

Bis(4-aminopyridinium) μ_6 -oxido-dodeca- μ_2 -oxido-hexaoxido[rhenium(VII)tetratungsten(VI)vanadium(V)]ate heptahydrate

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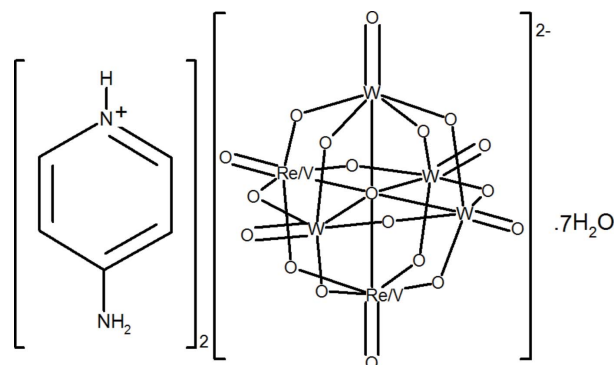
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.014$ Å; disorder in main residue; R factor = 0.069; wR factor = 0.192; data-to-parameter ratio = 31.8.

In the title organic–inorganic hybrid compound, $(\text{C}_5\text{H}_7\text{N}_2)_2[\text{ReVW}_4\text{O}_{19}]\cdot 7\text{H}_2\text{O}$, the Lindqvist-type polyoxido anion has crystallographically imposed $mm2$ symmetry and is built up by six MO_6 ($M = \text{W}, \text{V}, \text{Re}$) edge-sharing distorted octahedra. The Re and V atoms share the same crystallographic site in a 0.5:0.5 ratio. The 4-aminopyridinium cations lie on a mirror plane. Three of the four independent water O atoms in the asymmetric unit are located on a mirror plane whereas the remaining O atom has $mm2$ site symmetry. In the crystal, the cations, anions and water molecules are linked into a three-dimensional network through $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions.

Related literature

For applications of polyoxidometalates, see: Pope & Müller (1991, 1994). For bond-valence calculations, see: Brown & Altermatt (1985). For related structures, see: Lindqvist (1953); Bannani *et al.* (2007); Besecker *et al.* (1982); Wang *et al.* (2011); Wang *et al.* (2006); Meng *et al.* (2006). For NMR investigations of related compounds, see: Chen *et al.* (2004); Domaille (1984); Fedotov & Maksimovskaya (2006); Leparulo-Loftus & Pope (1987).



Experimental

Crystal data

$(\text{C}_5\text{H}_7\text{N}_2)_2[\text{ReVW}_4\text{O}_{19}]\cdot 7\text{H}_2\text{O}$
 $M_r = 1592.90$
Orthorhombic, $Pnma$
 $a = 17.837$ (2) Å
 $b = 9.163$ (4) Å
 $c = 10.552$ (3) Å
 $V = 1724.5$ (9) Å³

$Z = 2$
Ag $K\alpha$ radiation
 $\lambda = 0.56087$ Å
 $\mu = 9.22$ mm⁻¹
 $T = 298$ K
 $0.43 \times 0.27 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: multi-scan (Blessing, 1995)
 $T_{\min} = 0.100$, $T_{\max} = 0.306$
6539 measured reflections

4385 independent reflections
2083 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.052$
2 standard reflections every 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.069$
 $wR(F^2) = 0.192$
 $S = 1.03$
4385 reflections
138 parameters

17 restraints
H-atom parameters constrained
 $\Delta\rho_{\max} = 2.94$ e Å⁻³
 $\Delta\rho_{\min} = -2.83$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N1}-\text{H1A}\cdots\text{O1W}$	0.86	2.40	3.078 (14)	136
$\text{N1}-\text{H1A}\cdots\text{O1E}$	0.86	2.58	3.184 (14)	129
$\text{N2}-\text{H2A}\cdots\text{O3}^i$	0.86	2.39	3.181 (12)	152
$\text{O1W}-\text{H1W1}\cdots\text{O1E}$	0.81	2.50	3.188 (18)	144
$\text{O2W}-\text{H1W2}\cdots\text{O3E}^{ii}$	0.85	2.10	2.836 (18)	144
$\text{O4W}-\text{H1W4}\cdots\text{O2W}$	0.85	1.87	2.40 (7)	119
$\text{O4W}-\text{H2W4}\cdots\text{O4W}^{iii}$	0.85	2.31	2.65 (15)	106

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ5088).

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supporting information

Acta Cryst. (2013). E69, m661–m662 [doi:10.1107/S1600536813030687]

Bis(4-aminopyridinium) μ_6 -oxido-dodeca- μ_2 -oxido-hexaoxido[rhenium(VII)tetratungsten(VI)vanadium(V)]ate heptahydrate

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S1. Comment

Polyoxidometalate are of great interest in different fields such as medicine, biology, catalysis, material sciences, chemical analysis (Pope & Müller, 1991; Pope & Müller, 1994). Among this large class of compounds, Lindqvist anions $[M_6O_{19}]^{n-}$ have been intensively studied since the early characterization of $Na_7HNb_6O_{19} \cdot 15H_2O$ (Lindqvist, 1953). However, studies of substituted hexatungstate $[M_nW_{6-n}O_{19}]^{(2+n)-}$ are relatively scarce. Up to now, few compounds are cited in the literature, such as $[(n-C_4H_9)_4N]_3MW_5O_{19}$ ($M = Nb, V$) (Bannani *et al.*, 2007), $\{[(C_7H_8)Rh]_5(Nb_2W_4O_{19})_2\}[(n-C_4H_9)N]_3$ (Besecker *et al.*, 1982), $[Cu(phen)(H_2O)_3]_2[V_2W_4O_{19}]$ and $[Cu(bpy)(H_2O)]_2[V_2W_4O_{19}] \cdot 4H_2O$ (Wang *et al.*, 2011) and $[Ni(bpy)_3]_2[W_4V_2O_{19}]$ (Wang *et al.*, 2006), whereas substituted Lindqvist-type polyoxotungstates based on $[M_nM'_pW_{6-n-p}O_{19}]^{(2+n+p)-}$ anions have not been reported hitherto. On the best of our knowledge the reported title salt, $(C_5H_7N_2)_2[ReVW_4O_{19}] \cdot 7H_2O$ (I), is the first example of this kind of substituted Lindqvist structure.

