Dimerization of A- α -[SiNb₃W₉O₄₀]⁷⁻ by pH-Controlled Formation of Individual Nb- μ -O-Nb Bonds

Gyu-Shik Kim,[†] Huadong Zeng,[‡] Wade A. Neiwert, Jennifer J. Cowan,[¥] Donald VanDerveer,[§] Craig L. Hill* and Ira A. Weinstock*

Department of Chemistry, 1515 Pierce Drive, Emory University, Atlanta, GA 30322

Contents

Experimental:

LiOH hydrolysis of A- α -[Si₂Nb₆W₁₈O₇₇]⁸⁻ (**4**) to A- α -[SiNb₃W₉O₄₀]⁷⁻ (**1**).

Re-condensation of **1** to **4** by DCl.

Reversible hydrolysis of A- α -H₈[Si₂Nb₆W₁₈O₇₇]•20H₂O (H₈**4**•20H₂O).

Preparation of A- α -TBA₄H₃[Si(NbO₂)₃W₉O₃₇].

Synthesis of A- α -Cs₈[Si₂Nb₆W₁₈O₇₇]•18H₂O (Cs₈**4**•18H₂O) by cation exchange.

Data collection and refinement for the structure of *syn*-A- α -

Cs₈H₂[Si₂Nb₆W₁₈O₇₈]•18H₂O (*syn*-Cs₈H₂**3**•18H₂O).

Table S1. Crystal data and structure refinement for *syn*-Cs₈H₂**3**•18H₂O.

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for *syn*-Cs₈H₂**3**•18H₂O.

Table S3. Bond lengths (Å) and angles (°) for *syn*-Cs₈H₂**3**•18H₂O.

Table S4. Anisotropic displacement parameters for *syn*-Cs₈H₂**3**•18H₂O.

LiOH Hydrolysis of A- α -[Si₂Nb₆W₁₈O₇₇]⁸⁻ (4**).** Cs₈**4**•18H₂O (2.62 g, 0.40 mmol) was dissolved along with 14 equivalents of LiClO₄ (0.60 g, 5.64 mmol) in 2.2 mL of pre-acidified (2.0 M DCl) D₂O. After 15 min of stirring, insoluble CsClO₄ was removed by filtration to give 3.6 mL of a 0.11 M solution of **4** which was 1.2 M in D⁺ (4.40 mmol), 1.6 M in Li⁺ (5.64 mmol), 0.7 M in ClO₄⁻ (2.4 mmol), 1.2 M in Cl⁻ (4.40 mmol), and 4.0 M in HDO (14.4 mmol); total ionic strength, μ , was 5.9 M. Once the solution was prepared, spectral (¹⁸³W NMR) acquisition was initiated immediately. After the first ¹⁸³W NMR spectrum was obtained, the solution pD was carefully adjusted to a pD value of ca. 0.3 by dropwise addition of LiOH (5.0 M in D₂O) solution. From this stage on, sample solutions were often stored for one to two weeks while awaiting available NMR time. Over these time periods, no changes in measured pD values were observed, and ¹⁸³W NMR spectra (checked by repeated acquisitions after two weeks) also remained unchanged. In this way, successive ¹⁸³W NMR spectra were obtained at various pD values (up to pD = 7.8). (Four months time was required to obtain eleven ¹⁸³W NMR spectra at successive, increasingly higher pD values. Between acquisitions, NMR samples were stored at ambient temperature.) The ¹⁸³W NMR spectra obtained documented the step-wise conversion of **4** to **3** (two isomers), to **2** and, finally to **1**. At the high pD limit of 7.8, **4** had been converted entirely to **1** (effectively quantitatively within the sensitivity of ¹⁸³W NMR). At this stage, ca. 1.36 mL of 5.0 M LiOH in D₂O (6.80 mmol; 4.40 mmol to neutralize D⁺, and 2.40 mmol to cleave the dimer) had been added, bringing the total volume to 5.0 mL. The solution was now 0.16 M in **1** (0.8

mmol), 2.5 M in Li^+ (12.4 mmol), 0.5 M in ClO_4^- (2.4 mmol), 0.9 M in Cl^- (4.40 mmol), and 4.3 M in HDO (21.2 mmol); total ionic strength, μ , was 5.9 M.

