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Bis(4,4'-bipyridinium) dodecatungsto-silicate 4,4'-bipyridine hexahydrate

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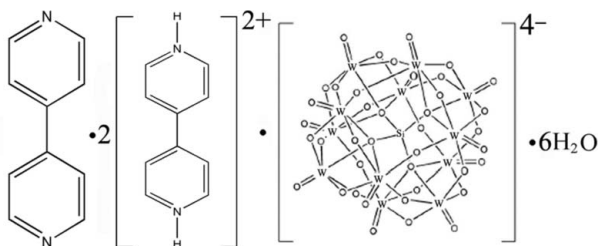
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.013$ Å;
R factor = 0.039; wR factor = 0.101; data-to-parameter ratio = 12.4.

The title compound, $(\text{C}_{10}\text{H}_{10}\text{N}_2)_2[\text{SiW}_{12}\text{O}_{40}] \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot 6\text{H}_2\text{O}$ or $(4,4'\text{-bipyH}_2)_2[\text{SiW}_{12}\text{O}_{40}] \cdot (4,4'\text{-bipy}) \cdot 6\text{H}_2\text{O}$ (4,4'-bipy is 4,4'-bipyridine), was prepared under hydrothermal conditions. The asymmetric unit contains a discrete Keggin-type $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anion (located on a twofold axis), one 4,4'-bipy (located on a twofold axis), two $(4,4'\text{-bipyH}_2)^{2+}$ cations and six uncoordinated water molecules. The polyoxoanion is constructed from a central SiO_4 tetrahedron which shares its O atoms with four trinuclear W_3O_{13} groups, each of which is made up of three edge-sharing WO_6 octahedra. The water molecules and $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions are linked through hydrogen bonds.

Related literature

For related literature, see: Hill (1998); Kurth *et al.* (2001); Misono (1987); Pope (1983). $\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot n\text{H}_2\text{O}$ was prepared according to literature procedures (Rocchiccioli-Deltcheff *et al.*, 1983).



Experimental

Crystal data

$(\text{C}_{10}\text{H}_{10}\text{N}_2)_2[\text{SiW}_{12}\text{O}_{40}] \cdot \text{C}_{10}\text{H}_8\text{N}_2 \cdot 6\text{H}_2\text{O}$

$M_r = 3454.85$
Monoclinic, $C2/c$

$a = 15.491$ (5) Å
 $b = 18.096$ (5) Å
 $c = 20.921$ (5) Å
 $\beta = 100.834$ (5)°
 $V = 5760$ (3) Å³

$Z = 4$
Mo $K\alpha$ radiation
 $\mu = 23.99$ mm⁻¹
 $T = 293$ (2) K
 $0.15 \times 0.12 \times 0.10$ mm

Data collection

Rigaku R-Axis RAPID diffractometer
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.041$, $T_{\max} = 0.095$

15853 measured reflections
5652 independent reflections
5214 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.101$
 $S = 1.10$
5652 reflections
455 parameters
8 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 3.60$ e Å⁻³
 $\Delta\rho_{\min} = -3.50$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1W}-\text{H1A} \cdots \text{O3W}$	0.89 (10)	2.15 (11)	2.699 (11)	119 (7)
$\text{O1W}-\text{H1B} \cdots \text{O2W}$	0.81 (9)	2.31 (9)	2.749 (12)	115 (10)
$\text{O1W}-\text{H1B} \cdots \text{O2O}$	0.81 (9)	2.54 (11)	2.844 (10)	104 (8)
$\text{N1}-\text{H1N} \cdots \text{O2W}$	0.78 (9)	1.97 (9)	2.754 (12)	172 (14)
$\text{O3W}-\text{H3A} \cdots \text{O18}$	0.91 (9)	2.24 (10)	2.878 (10)	127 (9)

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2097).

References

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supplementary materials

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Bis(4,4'-bipyridinium) dodecatungstosilicate 4,4'-bipyridine hexahydrate

F.-X. Ma and Q. Zhao

Comment

Polyoxometalates (*POMs*) have been known for more than 200 years, but continue to receive attention due to their versatile structures and applications in medicine, materials science, catalysis (Misono, 1987; Pope, 1983; Hill, 1998).