The asymmetric unit of (I) contains 1.75 water molecules, one half of a 4-aminopyridinium cation and one fourth of a $[ReVW_4O_{19}]^{2-}$ polyanion, in which Re and V metals share the same site in a 0.5:0.5 ratio. All constituents are completed by imposed crystallographic symmetries (Fig. 1). Three out of the four independent water O atoms in the asymmetric unit have mirror symmetry, while a fourth O atom has *mm2* site symmetry. It is to be mentioned that the O3W and O4W oxygen atoms associated to water molecules have relatively high thermal disorder and could not be anisotropically refined. In the crystal packing, cations and solvent water molecules assemble the discrete $[ReVW_4O_{19}]^{2-}$ anion complexes through $OW \cdots H \cdots O$ and $N \cdots H \cdots O$ hydrogen bonding interactions (Table 1) to form a supramolecular three-dimensional network as shown in Figure 2. The structure of the $[ReVW_4O_{19}]^{2-}$ polyanion is basically the same as that of Lindqvist-type anion (Lindqvist, 1953). It is built up by six MO_6 ($M = W, V, Re$) edge-sharing distorted octahedra and exhibits the characteristic $M-O$ bond-length range, with the shortest bonds being the $M-O$ terminal bonds and the longest being those involving the central O atom. The geometry features of the polyanion are in agreement with those of the Lindqvist-type polyoxidotungstate reported by Meng *et al.* (2006). The valence bond calculation (Brown & Altermatt, 1985) gives effective bond valences of 4.9847 for the V cation, 7.1447 for the Re cation and 6.0697 and 6.1369 for the two independent W cations. These values are consistent with the oxidation states V(V), Re(VII) and W(VI). In an attempt to shed more light on the structure of the hexametalate anion, we contemplated ^{51}V and ^{183}W NMR studies on the title complex. In fact, regarding the $[M_6O_{19}]^{n-}$ complex structure, the vanadium and rhenium heteroatoms may occupy *cis* or *trans* positions in the octahedral structure. The ^{183}W NMR study shows two signals with relative intensity of *ca* 2:2, which can be assigned to the two equatorial (W_{eq}) and the two axial (W_{ax}) tungsten atoms respectively. On the other hand, the ^{51}V NMR spectrum presents one signal at 508.7 ppm. These results are consistent with the C_{2v} symmetry of the disubstituted hexametalate structure with preferential *cis* configuration as reported in literature (Chen *et al.*, 2004; Domaille, 1984; Fedotov & Maksimovskaya, 2006; Leparulo-Loftus & Pope, 1987). All these observations corroborate

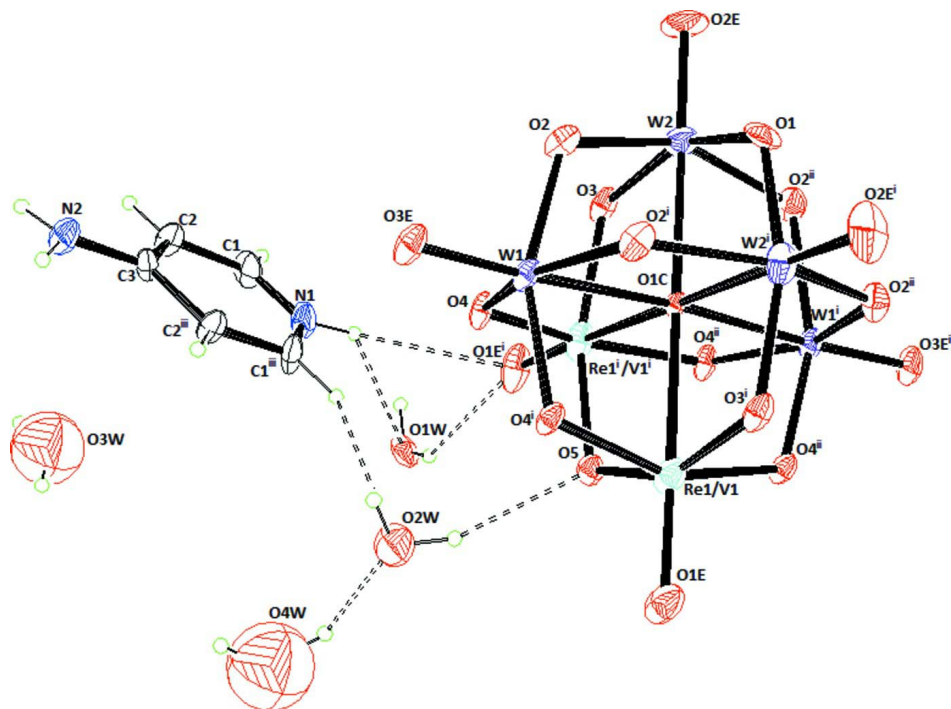
the structural results in suggesting that both rhenium and vanadium atoms (with 0.5/0.5 occupation) occupy preferentially the same site thus leading to a *cis*-[X₂W₄O₁₉]²⁻ (X = Re_{0.5}V_{0.5}) anion configuration.