Re-Condensation of 1 to 4 by DCl. To the pD 7.8 solution of 1 described immediately above, increments of conc. DCl (12 M DCl in D_2O) were added. W-183 NMR spectra were acquired at a series of increasingly lower pD values until the high $[\text{D}^+]$ limit of 1.2 M D^+ had been restored (a total of 0.57 mL of conc. DCl, 6.88 mmol D^+ was added). At identical pD values, the same ^{183}W NMR spectra as had been seen during incremental additions of LiOH (previous paragraph) were reproduced. Again, a number of weeks were required to obtain ^{183}W NMR spectra at successively lower pD values. As before, no changes in ^{183}W NMR spectra were observed when spectra were re-acquired from solutions stored at pD values greater than ca. 0.3 at ambient temperature for several weeks. The ^{183}W NMR spectra obtained documented the step-wise conversion of 1 to 2 to 3 (two isomers), and finally to 4. At the low-pD (1.2 M D^+) limit, monomeric 1 had been entirely re-condensed to 4. The solution (now 5.73 mL in volume) contained an additional 6.88 mmol Cl^- (13.7 mmol Cl^- , 2.4 M, in total); total ionic strength, μ , was 5.3 M.

Reversible Hydrolysis of $\text{A-}\alpha\text{-H}_8[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{77}]\cdot 20\text{H}_2\text{O}$ ($\text{H}_8\mathbf{4}\cdot 20\text{H}_2\text{O}$). Results effectively identical to those immediately above were obtained when the full experiment was carried out using $\text{H}_8\mathbf{4}\cdot 20\text{H}_2\text{O}$ (free acid). $\text{H}_8\mathbf{4}\cdot 20\text{H}_2\text{O}$ (1.4 g, 0.25 mmol) was dissolved in 2.0 mL of pre-acidified (2.0 M DCl) D_2O along with 7.8 equivalents of LiClO_4 (0.21 g, 1.97 mmol) to give 3.0 mL of a 0.084 M solution of 4, which was 1.33 M in D^+ (4.00 mmol), 0.67 M in " H^+ " (2.03 mmol), and 0.7 M in Li^+ and in ClO_4^- . (The H^+ introduced as counter-cation to $\text{H}_8\mathbf{4}\cdot 20\text{H}_2\text{O}$ resulted, on average, in the formation of 0.67 M HDO and an equivalent concentration of D_3O^+ , so that the total initial concentration of D^+ was ca. 2.0 M.) Subsequent sequential hydrolysis by addition of LiOH to high pD (7.8) and sequential condensation (dimerization) by addition of DCl to high (1.2 M) $[\text{D}^+]$, and acquisitions of ^{183}W NMR spectra, were as described in the paragraph immediately above. Within slight variation due to differences in ionic strength, and cation and anion concentrations, the ^{183}W NMR spectra acquired at specific pD values matched those obtained when the experiment was begun using $\text{Cs}_8\mathbf{4}\cdot 18\text{H}_2\text{O}$.

Preparation of $\text{A-}\alpha\text{-TBA}_4\text{H}_3[\text{Si}(\text{NbO}_2)_3\text{W}_9\text{O}_{37}]\cdot 13\text{H}_2\text{O}$ ($\text{K}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 13\text{H}_2\text{O}$). 4.18 g, 3.05 mmol) was dissolved in 500 mL of 0.5 M aqueous H_2O_2 , and to this was added 7.2 mL of 6.0 M aqueous HCl to give a bright yellow solution. Solid $\text{A-a-Na}_{10}[\text{SiW}_9\text{O}_{34}]\cdot 23\text{H}_2\text{O}$ (17.5 g; 6.10 mmol) was then added rapidly, and the mixture was stirred until all of the solid had dissolved. Addition of Bu_4NCl (10.2 g, 36.5 mmol) dissolved in 50 mL of water then gave a yellow precipitate. The mixture was stirred for 3 h. The yellow product was collected on a medium glass frit and washed with two 20-mL portions of diethyl ether. Drying in air gave 17.95 g of yellow powder (75.2% based on the hexaniobate precursor). This product sometimes contained a trace amount of insoluble white byproduct, which could be removed by dissolution in acetonitrile followed by filtration through Celite. Crystalline material was obtained by diffusion of diethyl ether into an acetonitrile solution. Anal. Calcd. (found) for $\text{C}_{64}\text{H}_{147}\text{N}_4\text{SiNb}_3\text{W}_9\text{O}_{43}$: C, 21.2 (21.8); H, 4.09 (4.19); N, 1.55 (1.57); Nb, 7.69 (7.77); W, 45.7 (45.1). FTIR (KBr, 1100-400 cm^{-1}): 1000 (w), 961 (m), 903 (vs), 866 (m, sh), 793 (vs), 600 (w), 533 (w) cm^{-1} .