The structure of the title compound is built from one independent 4,4'-bipyridines (4,4'-bipy) (placed on twofold axis by N3/C13/C14/N4) and two protonated 4,4'-bipyridines (4,4'-bipyH₂)²⁺, and Keggin-type anion [SiW₁₂O₄₀]⁴⁻ (placed on twofold axis) and six water molecules (Fig. 1). In the well known Keggin structure, there are 12 WO₆-octahedra and one SiO₄-tetrahedron. The 12 WO₆-octahedra can be categorized into four W₃O₁₃ trinuclear groups, each of which is made of three edge-sharing WO₆-octahedra and are joined to each other by sharing corners. The SiO₄-tetrahedron is located in the centre of the polyoxoanion by sharing its O atoms with the four W₃O₁₃-groups. In the Keggin anion, the Si—O and W—O distances as well as the corresponding angles are very similar to those of H₄SiW₁₂O₄₀ (Kurth *et al.*, 2001). The water molecules and [SiW₁₂O₄₀]⁴⁻ anions are linked through hydrogen bonds. It can be seen that all of the H atoms come from water molecules. The O atoms, which come from the [SiW₁₂O₄₀]⁴⁻ anions, are also involved in hydrogen bonds and play the role of acceptors.

Experimental

The H₄SiW₁₂O₄₀·nH₂O was prepared according to the method given by Rocchiccioli-Deltcheff *et al.*, (1983). The starting mixture of H₄SiW₁₂O₄₀·nH₂O (0.302 g), 4,4'-bipy (0.026 g), and H₂O (10 ml) was adjusted to pH = 5.6 by addition of 2 mol.L⁻¹ NaOH under stirring for 30 min. The final solution was transferred into a 25 ml teflon lined autoclave and was heated at 453 K for 96 h. Then, the autoclave was cooled with a rate of 10 K.h⁻¹ to room temperature. Black block-like crystals were filtered off, washed with distilled water and dried at ambient temperature (45% yield on W).

Refinement

All H atoms on C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. The H atoms bonded to N atom and O atoms of water molecules were located in a difference Fourier map and refined isotropically. In the final Fourier map, the highest peak is 0.85 Å away from W3 and the deepest hole is 0.55 Å from W4.

Figures

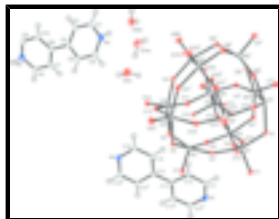


Fig. 1. A view of the structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius. Symmetry codes: $i = -x+2, y, -z+3/2$; $ii = -x+1, y, -z+3/2$.

Bis(4,4'-bipyridinium) dodecatungstosilicate 4,4'-bipyridine hexahydrate

Crystal data

$(C_{10}H_{10}N_2)_2[SiW_{12}O_{40}] \cdot C_{10}H_8N_2 \cdot 6H_2O$

$M_r = 3454.85$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 15.491 (5) \text{ \AA}$

$b = 18.096 (5) \text{ \AA}$

$c = 20.921 (5) \text{ \AA}$

$\beta = 100.834 (5)^\circ$

$V = 5760 (3) \text{ \AA}^3$

$Z = 4$

$F_{000} = 6128$

$D_x = 3.984 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 5214 reflections

$\theta = 1.8\text{--}26.0^\circ$

$\mu = 23.99 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Block, black

$0.15 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Rigaku R-Axis RAPID
diffractometer

Radiation source: Rotor target

Monochromator: graphite

Detector resolution: $10.0 \text{ pixels mm}^{-1}$

$T = 293(2) \text{ K}$

ω scans

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.041, T_{\max} = 0.095$

15853 measured reflections

5652 independent reflections

5214 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 1.8^\circ$

$h = -19 \rightarrow 14$

$k = -22 \rightarrow 22$

$l = -23 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.101$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 129.9363P]$