S2. Experimental

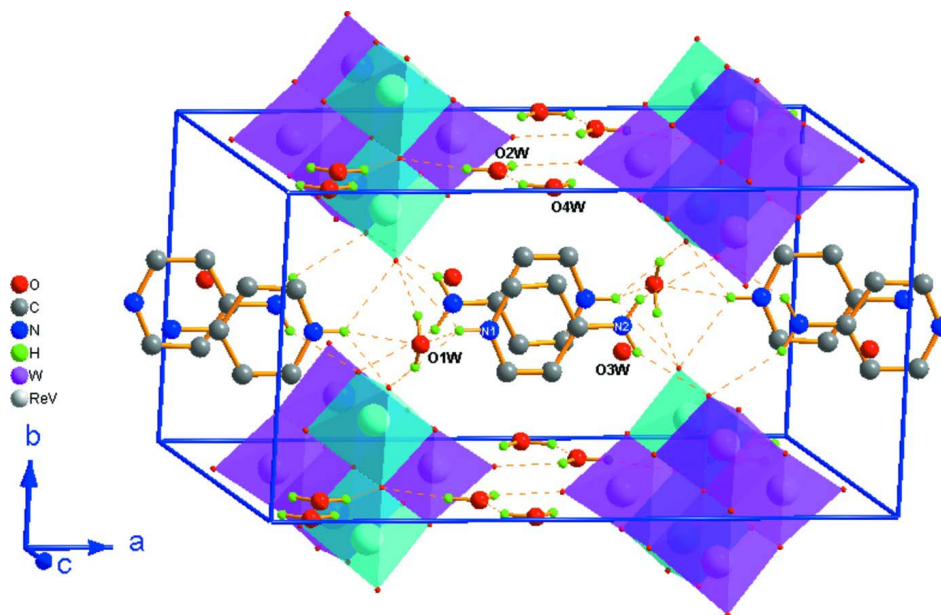
The title compound was prepared by the reaction of vanadium(V) oxide (0.18 g, 1 mmol), rhenium(VII) oxide (0.48 g, 1 mmol), Na₂WO₄·2H₂O (2 g, 6 mmol) and 4-aminopyridine (0.19 g, 2 mmol) dissolved in 50 ml of distilled water and then stirred for 1 h. Yellowish single crystals were obtained after two weeks by slow evaporation at room temperature (yield: 59% based on W). Anal. Calc. for C₁₀H₂₈N₄O₂₆ReVW₄: H 1.76, C 7.53, N 3.52, Re 11.69, V 3.20, W 46.16%; Found: H 1.81, C 7.57, N 3.50, Re 11.71, V 3.23, W 46.14%. ¹⁸³W NMR δ (p.p.m.): 86.5, 65.4; ⁵¹V NMR δ (p.p.m.): 508.7.

S3. Refinement

An initial attempt to refine the crystal structure with the Re atom disordered over three independent sites resulted in rather high atomic displacement parameters for the heaviest atoms (Re1, W1 and W2) as a possible consequence of the large number of restraints required by this model. The refinement of a model implying the Re atom sharing only the site occupied by the vanadium atom with an occupancy factor of 0.5 rapidly converged to a plausible result with low residuals. These observations are also supported by NMR study as detailed in Comment section. In spite the crystal selected for the X-ray analysis appeared to be of good quality, its diffraction ability was very poor. This may account for the rather high residual peaks, high R values and unresolved disorder affecting part of the water molecules. In fact, anisotropic refinement of the O atoms associated to water molecules resulted in unreasonable U_{ij} values for atoms O3W and O4W, which were therefore isotropically refined. The water H atoms could not be located and were placed geometrically sensible positions using restraints [O—H = 0.85 (1) Å, H···H = 1.44 (2) Å and $U_{iso}(H) = 1.5U_{eq}(O)$]. H atoms attached to C and N atoms were fixed geometrically and treated as riding, with C—H = 0.93 Å and N—H = 0.86 Å with $U_{iso}(H) = 1.2U_{eq}(C, N)$. In the final difference Fourier map, the highest residual electron density peak and the deepest hole are located 0.78 and 0.64 Å respectively from W2.


Figure 1

A view of the title compound with displacement ellipsoids drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Symmetry codes: (i) $1/2 + x, -y, 1 - z$; (ii) $1/2 + x, y, 1 - z$; (iii) $x, 1 - y, z$.


Figure 2

Packing diagram of the title compound. Hydrogen bonds are shown as dashed lines. Hydrogen atoms not involved in hydrogen bonding are omitted.

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Crystal data

(C₅H₇N₂)₂[ReVW₄O₁₉]·7H₂O

$M_r = 1592.90$

Orthorhombic, *Pmma*

Hall symbol: -P 2a 2a

$a = 17.837$ (2) Å

$b = 9.163$ (4) Å

$c = 10.552$ (3) Å

$V = 1724.5$ (9) Å³

$Z = 2$

$F(000) = 1436$

$D_x = 3.068$ Mg m⁻³

Ag $K\alpha$ radiation, $\lambda = 0.56087$ Å

Cell parameters from 25 reflections

$\theta = 9\text{--}11^\circ$

$\mu = 9.22$ mm⁻¹

$T = 298$ K

Prism, yellow

$0.43 \times 0.27 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

non-profiled ω scans

Absorption correction: multi-scan

(Blessing, 1995)

$T_{\min} = 0.100$, $T_{\max} = 0.306$

6539 measured reflections

4385 independent reflections

2083 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.052$

$\theta_{\max} = 28.0^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -29 \rightarrow 2$

