A*···O1^{ii}	0.85 (2)	2.252 (19)	2.9914 (14)	145.5 (17)
N15—H15*B*···O1^{vi}	0.882 (19)	2.570 (19)	3.0641 (13)	116.2 (15)
N15—H15*B*···O2^{vi}	0.882 (19)	2.01 (2)	2.8926 (14)	175.9 (19)
N16—H16*A*···O4^{ii}	0.887 (18)	1.990 (18)	2.8695 (13)	170.5 (16)
N16—H16*B*···O3	0.843 (19)	2.085 (19)	2.9156 (12)	168.5 (17)

N18—H18···O1ⁱⁱ	0.917 (19)	1.993 (19)	2.8541 (12)	155.7 (16)
O*W*1—H1*A*···O5	0.92 (2)	1.79 (2)	2.6550 (13)	155.8 (19)
O*W*1—H1*B*···O*W*2^{vii}	0.90 (2)	1.84 (2)	2.7270 (13)	169 (2)
O*W*2—H2*A*···O*W*1ⁱⁱ	0.87 (2)	1.87 (3)	2.7384 (14)	173 (2)
O*W*2—H2*B*···O6	0.90 (3)	1.93 (3)	2.7896 (13)	160 (2)
O*W*3—H3*A*···O8^{viii}	0.79 (2)	2.10 (2)	2.8621 (10)	161 (2)

Symmetry codes: (ii) *x*, *y*−1, *z*; (iii) −*x*+1/2, −*y*+3/2, −*z*+1; (iv) *x*, −*y*+2, *z*−1/2; (v) *x*, *y*+1, *z*; (vi) −*x*+1, −*y*, −*z*+1; (vii) −*x*+1/2, *y*+1/2, −*z*+1/2; (viii) −*x*+1, −*y*+1, −*z*+1.