$S = 1.10$	where $P = (F_o^2 + 2F_c^2)/3$
5652 reflections	$(\Delta/\sigma)_{\max} = 0.002$
455 parameters	$\Delta\rho_{\max} = 3.60 \text{ e } \text{\AA}^{-3}$
8 restraints	$\Delta\rho_{\min} = -3.50 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Si1	1.0000	0.14417 (15)	0.7500	0.0055 (5)
W1	0.98109 (2)	0.004870 (18)	0.865205 (16)	0.01358 (10)
W2	0.81326 (2)	0.150489 (19)	0.823667 (17)	0.01562 (10)
W3	0.83728 (2)	0.008359 (18)	0.701365 (16)	0.01280 (10)
W4	0.86857 (2)	0.136541 (19)	0.593364 (17)	0.01711 (10)
W5	0.83464 (2)	0.280029 (18)	0.712749 (16)	0.01327 (10)
W6	1.03445 (2)	0.282564 (18)	0.639007 (16)	0.01417 (10)
C1	0.7254 (7)	0.6611 (5)	0.4178 (5)	0.0264 (14)
H1	0.7714	0.6664	0.3953	0.032*
C2	0.6599 (7)	0.7125 (5)	0.4101 (5)	0.0254 (13)
H2	0.6598	0.7520	0.3816	0.031*
C3	0.5934 (6)	0.7045 (5)	0.4454 (5)	0.0210 (13)
C4	0.5952 (7)	0.6445 (5)	0.4877 (5)	0.0223 (13)
H4	0.5515	0.6386	0.5123	0.027*
C5	0.6624 (7)	0.5948 (5)	0.4922 (5)	0.0266 (13)
H5	0.6649	0.5544	0.5200	0.032*
C6	0.5183 (6)	0.7587 (5)	0.4376 (5)	0.0210 (13)
C7	0.4350 (6)	0.7337 (5)	0.4437 (5)	0.0219 (13)
H7	0.4262	0.6843	0.4530	0.026*
C8	0.3650 (7)	0.7838 (5)	0.4357 (5)	0.0228 (14)
H8	0.3090	0.7681	0.4396	0.027*
C9	0.4582 (6)	0.8799 (5)	0.4160 (5)	0.0240 (14)
H9	0.4648	0.9297	0.4069	0.029*
C10	0.5303 (7)	0.8325 (5)	0.4228 (5)	0.0227 (13)
H10	0.5850	0.8498	0.4175	0.027*