$k = -2 \rightarrow 15$

$l = -17 \rightarrow 2$

2 standard reflections every 120 min

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.069$

$wR(F^2) = 0.192$

$S = 1.03$

4385 reflections

138 parameters

17 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 4.9537P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.003$

$\Delta\rho_{\max} = 2.94$ e Å⁻³

$\Delta\rho_{\min} = -2.83$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
W1	0.37770 (3)	0.0000	0.34550 (7)	0.03479 (18)	
W2	0.2500	0.17748 (8)	0.18441 (8)	0.0497 (2)	
Re1	0.2500	0.18032 (13)	0.49071 (13)	0.0505 (3)	0.50

V1	0.2500	0.18032 (13)	0.49071 (13)	0.0505 (3)	0.50
O1C	0.2500	0.0000	0.3367 (12)	0.023 (2)	
O1E	0.2500	0.3071 (16)	0.6049 (16)	0.068 (4)	
O2E	0.2500	0.3115 (18)	0.0720 (17)	0.081 (5)	
O3E	0.4740 (6)	0.0000	0.3427 (13)	0.050 (3)	
O1	0.2500	0.0000	0.0922 (13)	0.048 (4)	
O2	0.3545 (4)	0.1420 (9)	0.2154 (9)	0.0466 (19)	
O3	0.2500	0.2888 (11)	0.3345 (12)	0.042 (3)	
O4	0.3529 (3)	0.1446 (8)	0.4650 (8)	0.0375 (16)	
O5	0.2500	0.0000	0.5902 (15)	0.039 (3)	
N1	0.3903 (7)	0.5000	0.6867 (14)	0.057 (4)	
H1A	0.3422	0.5000	0.6901	0.068*	
N2	0.6091 (7)	0.5000	0.6435 (17)	0.057 (4)	
H2A	0.6343	0.4198	0.649	0.069*	
C1	0.4219 (6)	0.6284 (14)	0.6845 (14)	0.056 (3)	
H1	0.3939	0.7134	0.6938	0.067*	
C2	0.4963 (6)	0.6327 (12)	0.6681 (13)	0.043 (3)	
H2	0.5214	0.7216	0.6642	0.052*	
C3	0.5363 (7)	0.5000	0.6570 (16)	0.038 (3)	
O1W	0.2500	0.5000	0.8564 (14)	0.063 (6)	
H1W1	0.2500	0.4226	0.8198	0.095*	
O2W	0.3772 (8)	0.0000	0.7518 (15)	0.079 (5)	
H1W2	0.410	0.0000	0.694	0.119*	
H2W2	0.332	0.0000	0.727	0.119*	
O3W	0.553 (3)	0.5000	0.960 (5)	0.27 (3)*	
H1W3	0.5644	0.5876	0.9741	0.402*	
O4W	0.429 (4)	0.0000	0.962 (6)	0.34 (3)*	
H1W4	0.386	0.0000	0.928	0.510*	
H2W4	0.466	0.0000	0.910	0.510*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.0230 (2)	0.0289 (3)	0.0525 (4)	0.000	0.0066 (2)	0.000
W2	0.0455 (4)	0.0462 (4)	0.0574 (5)	0.000	0.000	0.0195 (3)
Re1	0.0337 (5)	0.0436 (6)	0.0743 (8)	0.000	0.000	-0.0133 (5)
V1	0.0337 (5)	0.0436 (6)	0.0743 (8)	0.000	0.000	-0.0133 (5)
O1C	0.019 (4)	0.017 (5)	0.032 (6)	0.000	0.000	0.000
O1E	0.035 (5)	0.062 (9)	0.108 (12)	0.000	0.000	-0.029 (9)
O2E	0.083 (11)	0.078 (11)	0.082 (10)	0.000	0.000	0.065 (9)
O3E	0.023 (4)	0.046 (6)	0.081 (9)	0.000	0.012 (5)	0.000
O1	0.066 (10)	0.061 (11)	0.016 (6)	0.000	0.000	0.000
O2	0.040 (4)	0.037 (4)	0.063 (5)	0.000 (4)	0.013 (4)	0.006 (4)
O3	0.030 (4)	0.021 (4)	0.076 (8)	0.000	0.000	0.000 (5)
O4	0.019 (2)	0.030 (3)	0.063 (5)	0.000 (3)	0.001 (3)	-0.012 (3)
O5	0.027 (6)	0.047 (9)	0.043 (8)	0.000	0.000	0.000
N1	0.028 (6)	0.076 (12)	0.066 (11)	0.000	-0.006 (6)	0.000
N2	0.029 (5)	0.077 (12)	0.066 (10)	0.000	0.013 (6)	0.000

C1	0.033 (5)	0.053 (7)	0.080 (10)	0.017 (5)	-0.014 (5)	0.006 (7)
C2	0.037 (4)	0.023 (4)	0.069 (8)	0.001 (4)	0.003 (5)	-0.001 (5)
C3	0.029 (5)	0.029 (6)	0.056 (9)	0.000	-0.015 (6)	0.000
O1W	0.034 (7)	0.13 (2)	0.027 (8)	0.000	0.000	0.000
O2W	0.057 (8)	0.109 (14)	0.071 (11)	0.000	0.007 (7)	0.000

Geometric parameters (Å, °)