Synthesis of $\text{A-}\alpha\text{-Cs}_8[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{77}]\cdot 18\text{H}_2\text{O}$ ($\text{Cs}_8\mathbf{4}\cdot 18\text{H}_2\text{O}$) by Cation Exchange. In a preliminary communication (*J. Chem. Soc., Chem. Comm.* **1999**, 1651-1652) we noted that $\text{Cs}_8\mathbf{4}\cdot 18\text{H}_2\text{O}$ could be prepared from $\text{TBA}_6\text{H}_2\mathbf{4}\cdot \text{Et}_2\text{O}$ in 90% yield. Details are

reported here: $\text{TBA}_6\text{H}_2\mathbf{4}\cdot\text{Et}_2\text{O}$ (6.94 g; 1.05 mmol) was dissolved in 140 mL of acetonitrile and filtered. Addition of a saturated solution of CsCl in methanol (70 mL) gave a white precipitate, which was filtered (aspirator suction) on a medium glass frit and washed sequentially with methanol (2×20 mL), CH_3CN (2×10 mL) and diethyl ether (2×30 mL). Drying in air gave 6.04 g of white powder (90.6%). The following analytical data (from ref. 20) are reproduced by permission of The Royal Society of Chemistry: Anal. Calcd. (found) for $\text{H}_{36}\text{Cs}_8\text{Nb}_6\text{O}_{95}\text{Si}_2\text{W}_{18}$: H, 0.55 (0.50); Cs, 16.3 (16.3); Nb, 8.52 (8.31); W, 50.6 (50.6). FTIR (KBr, $1100\text{--}400\text{ cm}^{-1}$): 1005 (w), 967 (m), 918 (vs), 789 (vs), 687 (m), 536 (w). FT Raman ($1050\text{--}850\text{ cm}^{-1}$): 984 (vs), 910 (w), 860 (sh).

Data Collection and Refinement for the Structure of *Syn-A- α* - $\text{Cs}_8\text{H}_2[\text{Si}_2\text{Nb}_6\text{W}_{18}\text{O}_{78}]\cdot 18\text{H}_2\text{O}$ (*Syn-Cs $_8\text{H}_2\mathbf{3}\cdot 18\text{H}_2\text{O}$*). A well-formed colorless thin plate crystal of dimensions $0.16 \times 0.11 \times 0.03\text{ mm}^3$ was mounted on a glass fiber. X-ray diffraction data were collected at $-100\text{ }^\circ\text{C}$ using a Siemens SMART (Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995) platform diffractometer equipped with a CCD area detector and a normal focus molybdenum-target X-ray tube ($\lambda = 0.71073\text{ \AA}$). Data frames were collected using a narrow frame method with scan width 0.30° in ω and an exposure time of 10 s/frame ($2\theta_{\text{max}} = 56.78^\circ$). The data were integrated using the Siemens SAINT program (Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995), with the intensities corrected for Lorentz factor and polarization. Crystals were face-indexed for absorption corrections. An empirical absorption correction based on the entire data set was applied using SADABS (Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1995). Redundant reflections were averaged. The corrected data were used in subsequent structure solutions and refinements. The structure was solved by direct methods using SHELXTL-PC v. 5.03 and refined by full-matrix-least-squares-on- F^2 techniques (with $F^2 > 2\sigma(F_o^2)$) using SHELXL-97, incorporated in SHELXTL-PC v.5.03 (Sheldrick, G. M. *SHELXTL5.03 (PC Version) Program Library for Structure Solution and Molecular Graphic*; Siemens Analytical Instruments Division: Madison, WI, 1997). Direct methods located the heavy atoms (W, Cs, and Nb); other non-hydrogen atoms were located by successive Fourier difference maps. Anisotropic temperature factors were applied to all the atoms, except O(4), O(6), O(13), O(21), O(22), and O(24) of the polyanion, and the water oxygens, for which isotropic temperature factors were applied. Disorder of the Cs^+ cations and of some of the water molecules was indicated by high thermal-temperature factors. The total number of Cs^+ cations in the asymmetric unit was restrained and successfully refined to 2. An occupancy of 50% was assigned to some water oxygen atoms with higher thermal-temperature factors.

