

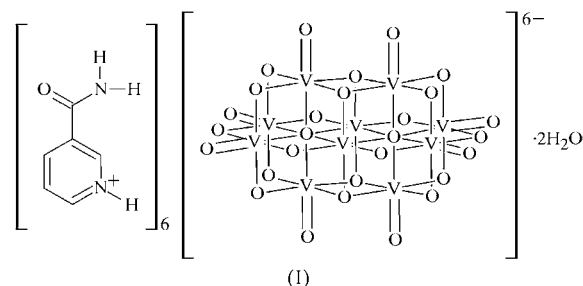
Hexakis[3-(aminocarbonyl)pyridinium]
decavanadate(V) dihydrateSilvia Pacigová,^a Erik Rakovský,^{a*} Michal Sivák^a and
Zdirad Žák^b^aDepartment of Inorganic Chemistry, Comenius University, Faculty of Natural Sciences, Mlynská dolina, 842 15 Bratislava, Slovak Republic, and ^bDepartment of Materials, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
Correspondence e-mail: rakovsky@fns.uniba.skReceived 20 April 2007
Accepted 11 June 2007
Online 17 August 2007

The structure of the title compound, $(C_6H_7N_2O)_6[V_{10}O_{28}] \cdot 2H_2O$, at 120 (2) K has monoclinic ($C2/c$) symmetry. The asymmetric unit consists of one half-decavanadate anion of C_i symmetry, three cations and one water molecule. Each water molecule is hydrogen bonded to two decavanadate anions, thus forming a one-dimensional chain of anions. The three-dimensional supramolecular structure is formed by a network of $N-H \cdots O$, $O-H \cdots O$ and $C-H \cdots O$ hydrogen bonds, in which the cations, anions and water molecules are involved,

and by nonparallel-displaced π -stacking interactions between pyridine rings. As a result of hydrogen bonding, the carboxamide groups of the cations are somewhat twisted from the pyridine ring plane.

Comment

The title compound, (I), was synthesized as part of our studies focused on interactions of both oxovanadium and oxoper-oxovanadium species with biologically important organic substrates. The oxovanadates(V) and peroxovanadium compounds are of great interest in biochemistry and medicine



because of their diverse biological activities; the former compounds also have applications in catalysis and materials science. The interaction of nicotinamide with vanadium(V) compounds and the nature of the products formed, are of interest with respect to the use of amides of pyridine- and pyrazinecarboxylic acids as antituberculotics, and the potential use of vanadium compounds as insulin-mimetic drugs in human medicine (Crans, 1998). From the same reaction