O1C—W1	2.2796 (8)	C2—C1	1.339 (15)
O1C—W1 ⁱ	2.2796 (8)	C2—H2	0.9300
O1C—W2 ⁱ	2.286 (9)	C1—N1	1.305 (13)
O1C—W2	2.286 (9)	C1—H1	0.9300
O1C—Re1	2.318 (9)	N1—C1 ⁱⁱ	1.305 (13)
O1C—V1 ⁱ	2.318 (9)	N1—H1A	0.8600
O1C—Re1 ⁱ	2.318 (9)	O2E—W2	1.707 (12)
O3—W2	1.883 (12)	W1—O4 ⁱⁱⁱ	1.882 (7)
O3—Re1	1.925 (12)	W1—O2 ⁱⁱⁱ	1.936 (9)
O1E—Re1	1.674 (14)	W1—Re1 ⁱ	3.2040 (11)
O4—W1	1.882 (7)	W1—Re1	3.2040 (11)
O4—Re1	1.885 (6)	W2—O2 ^{iv}	1.921 (8)
O5—V1 ⁱ	1.958 (9)	W2—Re1	3.2322 (18)
O5—Re1 ⁱ	1.958 (9)	Re1—O4 ^{iv}	1.885 (6)
O5—Re1	1.958 (9)	Re1—W1 ⁱ	3.2040 (11)
O3E—W1	1.718 (10)	N2—H2A	0.8600
O2—W2	1.921 (8)	O1W—H1W1	0.81
O2—W1	1.936 (9)	O2W—H1W2	0.85
O1—W2	1.895 (7)	O2W—H2W2	0.85
O1—W2 ⁱ	1.895 (7)	O3W—H1W3	0.84
C3—N2	1.307 (17)	O4W—H1W4	0.85
C3—C2 ⁱⁱ	1.414 (12)	O4W—H2W4	0.85
C3—C2	1.414 (12)		
W1—O1C—W1 ⁱ	175.3 (6)	O2—W1—Re1	80.8 (2)
W1—O1C—W2 ⁱ	91.6 (2)	O1C—W1—Re1	46.3 (2)
W1 ⁱ —O1C—W2 ⁱ	91.6 (2)	Re1 ⁱ —W1—Re1	62.09 (5)
W1—O1C—W2	91.6 (2)	O2E—W2—O3	101.2 (8)
W1 ⁱ —O1C—W2	91.6 (2)	O2E—W2—O1	105.1 (8)
W2 ⁱ —O1C—W2	90.7 (4)	O3—W2—O1	153.7 (5)
W1—O1C—Re1	88.4 (2)	O2E—W2—O2	103.9 (3)
W1 ⁱ —O1C—Re1	88.4 (2)	O3—W2—O2	87.1 (3)
W2 ⁱ —O1C—Re1	179.9 (4)	O1—W2—O2	86.7 (3)
W2—O1C—Re1	89.19 (5)	O2E—W2—O2 ^{iv}	103.9 (3)
W1—O1C—V1 ⁱ	88.4 (2)	O3—W2—O2 ^{iv}	87.1 (3)
W1 ⁱ —O1C—V1 ⁱ	88.4 (2)	O1—W2—O2 ^{iv}	86.7 (3)
W2 ⁱ —O1C—V1 ⁱ	89.19 (5)	O2—W2—O2 ^{iv}	152.2 (5)
W2—O1C—V1 ⁱ	179.9 (4)	O2E—W2—O1C	179.4 (7)
Re1—O1C—V1 ⁱ	90.9 (4)	O3—W2—O1C	78.1 (4)
W1—O1C—Re1 ⁱ	88.4 (2)	O1—W2—O1C	75.6 (4)