supplementary materials

C11	0.5736 (6)	-0.0110 (5)	0.7442 (4)	0.0195 (13)
H11	0.6235	-0.0379	0.7401	0.023*
C12	0.5755 (6)	0.0660 (5)	0.7443 (4)	0.0174 (12)
H12	0.6269	0.0908	0.7406	0.021*
C13	0.5000	0.1061 (7)	0.7500	0.0159 (14)
C14	0.5000	0.1881 (6)	0.7500	0.0146 (14)
C15	0.5682 (6)	0.2278 (5)	0.7320 (4)	0.0174 (12)
H15	0.6147	0.2029	0.7193	0.021*
C16	0.5676 (6)	0.3045 (5)	0.7328 (4)	0.0206 (13)
H16	0.6141	0.3307	0.7214	0.025*
N1	0.7246 (6)	0.6045 (5)	0.4565 (4)	0.0265 (13)
H1N	0.770 (5)	0.584 (6)	0.461 (6)	0.040*
N2	0.3794 (6)	0.8539 (4)	0.4226 (4)	0.0252 (14)
H2N	0.334 (5)	0.875 (6)	0.419 (6)	0.038*
N3	0.5000	-0.0457 (6)	0.7500	0.0192 (16)
N4	0.5000	0.3407 (6)	0.7500	0.0192 (16)
O1	0.9447 (4)	-0.0617 (3)	0.9112 (3)	0.0163 (12)
O2	1.0599 (4)	0.0597 (3)	0.9308 (3)	0.0120 (10)
O3	1.0822 (4)	-0.0439 (3)	0.8440 (3)	0.0122 (10)
O5	0.8959 (4)	0.0815 (3)	0.8665 (3)	0.0116 (9)
O6	0.8667 (4)	0.2281 (3)	0.8797 (3)	0.0134 (9)
O7	0.7236 (4)	0.1323 (3)	0.8568 (3)	0.0165 (11)
O8	0.7635 (4)	0.2270 (3)	0.7623 (3)	0.0146 (8)
O9	0.7957 (4)	0.0824 (3)	0.7520 (3)	0.0141 (8)
O10	0.9299 (4)	0.1957 (3)	0.7773 (3)	0.0104 (8)
O11	0.9167 (4)	-0.0197 (3)	0.7808 (3)	0.0135 (9)
O12	0.7571 (4)	-0.0570 (3)	0.6969 (3)	0.0198 (12)
O13	0.9484 (4)	0.0926 (3)	0.6913 (3)	0.0096 (8)
O14	0.7932 (4)	0.0625 (3)	0.6220 (3)	0.0135 (9)
O15	0.8026 (4)	0.1562 (3)	0.5197 (3)	0.0184 (12)
O16	0.9609 (4)	0.2067 (3)	0.5959 (3)	0.0136 (9)
O17	0.8220 (4)	0.2048 (3)	0.6488 (3)	0.0146 (9)
O18	0.7599 (4)	0.3442 (3)	0.6770 (3)	0.0198 (12)
O19	1.1124 (4)	0.3313 (3)	0.7084 (3)	0.0136 (10)
O20	1.0266 (5)	0.3501 (3)	0.5807 (3)	0.0214 (13)
O21	0.9400 (4)	0.3087 (3)	0.6807 (3)	0.0159 (9)
O1W	0.9247 (5)	0.4797 (4)	0.5870 (4)	0.0332 (12)
H1A	0.890 (7)	0.469 (7)	0.615 (4)	0.050*
H1B	0.920 (8)	0.457 (6)	0.553 (4)	0.050*
O2W	0.8790 (5)	0.5277 (4)	0.4605 (4)	0.0319 (13)
H2A	0.932 (7)	0.547 (6)	0.463 (5)	0.048*
H2B	0.859 (7)	0.506 (6)	0.427 (4)	0.048*
O3W	0.7508 (5)	0.4587 (4)	0.5805 (4)	0.0380 (13)
H3A	0.780 (8)	0.416 (4)	0.594 (5)	0.057*
H3B	0.763 (9)	0.487 (5)	0.618 (4)	0.057*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0050 (12)	0.0012 (11)	0.0111 (12)	0.000	0.0033 (10)	0.000
W1	0.0161 (2)	0.00723 (17)	0.01860 (19)	0.00094 (13)	0.00648 (14)	0.00361 (12)
W2	0.0143 (2)	0.01192 (18)	0.02205 (19)	0.00164 (13)	0.00714 (14)	-0.00002 (13)
W3	0.0121 (2)	0.00709 (17)	0.01982 (18)	-0.00403 (12)	0.00457 (13)	-0.00200 (12)
W4	0.0176 (2)	0.01453 (19)	0.01848 (19)	0.00010 (14)	0.00146 (14)	0.00044 (13)
W5	0.0137 (2)	0.00674 (17)	0.01943 (18)	0.00445 (12)	0.00332 (13)	0.00175 (12)