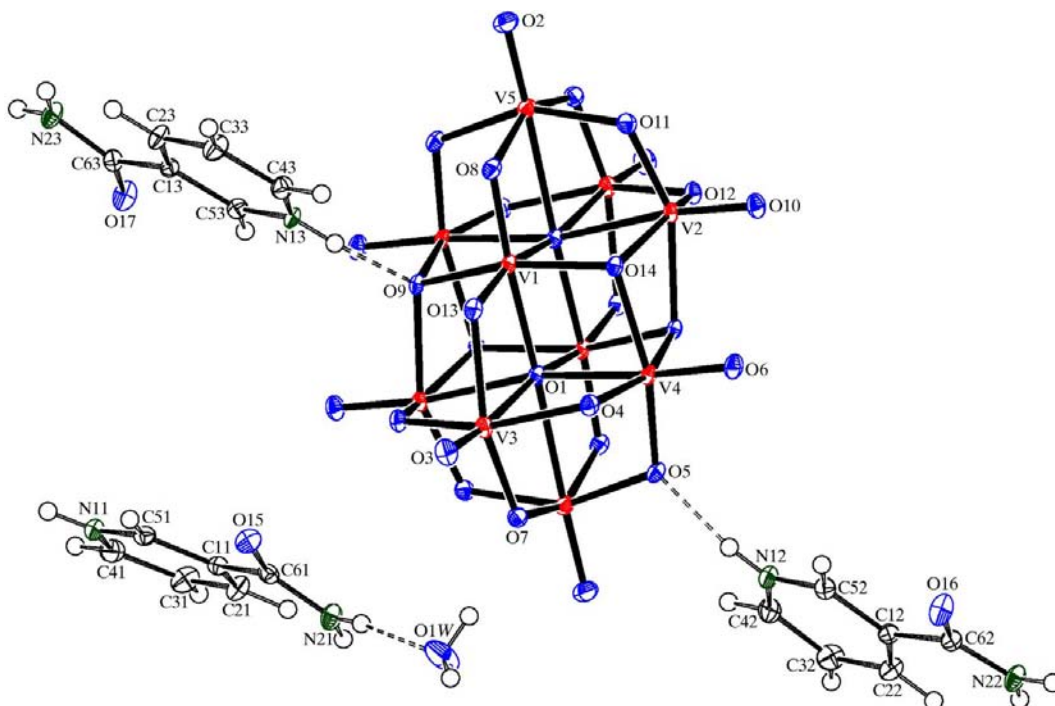


Figure 1

The structure of (I), showing the atom-labelling scheme and cation–anion and cation–water $N-H \cdots O$ hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level. The symmetry operation relating labelled atoms to unlabelled atoms is $(-x, -y + 1, -z)$.

metal-organic compounds

solution, *viz.* $V_2O_5-H_2O_2-H_2O$, but containing picolinamide or pyrazinamide, we have isolated and structurally characterized monoperoxovanadium(V) complexes (Sivák *et al.*, 2000; Mad'arová *et al.*, 2004; Pacigová *et al.*, 2007).

The asymmetric unit of (I) consists of one-half decavanadate anion of C_i symmetry (although its symmetry is close to the D_{2h} point group) lying on a special position on the glide plane, three 1*H*-nicotinamidium(1+) cations and one water molecule of crystallization (Fig. 1). The angle between the