Table S1. Crystal data and structure refinement for *syn*-Cs₈H₂**3**•18H₂O.

Identification code	hill12	
Empirical formula	H38 Cs8 Nb6 O96 Si2 W18	
Formula weight	6560.21	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Cmcm	
Unit cell dimensions	a = 40.847(2) Å	a = 90°.
	b = 13.2130(7) Å	b = 90°.
	c = 16.8179(9) Å	g = 90°.
Volume	9076.7(8) Å ³	
Z	4	
Density (calculated)	4.804 Mg/m ³	
Absorption coefficient	26.742 mm ⁻¹	
F(000)	11360	
Crystal size	0.16 x 0.11 x 0.03 mm ³	
Theta range for data collection	1.00 to 28.32°.	
Index ranges	-35<=h<=53, -16<=k<=17, -21<=l<=22	
Reflections collected	26621	
Independent reflections	5733 [R(int) = 0.1374]	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	5733 / 1 / 294	
Goodness-of-fit on F ²	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0685, wR2 = 0.1407	
R indices (all data)	R1 = 0.1353, wR2 = 0.1647	
Extinction coefficient	0.000000(2)	
Largest diff. peak and hole	3.658 and -4.552 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *syn*-Cs₈H₂3•18H₂O. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	1920(1)	2287(1)	3499(1)	22(1)
W(2)	1641(1)	238(1)	2500	23(1)
W(3)	1434(1)	4661(1)	3503(1)	23(1)
W(4)	1139(1)	2393(1)	4622(1)	20(1)
W(5)	858(1)	362(1)	3610(1)	19(1)
Nb(1)	716(1)	4823(2)	2500	20(1)
Nb(2)	438(1)	2549(1)	3592(1)	18(1)
Si(1)	1157(2)	2470(5)	2500	9(1)
Cs(1)	1098(1)	-2398(2)	2500	74(1)
Cs(2)	0	418(5)	5268(4)	87(3)
Cs(3)	1996(1)	2300(2)	5888(1)	56(1)
Cs(4)	622(1)	5000	5000	41(1)
Cs(5)	0	-111(6)	2500	52(3)
O(1)	2243(4)	2334(11)	4135(9)	39(4)
O(2)	1577(3)	2070(10)	4211(8)	27(3)
O(3)	1926(3)	853(10)	3306(8)	24(3)
O(4)	2144(5)	2470(13)	2500	29(5)
O(5)	1782(3)	3629(10)	3416(8)	25(3)
O(6)	1775(5)	-997(14)	2500	26(5)
O(7)	1314(3)	147(11)	3268(9)	37(4)
O(8)	1623(3)	5487(10)	4138(8)	25(3)
O(9)	1591(5)	5166(14)	2500	30(5)
O(10)	1036(3)	5321(10)	3326(8)	28(3)
O(11)	1225(3)	3732(10)	4220(8)	24(3)
O(12)	1220(3)	2516(9)	5613(9)	29(4)
O(13)	1049(3)	993(9)	4542(8)	25(3)
O(14)	686(3)	2670(9)	4599(8)	25(3)
O(15)	755(3)	-808(10)	3920(9)	32(4)
O(16)	460(3)	1025(10)	3797(8)	22(3)
O(17)	763(4)	256(13)	2500	21(4)
O(18)	439(5)	5810(15)	2500	37(6)
O(19)	539(3)	3875(9)	3323(8)	25(3)
O(20)	0	2625(13)	3979(12)	26(5)
O(21)	363(4)	2238(12)	2500	13(4)
O(22)	1527(4)	1972(13)	2500	18(4)
O(23)	1185(4)	3690(12)	2500	12(4)
O(24)	960(3)	2112(8)	3289(7)	16(3)
OW1	1740(5)	0	5000	31(5)
OW2	2185(8)	3206(22)	7500	86(10)
OW3	0	5766(28)	4028(24)	126(14)
OW4	2673(9)	-305(27)	2279(31)	99(17)
OW5	2406(10)	424(27)	6185(23)	194(15)