W6	0.0179 (2)	0.00714 (17)	0.01819 (18)	-0.00104 (13)	0.00512 (14)	0.00300 (12)
C1	0.022 (3)	0.022 (3)	0.037 (3)	0.000 (2)	0.010 (2)	-0.002 (2)
C2	0.023 (3)	0.019 (2)	0.035 (3)	0.001 (2)	0.008 (2)	0.000 (2)
C3	0.018 (3)	0.017 (2)	0.029 (3)	0.000 (2)	0.007 (2)	-0.002 (2)
C4	0.019 (2)	0.018 (2)	0.031 (2)	0.001 (2)	0.007 (2)	-0.001 (2)
C5	0.023 (3)	0.022 (3)	0.034 (3)	0.001 (2)	0.005 (2)	0.001 (2)
C6	0.020 (3)	0.015 (2)	0.028 (3)	0.002 (2)	0.005 (2)	0.000 (2)
C7	0.020 (3)	0.017 (2)	0.030 (3)	0.003 (2)	0.006 (2)	0.000 (2)
C8	0.019 (3)	0.019 (3)	0.032 (3)	0.003 (3)	0.009 (3)	0.002 (3)
C9	0.023 (3)	0.016 (3)	0.033 (3)	0.002 (3)	0.006 (3)	-0.002 (3)
C10	0.021 (3)	0.016 (2)	0.031 (3)	0.000 (2)	0.007 (2)	0.000 (2)
C11	0.018 (2)	0.012 (2)	0.029 (2)	0.001 (2)	0.003 (2)	-0.002 (2)
C12	0.016 (2)	0.011 (2)	0.025 (2)	0.000 (2)	0.003 (2)	0.000 (2)
C13	0.015 (3)	0.010 (3)	0.022 (3)	0.000	0.002 (2)	0.000
C14	0.014 (3)	0.009 (3)	0.021 (3)	0.000	0.004 (2)	0.000
C15	0.016 (2)	0.011 (2)	0.025 (2)	0.000 (2)	0.004 (2)	0.000 (2)
C16	0.020 (3)	0.014 (2)	0.028 (3)	-0.002 (2)	0.004 (2)	0.002 (2)
N1	0.020 (3)	0.021 (2)	0.038 (3)	0.004 (2)	0.005 (2)	-0.004 (2)
N2	0.023 (3)	0.019 (3)	0.034 (3)	0.006 (2)	0.008 (2)	0.001 (2)
N3	0.018 (3)	0.011 (3)	0.029 (3)	0.000	0.004 (3)	0.000
N4	0.019 (3)	0.013 (3)	0.025 (3)	0.000	0.002 (3)	0.000
O1	0.018 (3)	0.010 (3)	0.023 (3)	0.001 (2)	0.007 (2)	0.007 (2)
O2	0.011 (2)	0.0089 (19)	0.016 (2)	0.0007 (18)	0.0036 (17)	0.0043 (17)
O3	0.013 (2)	0.005 (2)	0.019 (2)	0.0014 (18)	0.0047 (18)	0.0035 (18)
O5	0.0132 (18)	0.0082 (17)	0.0149 (17)	-0.0005 (16)	0.0060 (15)	0.0017 (15)
O6	0.0144 (19)	0.0075 (18)	0.0190 (18)	0.0021 (16)	0.0049 (17)	-0.0011 (16)
O7	0.015 (3)	0.014 (2)	0.021 (2)	0.003 (2)	0.006 (2)	0.000 (2)
O8	0.0131 (17)	0.0107 (16)	0.0201 (16)	0.0028 (15)	0.0037 (15)	0.0016 (15)
O9	0.0138 (16)	0.0097 (15)	0.0194 (15)	0.0000 (14)	0.0050 (14)	-0.0002 (14)
O10	0.0116 (17)	0.0047 (16)	0.0155 (16)	0.0012 (15)	0.0039 (15)	0.0004 (14)
O11	0.0158 (18)	0.0084 (17)	0.0171 (18)	-0.0005 (16)	0.0049 (16)	0.0026 (16)
O12	0.016 (3)	0.014 (3)	0.030 (3)	-0.004 (2)	0.007 (2)	-0.002 (2)
O13	0.0106 (16)	0.0052 (16)	0.0142 (16)	0.0010 (15)	0.0054 (14)	-0.0004 (14)
O14	0.0119 (18)	0.0090 (17)	0.0194 (17)	-0.0019 (16)	0.0025 (16)	-0.0018 (16)
O15	0.019 (3)	0.016 (3)	0.019 (3)	0.002 (2)	0.002 (2)	0.004 (2)
O16	0.0141 (19)	0.0090 (18)	0.0189 (18)	0.0006 (17)	0.0061 (16)	0.0016 (16)
O17	0.0140 (17)	0.0103 (16)	0.0193 (16)	0.0017 (15)	0.0023 (15)	0.0004 (15)
O18	0.022 (3)	0.016 (2)	0.023 (3)	0.009 (2)	0.007 (2)	0.007 (2)