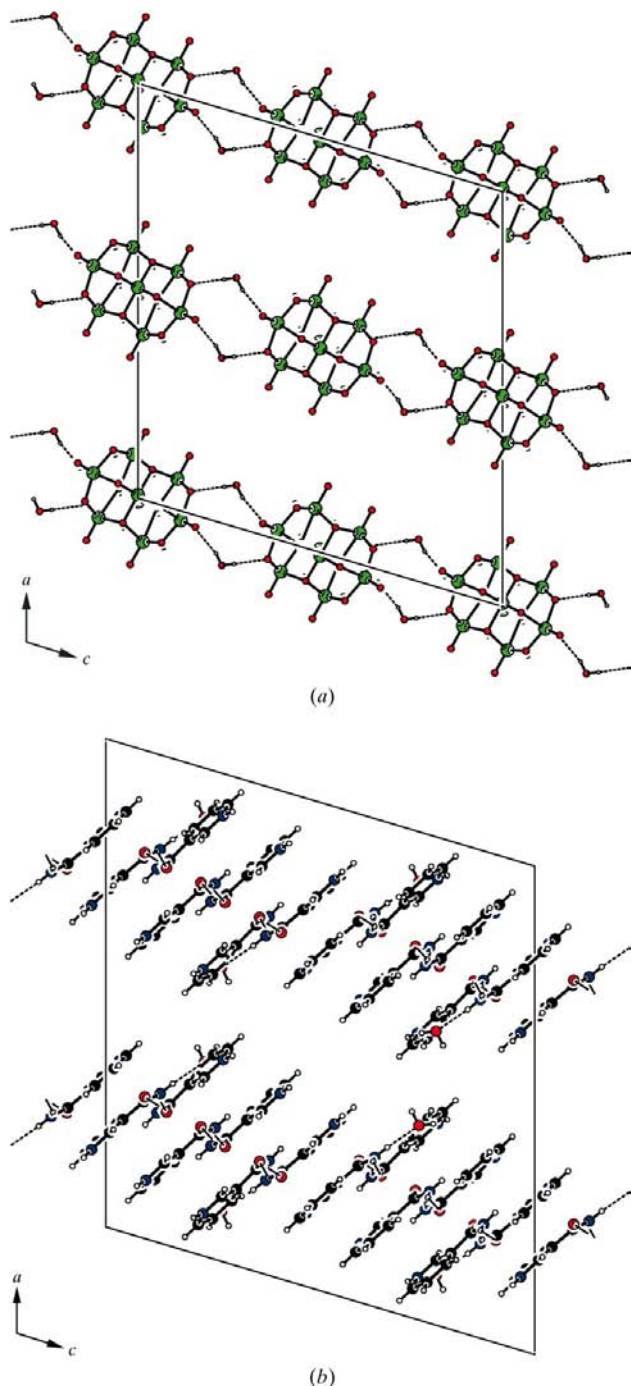


Figure 2
(a) A view of the anionic chains packing along the *b* axis. (b) A view of the cationic chains packing along the *b* axis, involving water molecule contacts. Dashed lines indicate hydrogen bonds.

(020) glide plane and the central plane of the $[V_{10}O_{28}]^{6-}$ anion [formed by atoms V1, V1ⁱ, V3, V3ⁱ, V5 and V5ⁱ; symmetry code: (i) $-x, -y + 1, -z$] is 86.29 (1)°. The terminal vanadium–oxygen bond lengths are in the range 1.601 (1)–1.618 (1) Å, with an average value of 1.609 (9) Å. The bond lengths of the bridging O atoms with coordination numbers two, three and six have mean values of 1.85 (12), 2.00 (7) and 2.24 (10) Å, respectively.

The supramolecular structure is formed by $D-H \cdots O$ hydrogen bonds [$D = N, O$ or C , with $H \cdots O \leq 2.72$ Å and $D-H \cdots O > 119^\circ$ (Brown, 1992)] between cations and anions, between cations and cations, between water molecules and anions, and between water molecules and cations, and by nonparallel-displaced π -stacking interactions between the pyridine rings.

Two $[V_{10}O_{28}]^{6-}$ anions are bridged *via* two water molecules, forming rings with graph-set $N_2 = R_4^4(12)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995) and subsequently chains along the *c* axis (Fig. 2*a*, detail in Fig. 3). The colinearly arranged atoms O5, O9 and O12 act as acceptors of pyridinium H atoms H12, H13 and H11, and terminal O atoms O6 and O10 are acceptors of amide H atoms H23*A* and H22*A*. The anion-bridging water molecule acts as an acceptor of the corresponding H21*A* atom. The 1*H*-nicotinamidium(1+) cations form two types of hydrogen-bonded chains along the *b* axis, almost parallel to the (10 $\bar{1}$) plane (Figs. 2*b* and 4). One type is formed by chains with graph set $N_1 = C(4)$, containing crystallographically equivalent nicotinamidium cations containing the C*x*1/N11 ($x = 1-5$) pyridinium ring. The next two chains, with graph set

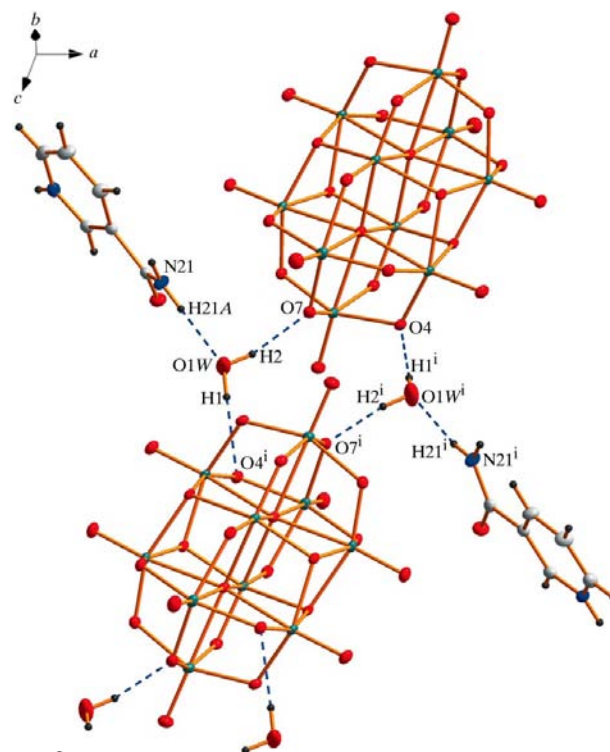


Figure 3
A detail of the $N_2 = R_4^4(12)$ rings (see *Comment*) in the anionic chains, involving interaction with the cationic chains *via* the water molecules. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