OW6	2243(11)	4636(33)	4978(40)	118(21)
OW7	-337(16)	-2080(46)	2500	245(29)
OW8	141(25)	2031(59)	5898(55)	275(51)

Table S3. Bond lengths (Å) and angles (°) for *syn*-Cs₈H₂3•18H₂O.

W(1)-O(1)	1.699(14)	Nb(1)-Cs(1)#2	3.991(4)	Cs(3)-OW1	3.543(6)
W(1)-O(2)	1.866(14)	Nb(1)-Cs(4)#1	4.2285(4)	Cs(3)-OW6	3.59(5)
W(1)-O(5)	1.866(14)	Nb(1)-Cs(4)	4.2285(4)	Cs(4)-O(14)#11	
W(1)-O(3)	1.922(13)	Nb(2)-O(19)	1.856(12)	Cs(4)-O(14)	3.162(12)
W(1)-O(4)	1.928(10)	Nb(2)-O(20)	1.905(7)	Cs(4)-OW3	3.18(2)
W(1)-O(22)	2.363(12)	Nb(2)-O(21)	1.907(5)	Cs(4)-OW3#13	
W(1)-Cs(3)	4.029(2)	Nb(2)-O(14)	1.981(14)	Cs(4)-O(19)	3.206(14)
W(2)-O(6)	1.72(2)	Nb(2)-O(16)	2.046(13)	Cs(4)-O(19)#11	
W(2)-O(7)	1.864(15)	Nb(2)-O(24)	2.270(12)	Cs(4)-O(11)#11	
W(2)-O(7)#1	1.864(15)	Nb(2)-Cs(4)	4.081(2)	Cs(4)-O(11)	3.257(13)
W(2)-O(3)#1	1.964(13)	Nb(2)-Cs(5)	4.351(6)	Cs(4)-O(10)#11	
W(2)-O(3)	1.964(13)	Nb(2)-Cs(2)	4.366(6)	Cs(4)-O(10)	3.313(14)
W(2)-O(22)	2.34(2)	Si(1)-O(24)#1	1.622(12)	Cs(4)-Nb(2)#11	
W(2)-Cs(1)	4.129(3)	Si(1)-O(24)	1.622(12)	Cs(5)-OW7	2.94(6)
W(3)-O(8)	1.712(12)	Si(1)-O(23)	1.62(2)	Cs(5)-OW7#4	2.94(6)
W(3)-O(10)	1.867(14)	Si(1)-O(22)	1.65(2)	Cs(5)-O(17)	3.15(2)
W(3)-O(11)	1.919(13)	Cs(1)-OW7#4	3.14(6)	Cs(5)-O(17)#4	3.15(2)
W(3)-O(9)	1.925(10)	Cs(1)-O(12)#5	3.216(14)	Cs(5)-O(16)#1	3.246(13)
W(3)-O(5)	1.976(14)	Cs(1)-O(12)#6	3.216(14)	Cs(5)-O(16)	3.246(13)
W(3)-O(23)	2.351(11)	Cs(1)-O(10)#7	3.328(13)	Cs(5)-O(16)#4	3.246(13)
W(3)-Cs(4)	4.188(2)	Cs(1)-O(10)#8	3.328(13)	Cs(5)-O(16)#9	3.246(13)
W(3)-Cs(1)#2	4.452(3)	Cs(1)-O(6)	3.33(2)	Cs(5)-O(21)	3.44(2)