supplementary materials

O19	0.015 (2)	0.005 (2)	0.021 (2)	-0.0026 (18)	0.0053 (18)	0.0020 (18)
O20	0.025 (3)	0.015 (3)	0.026 (3)	0.000 (2)	0.008 (2)	0.012 (2)
O21	0.0165 (18)	0.0096 (17)	0.0224 (18)	0.0011 (16)	0.0053 (16)	0.0014 (16)
O1W	0.029 (2)	0.026 (2)	0.044 (2)	-0.001 (2)	0.006 (2)	0.005 (2)
O2W	0.025 (3)	0.026 (3)	0.045 (3)	0.001 (2)	0.008 (2)	-0.003 (2)
O3W	0.032 (3)	0.033 (2)	0.048 (3)	0.001 (2)	0.005 (2)	0.007 (2)

Geometric parameters (Å, °)

Si1—O10	1.614 (6)	C3—C4	1.397 (13)
Si1—O10 ⁱ	1.614 (6)	C3—C6	1.507 (13)
Si1—O13	1.627 (5)	C4—C5	1.366 (13)
Si1—O13 ⁱ	1.627 (5)	C4—H4	0.9300
W1—O1	1.703 (6)	C5—N1	1.337 (14)
W1—O11	1.911 (5)	C5—H5	0.9300
W1—O5	1.918 (6)	C6—C10	1.391 (13)
W1—O3	1.921 (6)	C6—C7	1.395 (14)
W1—O2	1.931 (6)	C7—C8	1.400 (13)
W1—O13 ⁱ	2.366 (5)	C7—H7	0.9300
W2—O7	1.697 (6)	C8—N2	1.325 (12)
W2—O5	1.889 (5)	C8—H8	0.9300
W2—O6	1.915 (6)	C9—N2	1.340 (13)
W2—O9	1.921 (6)	C9—C10	1.394 (14)
W2—O8	1.945 (6)	C9—H9	0.9300
W2—O10	2.353 (6)	C10—H10	0.9300
W3—O12	1.706 (6)	C11—N3	1.327 (11)
W3—O9	1.894 (6)	C11—C12	1.395 (12)
W3—O14	1.939 (6)	C11—H11	0.9300
W3—O11	1.940 (5)	C12—C13	1.400 (11)
W3—O3 ⁱ	1.948 (6)	C12—H12	0.9300
W3—O13	2.338 (5)	C13—C12 ⁱⁱ	1.400 (11)
W4—O15	1.719 (6)	C13—C14	1.483 (17)
W4—O2 ⁱ	1.904 (6)	C14—C15 ⁱⁱ	1.388 (11)
W4—O16	1.907 (6)	C14—C15	1.388 (11)
W4—O17	1.924 (6)	C15—C16	1.387 (12)
W4—O14	1.943 (6)	C15—H15	0.9300
W4—O13	2.325 (5)	C16—N4	1.341 (11)
W5—O18	1.709 (6)	C16—H16	0.9300
W5—O17	1.894 (6)	N1—H1N	0.79 (6)
W5—O8	1.909 (6)	N2—H2N	0.79 (6)
W5—O19 ⁱ	1.935 (6)	N3—C11 ⁱⁱ	1.327 (11)
W5—O21	1.948 (6)	N4—C16 ⁱⁱ	1.341 (11)
W5—O10	2.363 (5)	O2—W4 ⁱ	1.904 (6)
W6—O20	1.715 (6)	O3—W3 ⁱ	1.948 (6)
W6—O21	1.898 (6)	O6—W6 ⁱ	1.923 (6)
W6—O16	1.900 (6)	O10—W6 ⁱ	2.341 (5)