$N_2 = C_2^2(8)$ and running in opposite directions, are formed by the alternation of the two remaining nicotinamidium cations; both types form sheet-like structures (Athimoolam & Natarajan, 2006). There are two types of C—H...O bond, the first containing decavanadate O atoms and the second containing carboxamide O atoms as acceptors. Bonds of the second type reinforce interactions in the cationic chains mentioned above. All nicotinamidium chains present are mutually π -stacked.

To evaluate the π - π interactions between the pyridine rings, least-squares planes n defined by atoms C1*n*–C5*n* and N1*n* were calculated. The mean distance of the plane 1 atoms from plane 3, $R(31)$, is 3.32 (17) Å, and the mean distance of the plane 3 atoms from plane 1, $R(13)$, is 3.32 (17) Å, with an angle between the planes, $\gamma(1)$, of 9.42 (9)°, a corresponding centroid–centroid distance, $R_{ct}(1)$, of 3.5 Å, and the closest interatomic distance, $R_{clo}(C51 \cdots N13)$, of 3.156 (2) Å; for planes 3 and 2, $R(32) = 3.44$ (11) Å, $R(23) = 3.40$ (11) Å, $\gamma(2) = 5.77$ (9)°, $R_{ct}(2) = 3.6$ Å and $R_{clo}(N12 \cdots C53) = 3.364$ (2) Å.