W1 ⁱ —O1C—Re1 ⁱ	88.4 (2)	O2—W2—O1C	76.1 (3)
W2 ⁱ —O1C—Re1 ⁱ	89.19 (5)	O2 ^{iv} —W2—O1C	76.1 (3)
W2—O1C—Re1 ⁱ	179.9 (4)	O2E—W2—Re1	133.6 (7)
Re1—O1C—Re1 ⁱ	90.9 (4)	O3—W2—Re1	32.3 (3)
W2—O3—Re1	116.1 (5)	O1—W2—Re1	121.4 (4)
W1—O4—Re1	116.6 (4)	O2—W2—Re1	80.3 (3)
V1 ⁱ —O5—Re1	115.1 (8)	O2 ^{iv} —W2—Re1	80.3 (3)
Re1 ⁱ —O5—Re1	115.1 (8)	O1C—W2—Re1	45.8 (2)
W2—O2—W1	116.2 (4)	O1E—Re1—O4	102.9 (2)
W2—O1—W2 ⁱ	118.2 (7)	O1E—Re1—O4 ^{iv}	102.9 (2)
N2—C3—C2 ⁱⁱ	120.6 (6)	O4—Re1—O4 ^{iv}	154.0 (4)
N2—C3—C2	120.6 (6)	O1E—Re1—O3	105.0 (7)
C2 ⁱⁱ —C3—C2	118.6 (12)	O4—Re1—O3	88.1 (3)
C1—C2—C3	119.0 (11)	O4 ^{iv} —Re1—O3	88.1 (3)
C1—C2—H2	120.5	O1E—Re1—O5	101.5 (7)
C3—C2—H2	120.5	O4—Re1—O5	86.0 (3)
N1—C1—C2	117.1 (12)	O4 ^{iv} —Re1—O5	86.0 (3)
N1—C1—H1	121.4	O3—Re1—O5	153.5 (5)
C2—C1—H1	121.4	O1E—Re1—O1C	178.5 (7)
C1 ⁱⁱ —N1—C1	128.8 (14)	O4—Re1—O1C	77.0 (2)
C1 ⁱⁱ —N1—H1A	115.6	O4 ^{iv} —Re1—O1C	77.0 (2)
C1—N1—H1A	115.6	O3—Re1—O1C	76.6 (4)
O3E—W1—O4	104.2 (4)	O5—Re1—O1C	77.0 (4)
O3E—W1—O4 ⁱⁱⁱ	104.2 (4)	O1E—Re1—W1 ⁱ	134.60 (4)
O4—W1—O4 ⁱⁱⁱ	89.5 (5)	O4—Re1—W1 ⁱ	122.3 (2)
O3E—W1—O2 ⁱⁱⁱ	101.6 (4)	O4 ^{iv} —Re1—W1 ⁱ	31.7 (2)
O4—W1—O2 ⁱⁱⁱ	154.0 (3)	O3—Re1—W1 ⁱ	81.8 (2)
O4 ⁱⁱⁱ —W1—O2 ⁱⁱⁱ	87.3 (4)	O5—Re1—W1 ⁱ	79.7 (3)
O3E—W1—O2	101.6 (4)	O1C—Re1—W1 ⁱ	45.33 (2)
O4—W1—O2	87.3 (4)	O1E—Re1—W1	134.60 (4)
O4 ⁱⁱⁱ —W1—O2	154.0 (3)	O4—Re1—W1	31.7 (2)
O2 ⁱⁱⁱ —W1—O2	84.4 (5)	O4 ^{iv} —Re1—W1	122.3 (2)
O3E—W1—O1C	176.7 (6)	O3—Re1—W1	81.8 (2)
O4—W1—O1C	78.1 (3)	O5—Re1—W1	79.7 (3)
O4 ⁱⁱⁱ —W1—O1C	78.1 (3)	O1C—Re1—W1	45.33 (2)
O2 ⁱⁱⁱ —W1—O1C	76.0 (3)	W1 ⁱ —Re1—W1	90.62 (4)
O2—W1—O1C	76.0 (3)	O1E—Re1—W2	136.5 (6)
O3E—W1—Re1 ⁱ	136.0 (3)	O4—Re1—W2	81.7 (3)
O4—W1—Re1 ⁱ	82.9 (2)	O4 ^{iv} —Re1—W2	81.7 (3)
O4 ⁱⁱⁱ —W1—Re1 ⁱ	31.75 (19)	O3—Re1—W2	31.5 (3)
O2 ⁱⁱⁱ —W1—Re1 ⁱ	80.8 (2)	O5—Re1—W2	122.0 (4)
O2—W1—Re1 ⁱ	122.3 (2)	O1C—Re1—W2	45.0 (2)
O1C—W1—Re1 ⁱ	46.3 (2)	W1 ⁱ —Re1—W2	61.16 (3)
O3E—W1—Re1	136.0 (3)	W1—Re1—W2	61.16 (3)
O4—W1—Re1	31.75 (19)	C3—N2—H2A	121
O4 ⁱⁱⁱ —W1—Re1	82.9 (2)	H1W2—O2W—H2W2	116
O2 ⁱⁱⁱ —W1—Re1	122.3 (2)	H1W4—O4W—H2W4	116