W6—O19	1.919 (6)	O13—W1 ⁱ	2.366 (5)
W6—O6 ⁱ	1.923 (6)	O19—W5 ⁱ	1.935 (6)
W6—O10 ⁱ	2.341 (5)	O1W—H1A	0.89 (6)
C1—N1	1.306 (13)	O1W—H1B	0.81 (6)
C1—C2	1.364 (14)	O2W—H2A	0.88 (9)
C1—H1	0.9300	O2W—H2B	0.80 (6)
C2—C3	1.383 (14)	O3W—H3A	0.92 (6)
C2—H2	0.9300	O3W—H3B	0.93 (6)
O10—Si1—O10 ⁱ	109.4 (4)	O19—W6—O6 ⁱ	88.7 (2)
O10—Si1—O13	109.3 (3)	O20—W6—O10 ⁱ	170.4 (3)
O10 ⁱ —Si1—O13	109.4 (3)	O21—W6—O10 ⁱ	85.3 (2)
O10—Si1—O13 ⁱ	109.4 (3)	O16—W6—O10 ⁱ	84.6 (2)
O10 ⁱ —Si1—O13 ⁱ	109.3 (3)	O19—W6—O10 ⁱ	73.5 (2)
O13—Si1—O13 ⁱ	110.0 (4)	O6 ⁱ —W6—O10 ⁱ	74.0 (2)
O1—W1—O11	100.7 (3)	N1—C1—C2	120.9 (10)
O1—W1—O5	101.7 (3)	N1—C1—H1	119.5
O11—W1—O5	86.6 (2)	C2—C1—H1	119.5
O1—W1—O3	100.2 (3)	C1—C2—C3	118.5 (10)
O11—W1—O3	89.2 (2)	C1—C2—H2	120.8
O5—W1—O3	158.2 (2)	C3—C2—H2	120.8
O1—W1—O2	101.2 (3)	C2—C3—C4	119.5 (9)
O11—W1—O2	158.0 (2)	C2—C3—C6	120.7 (9)
O5—W1—O2	87.9 (2)	C4—C3—C6	119.8 (9)
O3—W1—O2	88.0 (2)	C5—C4—C3	118.6 (10)
O1—W1—O13 ⁱ	172.0 (2)	C5—C4—H4	120.7
O11—W1—O13 ⁱ	84.5 (2)	C3—C4—H4	120.7
O5—W1—O13 ⁱ	84.6 (2)	N1—C5—C4	119.7 (9)
O3—W1—O13 ⁱ	73.7 (2)	N1—C5—H5	120.2
O2—W1—O13 ⁱ	73.8 (2)	C4—C5—H5	120.2
O7—W2—O5	102.2 (3)	C10—C6—C7	119.7 (9)
O7—W2—O6	100.6 (3)	C10—C6—C3	121.1 (9)
O5—W2—O6	91.0 (2)	C7—C6—C3	119.2 (8)
O7—W2—O9	100.8 (3)	C6—C7—C8	119.3 (9)
O5—W2—O9	86.0 (2)	C6—C7—H7	120.4
O6—W2—O9	158.5 (3)	C8—C7—H7	120.4
O7—W2—O8	98.9 (3)	N2—C8—C7	119.2 (9)
O5—W2—O8	158.8 (3)	N2—C8—H8	120.4
O6—W2—O8	87.4 (2)	C7—C8—H8	120.4
O9—W2—O8	87.8 (2)	N2—C9—C10	120.0 (9)
O7—W2—O10	170.8 (2)	N2—C9—H9	120.0
O5—W2—O10	85.5 (2)	C10—C9—H9	120.0
O6—W2—O10	73.8 (2)	C6—C10—C9	118.4 (9)
O9—W2—O10	84.7 (2)	C6—C10—H10	120.8
O8—W2—O10	73.8 (2)	C9—C10—H10	120.8
O12—W3—O9	101.6 (3)	N3—C11—C12	119.3 (9)
O12—W3—O14	99.7 (3)	N3—C11—H11	120.3