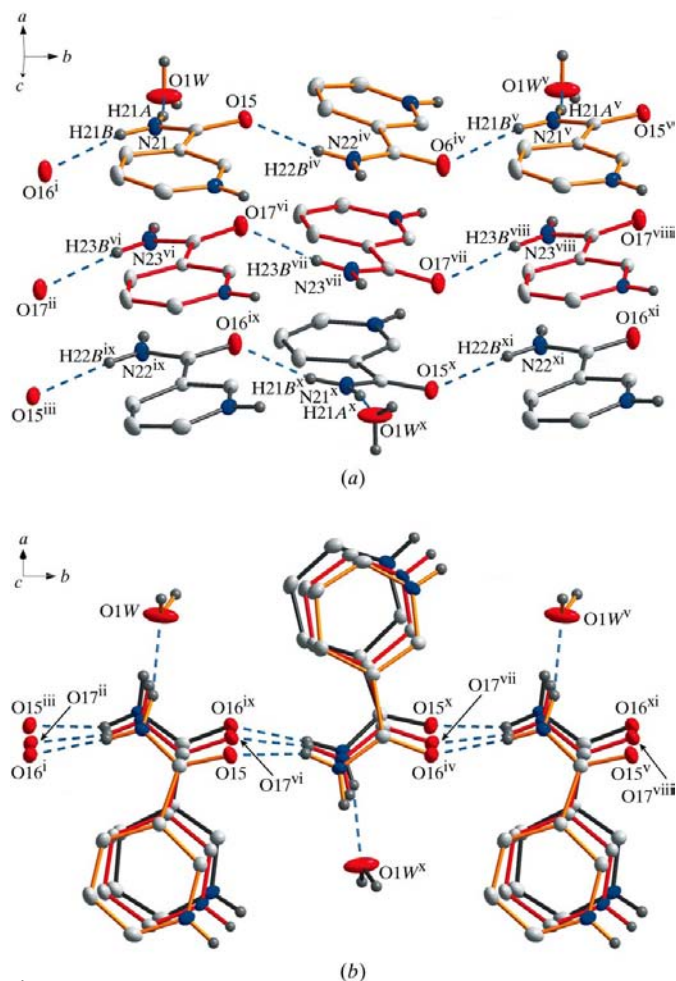


Figure 4
 (a) The formation of two types of 1*H*-nicotinamidium(1+) chains along the *b* axis and (b) π -stacking patterns of the 1*H*-nicotinamidium(1+) chains viewed towards the (203) plane. H atoms bonded to C atoms have been omitted for clarity. [Symmetry codes: (i) $-x, y, -z + \frac{1}{2}$; (ii) $x, -y + 1, z + \frac{1}{2}$; (iii) $-x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x, y + 1, -z + \frac{1}{2}$; (v) $x, y + 1, z$; (vi) $-x - \frac{1}{2}, -y + \frac{3}{2}, -z$; (vii) $x, -y + 2, z + \frac{1}{2}$; (viii) $-x - \frac{1}{2}, -y + \frac{5}{2}, -z$; (ix) $x - \frac{1}{2}, y + \frac{1}{2}, z$; (x) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (xi) $x - \frac{1}{2}, y + \frac{3}{2}, z$.]

The carboxamide groups of the cations are somewhat twisted from the pyridine ring planes n by 13.61 (14)° (for 1), 5.21 (11)° (for 2) and 6.84 (10)° (for 3), respectively, which is obvious for 1*H*-nicotinamidium(1+) compounds (Athimoolam & Natarajan, 2007*a,b*). In comparison with other 1*H*-nicotinamidium(1+) compounds from the Cambridge Structural Database (Version 5.27, update to September 2006; Allen, 2002), the R_{ct} and R_{clo} distances in (I) are the shortest among all nonparallel displaced structures (R_{ct} in the other nonparallel displaced structures lies between 3.8 and 4.9 Å, and R_{clo} lies between 3.3 and 3.6 Å) and the R_{ct} values are close to the interplanar distances of parallel-displaced π -stacked structures containing 1*H*-nicotinamidium(1+) cations, which lie between 3.1 and 3.5 Å (R_{ct} in the parallel-displaced structures lies between 3.4 and 3.9 Å).

Experimental

Orange crystals of $(C_6H_7N_2O)_6[V_{10}O_{28}] \cdot 2H_2O$ crystallized within 6–7 d from a V_2O_5 – H_2O_2 –nicotinamide– H_2O solution prepared as follows. For the preparation of solution A, V_2O_5 (0.181 g, 1 mmol) was dissolved in H_2O_2 (3 ml, $w = 0.3$) under continuous stirring in an ice bath. For the preparation of solution B, nicotinamide (0.122 g, 1 mmol) was dissolved in 5 ml of water. Solution B was added dropwise to A and the resulting solution was acidified with two drops of concentrated $HClO_4$. The obtained solution (pH 1.8) was allowed to crystallize in a refrigerator at 279 K. The crystals were dried in a desiccator over silica gel at the same temperature.

Crystal data

$(C_6H_7N_2O)_6[V_{10}O_{28}] \cdot 2H_2O$	$V = 5566$ (3) Å ³
$M_r = 1732.25$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 25.806$ (9) Å	$\mu = 1.71$ mm ⁻¹
$b = 9.5460$ (13) Å	$T = 120$ (2) K
$c = 23.577$ (10) Å	$0.50 \times 0.25 \times 0.15$ mm
$\beta = 106.60$ (4)°	

Data collection

Kuma KM-4 CCD diffractometer	34597 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2006)	5811 independent reflections
$T_{min} = 0.481$, $T_{max} = 0.783$	5173 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.012$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$	H atoms treated by a mixture of restrained and constrained refinement
$wR(F^2) = 0.062$	$\Delta\rho_{max} = 0.50$ e Å ⁻³
$S = 1.07$	$\Delta\rho_{min} = -0.51$ e Å ⁻³
5811 reflections	
431 parameters	
1 restraint	