W(4)-O(12)	1.707(15)	Cs(1)-O(15)	3.48(2)	Cs(5)-O(21)#4	3.44(2)
W(4)-O(14)	1.886(13)	Cs(1)-O(15)#1	3.48(2)	Cs(5)-Cs(2)#14	
W(4)-O(13)	1.891(12)	Cs(1)-O(18)#8	3.59(2)	Cs(5)-Cs(2)#3	3.776(7)
W(4)-O(11)	1.927(13)	Cs(1)-O(7)#1	3.71(2)	O(1)-Cs(3)#10	3.144(15)
W(4)-O(2)	1.964(13)	Cs(1)-O(7)	3.71(2)	O(4)-W(1)#1	1.928(10)
W(4)-O(24)	2.386(12)	Cs(1)-O(17)	3.76(2)	O(6)-Cs(3)#5	3.337(11)
W(4)-Cs(4)	4.091(2)	Cs(2)-OW8	2.45(8)	O(6)-Cs(3)#6	3.337(11)
W(4)-Cs(3)	4.100(2)	Cs(2)-OW8#9	2.45(8)	O(8)-Cs(3)#11	3.298(13)
W(5)-O(15)	1.685(12)	Cs(2)-O(16)#6	3.103(13)	O(9)-W(3)#1	1.925(10)
W(5)-O(16)	1.873(13)	Cs(2)-O(16)#3	3.103(13)	O(9)-Cs(1)#2	3.80(2)
W(5)-O(17)	1.912(4)	Cs(2)-O(16)#9	3.207(13)	O(10)-Cs(1)#2	3.328(13)
W(5)-O(13)	1.940(13)	Cs(2)-O(16)	3.207(13)	O(12)-Cs(1)#12	
W(5)-O(7)	1.970(14)	Cs(2)-O(15)#6	3.41(2)	O(15)-Cs(2)#3	3.41(2)
W(5)-O(24)	2.411(11)	Cs(2)-O(15)#3	3.41(2)	O(16)-Cs(2)#3	3.103(13)
W(5)-Cs(5)	4.0184(15)	Cs(2)-O(20)	3.63(2)	O(17)-W(5)#1	1.912(4)
W(5)-Cs(2)#3	4.110(3)	Cs(2)-W(5)#6	4.110(3)	O(18)-Cs(1)#2	3.59(2)
W(5)-Cs(1)	4.214(3)	Cs(3)-OW5	3.03(4)	O(20)-Nb(2)#9	1.905(7)
W(5)-Cs(2)	4.477(4)	Cs(3)-OW2	3.063(14)	O(21)-Nb(2)#1	1.907(5)
Nb(1)-O(18)	1.73(2)	Cs(3)-O(1)	3.11(2)	O(22)-W(1)#1	2.363(12)
Nb(1)-O(19)	2.001(13)	Cs(3)-O(1)#10	3.144(15)	O(23)-W(3)#1	2.351(11)
Nb(1)-O(19)#1	2.001(13)	Cs(3)-O(12)	3.219(14)	OW1-Cs(3)#6	3.543(6)
Nb(1)-O(10)#1	2.019(14)	Cs(3)-O(8)#11	3.298(13)	OW2-Cs(3)#15	
Nb(1)-O(10)	2.019(14)	Cs(3)-O(2)	3.313(14)	OW3-Cs(4)#13	
Nb(1)-O(23)	2.43(2)	Cs(3)-O(6)#12	3.337(11)	OW7-Cs(1)#4	3.14(6)