supplementary materials

O9—W3—O14	91.1 (2)	C12—C11—H11	120.3
O12—W3—O11	101.7 (3)	C11—C12—C13	120.1 (9)
O9—W3—O11	86.2 (2)	C11—C12—H12	119.9
O14—W3—O11	158.5 (2)	C13—C12—H12	119.9
O12—W3—O3 ⁱ	99.4 (3)	C12 ⁱⁱ —C13—C12	117.5 (11)
O9—W3—O3 ⁱ	158.7 (2)	C12 ⁱⁱ —C13—C14	121.2 (6)
O14—W3—O3 ⁱ	89.0 (2)	C12—C13—C14	121.2 (6)
O11—W3—O3 ⁱ	85.9 (2)	C15 ⁱⁱ —C14—C15	117.5 (11)
O12—W3—O13	171.3 (2)	C15 ⁱⁱ —C14—C13	121.2 (6)
O9—W3—O13	85.6 (2)	C15—C14—C13	121.2 (5)
O14—W3—O13	74.9 (2)	C16—C15—C14	120.5 (9)
O11—W3—O13	83.6 (2)	C16—C15—H15	119.7
O3 ⁱ —W3—O13	73.9 (2)	C14—C15—H15	119.7
O15—W4—O2 ⁱ	101.0 (3)	N4—C16—C15	120.0 (9)
O15—W4—O16	101.7 (3)	N4—C16—H16	120.0
O2 ⁱ —W4—O16	91.3 (2)	C15—C16—H16	120.0
O15—W4—O17	100.4 (3)	C1—N1—C5	122.8 (9)
O2 ⁱ —W4—O17	158.6 (2)	C1—N1—H1N	109 (9)
O16—W4—O17	85.4 (3)	C5—N1—H1N	127 (9)
O15—W4—O14	97.4 (3)	C8—N2—C9	123.4 (9)
O2 ⁱ —W4—O14	89.5 (2)	C8—N2—H2N	108 (9)
O16—W4—O14	160.3 (2)	C9—N2—H2N	129 (9)
O17—W4—O14	86.7 (2)	C11 ⁱⁱ —N3—C11	123.6 (11)
O15—W4—O13	171.5 (2)	C16 ⁱⁱ —N4—C16	121.4 (11)
O2 ⁱ —W4—O13	75.2 (2)	W4 ⁱ —O2—W1	120.5 (3)
O16—W4—O13	86.1 (2)	W1—O3—W3 ⁱ	121.0 (3)
O17—W4—O13	83.5 (2)	W2—O5—W1	151.4 (3)
O14—W4—O13	75.1 (2)	W2—O6—W6 ⁱ	121.3 (3)
O18—W5—O17	102.0 (3)	W5—O8—W2	121.2 (3)
O18—W5—O8	99.6 (3)	W3—O9—W2	151.4 (3)
O17—W5—O8	91.6 (3)	Si1—O10—W6 ⁱ	125.0 (3)
O18—W5—O19 ⁱ	101.0 (3)	Si1—O10—W2	124.4 (3)
O17—W5—O19 ⁱ	156.7 (2)	W6 ⁱ —O10—W2	90.93 (19)
O8—W5—O19 ⁱ	88.5 (3)	Si1—O10—W5	124.1 (3)
O18—W5—O21	102.2 (3)	W6 ⁱ —O10—W5	91.59 (19)
O17—W5—O21	86.0 (3)	W2—O10—W5	90.8 (2)
O8—W5—O21	158.1 (2)	W1—O11—W3	150.2 (3)
O19 ⁱ —W5—O21	85.3 (2)	Si1—O13—W4	125.0 (3)
O18—W5—O10	171.0 (3)	Si1—O13—W3	124.9 (3)
O17—W5—O10	84.8 (2)	W4—O13—W3	91.37 (19)
O8—W5—O10	74.2 (2)	Si1—O13—W1 ⁱ	123.6 (3)
O19 ⁱ —W5—O10	72.7 (2)	W4—O13—W1 ⁱ	90.46 (18)
O21—W5—O10	84.0 (2)	W3—O13—W1 ⁱ	91.39 (18)
O20—W6—O21	101.0 (3)	W3—O14—W4	118.5 (3)

O20—W6—O16	102.7 (3)	W6—O16—W4	150.9 (3)
O21—W6—O16	87.3 (3)	W5—O17—W4	152.4 (3)
O20—W6—O19	99.3 (3)	W6—O19—W5 ⁱ	122.0 (3)
O21—W6—O19	88.2 (3)	W6—O21—W5	149.3 (3)
O16—W6—O19	158.0 (2)	H1A—O1W—H1B	119 (9)
O20—W6—O6 ⁱ	99.9 (3)	H2A—O2W—H2B	117 (10)
O21—W6—O6 ⁱ	159.0 (2)	H3A—O3W—H3B	102 (6)
O16—W6—O6 ⁱ	87.8 (2)		

Symmetry codes: (i) $-x+2, y, -z+3/2$; (ii) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1W—H1A...O3W	0.89 (10)	2.15 (11)	2.699 (11)	119 (7)
O1W—H1B...O2W	0.81 (9)	2.31 (9)	2.749 (12)	115 (10)
O1W—H1B...O20	0.81 (9)	2.54 (11)	2.844 (10)	104 (8)
N1—H1N...O2W	0.78 (9)	1.97 (9)	2.754 (12)	172 (14)
O3W—H3A...O18	0.91 (9)	2.24 (10)	2.878 (10)	127 (9)

Fig. 1