H atoms of the cations were placed in geometrically idealized positions (C—H = 0.95 Å and N—H = 0.89 Å) and constrained to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C,N)$]. H atoms of the water molecules were located in a difference map and refined with O—H interatomic distances restrained to be equal, with the standard deviation set at 0.05 Å and with $U_{iso}(H)$ values of $1.5U_{eq}(O)$, which leads to reasonable geometry [O1W—H1 = O1W—H2 = 0.83 (3) Å and H1—O1W—H2 = 108 (3)°].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11...O12 ⁱ	0.88	1.78	2.6257 (19)	161
N21—H21A...O1W	0.88	2.04	2.909 (2)	168
N21—H21B...O16 ⁱⁱ	0.88	2.01	2.855 (2)	161
N12—H12...O5	0.88	1.81	2.679 (2)	167
N22—H22A...O10 ⁱⁱⁱ	0.88	2.07	2.929 (2)	163
N22—H22B...O15 ^{iv}	0.88	2.03	2.808 (2)	146
N13—H13...O9	0.88	1.67	2.5492 (18)	173
N23—H23A...O6 ^v	0.88	2.03	2.869 (2)	160
N23—H23B...O17 ^{vi}	0.88	2.05	2.878 (2)	156
O1W—H1...O4 ⁱⁱ	0.83 (3)	2.21 (3)	3.039 (2)	172 (3)
O1W—H2...O7	0.83 (3)	1.95 (3)	2.768 (2)	166 (3)
C21—H21...O16 ⁱⁱ	0.95	2.41	3.216 (2)	142
C31—H31...O11 ^{vii}	0.95	2.21	3.066 (2)	149
C51—H51...O10 ⁱ	0.95	2.45	3.265 (2)	144
C22—H22...O15 ^{iv}	0.95	2.72	3.617 (2)	158
C32—H32...O3 ^{viii}	0.95	2.63	3.222 (2)	121
C42—H42...O2 ^{ix}	0.95	2.64	3.218 (2)	119
C42—H42...O3 ^{viii}	0.95	2.53	3.176 (2)	125
C23—H23...O17 ^{vi}	0.95	2.55	3.422 (2)	153
C33—H33...O4 ^x	0.95	2.52	3.267 (2)	136
C33—H33...O14 ^x	0.95	2.39	3.269 (2)	154
C43—H43...O13 ^x	0.95	2.68	3.314 (2)	125
C53—H53...O6 ^{ix}	0.95	2.44	3.173 (2)	134

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

(Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*, *DIAMOND* and *publCIF* (Westrip, 2007).

This work was supported by the Ministry of Education of the Slovak Republic (VEGA grant No. 1/4462/07).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3044). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Athimoolam, S. & Natarajan, S. (2006). *Acta Cryst.* **C62**, o612–o617.
- Athimoolam, S. & Natarajan, S. (2007a). *Acta Cryst.* **E63**, o1811–o1813.
- Athimoolam, S. & Natarajan, S. (2007b). *Acta Cryst.* **E63**, o2430–o2432.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Brandenburg, K. (2007). *DIAMOND*. Release 3.1e. Crystal Impact GbR, Bonn, Germany.
- Brown, I. D. (1992). *Acta Cryst.* **B48**, 553–572.
- Crans, D. C. (1998). *Peroxo, Hydroxylamido, and acac Derived Vanadium Complexes: Chemistry, Biochemistry and Insulin-Mimetic Action of Selected Vanadium Compounds*. ACS Symposium Series 711, edited by Al. S. Tracey & D. C. Crans. Oxford University Press.
- Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* **B46**, 256–262.
- Mad'arová, M., Sivák, M., Kuchta, L., Marek, J. & Benko, J. (2004). *Dalton Trans.* pp. 3313–3320.
- Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
- Pacigová, S., Gyepes, R., Sivák, M. & Tatiersky, J. (2007). Unpublished results.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Sivák, M., Mad'arová, M., Marek, J. & Benko, J. (2000). *Chem. Pap. Chem. Zvesti.* **94**, 906–907.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Westrip, S. P. (2007). *publCIF*. In preparation.