N2—C3—C2—C1	-178.7 (16)	W1 ⁱ —O1C—Re1—W2	-91.7 (2)
C2 ⁱⁱ —C3—C2—C1	-2 (3)	O3E—W1—Re1—O1E	-5.6 (10)
C3—C2—C1—N1	-1 (2)	O4—W1—Re1—O1E	-3.2 (10)
C2—C1—N1—C1 ⁱⁱ	6 (3)	O4 ⁱⁱⁱ —W1—Re1—O1E	97.6 (9)
Re1—O4—W1—O3E	178.3 (5)	O2—W1—Re1—O1E	-102.8 (9)
Re1—O4—W1—O4 ⁱⁱⁱ	-77.1 (5)	O1C—W1—Re1—O1E	177.8 (9)
Re1—O4—W1—O2 ⁱⁱⁱ	5.6 (11)	Re1 ⁱ —W1—Re1—O1E	122.9 (9)
Re1—O4—W1—O2	77.0 (5)	O3E—W1—Re1—O4	-2.4 (7)
Re1—O4—W1—O1C	0.7 (4)	O4 ⁱⁱⁱ —W1—Re1—O4	100.7 (7)
Re1—O4—W1—Re1 ⁱ	-46.0 (4)	O2 ⁱⁱⁱ —W1—Re1—O4	-177.1 (6)
W2—O2—W1—O3E	179.7 (5)	O2—W1—Re1—O4	-99.7 (6)
W2—O2—W1—O4	-76.3 (5)	O1C—W1—Re1—O4	-179.0 (6)
W2—O2—W1—O4 ⁱⁱⁱ	6.9 (12)	Re1 ⁱ —W1—Re1—O4	126.1 (5)
W2—O2—W1—O2 ⁱⁱⁱ	78.9 (5)	O3E—W1—Re1—O4 ^{iv}	179.8 (6)
W2—O2—W1—O1C	2.0 (4)	O4—W1—Re1—O4 ^{iv}	-177.8 (8)
W2—O2—W1—Re1 ⁱ	3.5 (6)	O4 ⁱⁱⁱ —W1—Re1—O4 ^{iv}	-77.05 (19)
W2—O2—W1—Re1	-45.1 (4)	O2 ⁱⁱⁱ —W1—Re1—O4 ^{iv}	5.1 (4)
W2 ⁱ —O1C—W1—O4	179.3 (4)	O2—W1—Re1—O4 ^{iv}	82.5 (4)
W2—O1C—W1—O4	88.6 (3)	O1C—W1—Re1—O4 ^{iv}	3.2 (4)
Re1—O1C—W1—O4	-0.5 (3)	Re1 ⁱ —W1—Re1—O4 ^{iv}	-51.7 (3)
V1 ⁱ —O1C—W1—O4	-91.5 (4)	O3E—W1—Re1—O3	97.4 (5)
Re1 ⁱ —O1C—W1—O4	-91.5 (4)	O4—W1—Re1—O3	99.8 (5)
W2 ⁱ —O1C—W1—O4 ⁱⁱⁱ	-88.6 (3)	O4 ⁱⁱⁱ —W1—Re1—O3	-159.5 (3)
W2—O1C—W1—O4 ⁱⁱⁱ	-179.3 (4)	O2 ⁱⁱⁱ —W1—Re1—O3	-77.3 (4)
Re1—O1C—W1—O4 ⁱⁱⁱ	91.5 (4)	O2—W1—Re1—O3	0.1 (3)
V1 ⁱ —O1C—W1—O4 ⁱⁱⁱ	0.5 (3)	O1C—W1—Re1—O3	-79.2 (4)
Re1 ⁱ —O1C—W1—O4 ⁱⁱⁱ	0.5 (3)	Re1 ⁱ —W1—Re1—O3	-134.1 (2)
W2 ⁱ —O1C—W1—O2 ⁱⁱⁱ	1.5 (3)	O3E—W1—Re1—O5	-101.6 (6)
W2—O1C—W1—O2 ⁱⁱⁱ	-89.2 (4)	O4—W1—Re1—O5	-99.2 (6)
Re1—O1C—W1—O2 ⁱⁱⁱ	-178.3 (4)	O4 ⁱⁱⁱ —W1—Re1—O5	1.5 (4)
V1 ⁱ —O1C—W1—O2 ⁱⁱⁱ	90.7 (3)	O2 ⁱⁱⁱ —W1—Re1—O5	83.7 (4)
Re1 ⁱ —O1C—W1—O2 ⁱⁱⁱ	90.7 (3)	O2—W1—Re1—O5	161.1 (4)
W2 ⁱ —O1C—W1—O2	89.2 (4)	O1C—W1—Re1—O5	81.8 (4)
W2—O1C—W1—O2	-1.5 (3)	Re1 ⁱ —W1—Re1—O5	26.9 (3)
Re1—O1C—W1—O2	-90.7 (3)	O3E—W1—Re1—O1C	176.6 (6)
V1 ⁱ —O1C—W1—O2	178.3 (4)	O4—W1—Re1—O1C	179.0 (6)
Re1 ⁱ —O1C—W1—O2	178.3 (4)	O4 ⁱⁱⁱ —W1—Re1—O1C	-80.3 (4)
W2 ⁱ —O1C—W1—Re1 ⁱ	-89.14 (5)	O2 ⁱⁱⁱ —W1—Re1—O1C	1.9 (4)
W2—O1C—W1—Re1 ⁱ	-179.9 (4)	O2—W1—Re1—O1C	79.3 (4)
Re1—O1C—W1—Re1 ⁱ	91.0 (4)	Re1 ⁱ —W1—Re1—O1C	-54.9 (3)
V1 ⁱ —O1C—W1—Re1 ⁱ	0.0	O3E—W1—Re1—W1 ⁱ	179.0 (5)
W2 ⁱ —O1C—W1—Re1	179.9 (4)	O4—W1—Re1—W1 ⁱ	-178.6 (5)
W2—O1C—W1—Re1	89.14 (5)	O4 ⁱⁱⁱ —W1—Re1—W1 ⁱ	-77.9 (2)
V1 ⁱ —O1C—W1—Re1	-91.0 (4)	O2 ⁱⁱⁱ —W1—Re1—W1 ⁱ	4.3 (3)
Re1 ⁱ —O1C—W1—Re1	-91.0 (4)	O2—W1—Re1—W1 ⁱ	81.7 (3)
Re1—O3—W2—O2	-76.4 (2)	O1C—W1—Re1—W1 ⁱ	2.4 (3)
Re1—O3—W2—O2 ^{iv}	76.4 (2)	Re1 ⁱ —W1—Re1—W1 ⁱ	-52.53 (4)
W2 ⁱ —O1—W2—O2	76.5 (3)	O3E—W1—Re1—W2	122.8 (5)

W2 ⁱ —O1—W2—O2 ^{iv}	-76.5 (3)	O4—W1—Re1—W2	125.2 (5)
W1—O2—W2—O2E	177.3 (8)	O4 ⁱⁱⁱ —W1—Re1—W2	-134.1 (2)
W1—O2—W2—O3	76.5 (6)	O2 ⁱⁱⁱ —W1—Re1—W2	-51.9 (3)
W1—O2—W2—O1	-78.0 (6)	O2—W1—Re1—W2	25.5 (3)
W1—O2—W2—O2 ^{iv}	-1.5 (16)	O1C—W1—Re1—W2	-53.8 (3)
W1—O2—W2—O1C	-2.0 (4)	Re1 ⁱ —W1—Re1—W2	-108.71 (2)
W1—O2—W2—Re1	44.6 (4)	O2—W2—Re1—O1E	100.0 (3)
W1—O1C—W2—O2	1.5 (3)	O2 ^{iv} —W2—Re1—O1E	-100.0 (3)
W1 ⁱ —O1C—W2—O2	178.2 (4)	O2E—W2—Re1—O4	-100.0 (2)
Re1—O1C—W2—O2	89.9 (3)	O3—W2—Re1—O4	-100.0 (2)
W1—O1C—W2—O2 ^{iv}	-178.2 (4)	O1—W2—Re1—O4	80.0 (2)
W1 ⁱ —O1C—W2—O2 ^{iv}	-1.5 (3)	O2—W2—Re1—O4	-0.1 (3)
Re1—O1C—W2—O2 ^{iv}	-89.9 (3)	O2 ^{iv} —W2—Re1—O4	160.0 (3)
W1—O4—Re1—O1E	177.7 (7)	O1C—W2—Re1—O4	80.0 (2)
W1—O4—Re1—O4 ^{iv}	4.3 (15)	O2E—W2—Re1—O4 ^{iv}	100.0 (2)
W1—O4—Re1—O3	-77.4 (5)	O3—W2—Re1—O4 ^{iv}	100.0 (2)
W1—O4—Re1—O5	76.8 (6)	O1—W2—Re1—O4 ^{iv}	-80.0 (2)
W1—O4—Re1—O1C	-0.7 (4)	O2—W2—Re1—O4 ^{iv}	-160.0 (3)
W1—O4—Re1—W1 ⁱ	1.6 (6)	O2 ^{iv} —W2—Re1—O4 ^{iv}	0.1 (3)
W1—O4—Re1—W2	-46.3 (4)	O1C—W2—Re1—O4 ^{iv}	-80.0 (2)
W2—O3—Re1—O4	77.1 (2)	O2E—W2—Re1—O3	0.000 (2)
W2—O3—Re1—O4 ^{iv}	-77.1 (2)	O1—W2—Re1—O3	180.000 (2)
W2—O3—Re1—W1 ⁱ	-45.92 (4)	O2—W2—Re1—O3	100.0 (3)
W2—O3—Re1—W1	45.92 (4)	O2 ^{iv} —W2—Re1—O3	-100.0 (3)
V1 ⁱ —O5—Re1—O4	-77.6 (2)	O1C—W2—Re1—O3	180.000 (2)
Re1 ⁱ —O5—Re1—O4	-77.6 (2)	O2E—W2—Re1—O5	180.000 (1)
V1 ⁱ —O5—Re1—O4 ^{iv}	77.6 (2)	O3—W2—Re1—O5	180.000 (1)
Re1 ⁱ —O5—Re1—O4 ^{iv}	77.6 (2)	O1—W2—Re1—O5	0.000 (1)
V1 ⁱ —O5—Re1—W1 ⁱ	46.26 (5)	O2—W2—Re1—O5	-80.0 (3)
Re1 ⁱ —O5—Re1—W1 ⁱ	46.26 (5)	O2 ^{iv} —W2—Re1—O5	80.0 (3)
V1 ⁱ —O5—Re1—W1	-46.26 (5)	O1C—W2—Re1—O5	0.000 (1)
Re1 ⁱ —O5—Re1—W1	-46.26 (5)	O2E—W2—Re1—O1C	180.0
W1—O1C—Re1—O4	0.5 (3)	O3—W2—Re1—O1C	180.0
W1 ⁱ —O1C—Re1—O4	177.2 (4)	O1—W2—Re1—O1C	0.0
V1 ⁱ —O1C—Re1—O4	88.9 (3)	O2—W2—Re1—O1C	-80.0 (3)
Re1 ⁱ —O1C—Re1—O4	88.9 (3)	O2 ^{iv} —W2—Re1—O1C	80.0 (3)
W1—O1C—Re1—O4 ^{iv}	-177.2 (4)	O2E—W2—Re1—W1 ⁱ	125.752 (18)
W1 ⁱ —O1C—Re1—O4 ^{iv}	-0.5 (3)	O3—W2—Re1—W1 ⁱ	125.752 (18)
V1 ⁱ —O1C—Re1—O4 ^{iv}	-88.9 (3)	O1—W2—Re1—W1 ⁱ	-54.248 (18)
Re1 ⁱ —O1C—Re1—O4 ^{iv}	-88.9 (3)	O2—W2—Re1—W1 ⁱ	-134.3 (3)
W1—O1C—Re1—O5	-88.3 (2)	O2 ^{iv} —W2—Re1—W1 ⁱ	25.8 (3)
W1 ⁱ —O1C—Re1—O5	88.3 (2)	O1C—W2—Re1—W1 ⁱ	-54.248 (18)
W1—O1C—Re1—W1 ⁱ	-176.7 (4)	O2E—W2—Re1—W1	-125.752 (18)
V1 ⁱ —O1C—Re1—W1 ⁱ	-88.3 (2)	O3—W2—Re1—W1	-125.752 (18)
Re1 ⁱ —O1C—Re1—W1 ⁱ	-88.3 (2)	O1—W2—Re1—W1	54.248 (18)
W1 ⁱ —O1C—Re1—W1	176.7 (4)	O2—W2—Re1—W1	-25.8 (3)
V1 ⁱ —O1C—Re1—W1	88.3 (2)	O2 ^{iv} —W2—Re1—W1	134.3 (3)

Re1 ⁱ —O1C—Re1—W1	88.3 (2)	O1C—W2—Re1—W1	54.248 (18)
W1—O1C—Re1—W2	91.7 (2)		

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1A \cdots O1W	0.86	2.40	3.078 (14)	136
N1—H1A \cdots O1E	0.86	2.58	3.184 (14)	129
N2—H2A \cdots O3 ^v	0.86	2.39	3.181 (12)	152
O1W—H1W1 \cdots O1E	0.81	2.50	3.188 (18)	144
O2W—H1W2 \cdots O3E ^{vi}	0.85	2.10	2.836 (18)	144
O4W—H1W4 \cdots O2W	0.85	1.87	2.40 (7)	119
O4W—H2W4 \cdots O4W ^{vii}	0.85	2.31	2.65 (15)	106

Symmetry codes: (v) $x+1/2, y, -z+1$; (vi) $-x+1, -y, -z+1$; (vii) $-x+1, -y, -z+2$.