O(1)-W(1)-O(2)	100.7(7)	O(8)-W(3)-O(5)	99.2(6)
O(1)-W(1)-O(5)	104.3(7)	O(10)-W(3)-O(5)	159.5(5)
O(2)-W(1)-O(5)	88.1(5)	O(11)-W(3)-O(5)	85.6(5)
O(1)-W(1)-O(3)	97.6(6)	O(9)-W(3)-O(5)	86.2(7)
O(2)-W(1)-O(3)	88.1(6)	O(8)-W(3)-O(23)	172.4(5)
O(5)-W(1)-O(3)	158.1(5)	O(10)-W(3)-O(23)	76.3(6)
O(1)-W(1)-O(4)	100.2(7)	O(11)-W(3)-O(23)	84.8(5)
O(2)-W(1)-O(4)	159.2(7)	O(9)-W(3)-O(23)	72.9(6)
O(5)-W(1)-O(4)	87.7(7)	O(5)-W(3)-O(23)	83.2(5)
O(3)-W(1)-O(4)	88.3(7)	O(8)-W(3)-Cs(4)	85.1(4)
O(1)-W(1)-O(22)	169.2(7)	O(10)-W(3)-Cs(4)	50.0(4)
O(2)-W(1)-O(22)	85.3(5)	O(11)-W(3)-Cs(4)	48.7(4)
O(5)-W(1)-O(22)	84.7(6)	O(9)-W(3)-Cs(4)	139.0(6)
O(3)-W(1)-O(22)	73.4(6)	O(5)-W(3)-Cs(4)	133.5(4)
O(4)-W(1)-O(22)	74.0(6)	O(23)-W(3)-Cs(4)	98.4(3)
O(1)-W(1)-Cs(3)	46.6(5)	O(8)-W(3)-Cs(1)#2	79.6(4)
O(2)-W(1)-Cs(3)	54.5(4)	O(10)-W(3)-Cs(1)#2	42.6(4)
O(5)-W(1)-Cs(3)	95.4(4)	O(11)-W(3)-Cs(1)#2	131.3(4)
O(3)-W(1)-Cs(3)	99.9(4)	O(9)-W(3)-Cs(1)#2	57.9(6)
O(4)-W(1)-Cs(3)	146.3(5)	O(5)-W(3)-Cs(1)#2	142.8(4)
O(22)-W(1)-Cs(3)	139.7(3)	O(23)-W(3)-Cs(1)#2	94.1(3)
O(6)-W(2)-O(7)	99.6(6)	Cs(4)-W(3)-Cs(1)#2	83.73(4)
O(6)-W(2)-O(7)#1	99.6(6)	O(12)-W(4)-O(14)	101.0(6)
O(7)-W(2)-O(7)#1	87.8(9)	O(12)-W(4)-O(13)	101.5(6)
O(6)-W(2)-O(3)#1	101.8(6)	O(14)-W(4)-O(13)	89.9(5)
O(7)-W(2)-O(3)#1	158.6(6)	O(12)-W(4)-O(11)	102.7(6)
O(7)#1-W(2)-O(3)#1	88.5(6)	O(14)-W(4)-O(11)	89.7(5)
O(6)-W(2)-O(3)	101.8(6)	O(13)-W(4)-O(11)	155.4(6)
O(7)-W(2)-O(3)	88.5(6)	O(12)-W(4)-O(2)	100.9(6)
O(7)#1-W(2)-O(3)	158.6(6)	O(14)-W(4)-O(2)	158.1(6)
O(3)#1-W(2)-O(3)	87.3(8)	O(13)-W(4)-O(2)	86.5(6)
O(6)-W(2)-O(22)	173.1(8)	O(11)-W(4)-O(2)	84.8(5)
O(7)-W(2)-O(22)	85.4(5)	O(12)-W(4)-O(24)	172.3(5)
O(7)#1-W(2)-O(22)	85.4(5)	O(14)-W(4)-O(24)	73.2(5)
O(3)#1-W(2)-O(22)	73.3(5)	O(13)-W(4)-O(24)	73.8(5)
O(3)-W(2)-O(22)	73.3(5)	O(11)-W(4)-O(24)	82.5(5)
O(6)-W(2)-Cs(1)	51.0(6)	O(2)-W(4)-O(24)	85.1(5)
O(7)-W(2)-Cs(1)	63.9(5)	O(12)-W(4)-Cs(4)	82.4(4)
O(7)#1-W(2)-Cs(1)	63.9(5)	O(14)-W(4)-Cs(4)	48.2(4)
O(3)#1-W(2)-Cs(1)	131.9(4)	O(13)-W(4)-Cs(4)	137.2(4)
O(3)-W(2)-Cs(1)	131.9(4)	O(11)-W(4)-Cs(4)	51.4(4)
O(22)-W(2)-Cs(1)	136.0(4)	O(2)-W(4)-Cs(4)	135.1(4)
O(8)-W(3)-O(10)	101.3(6)	O(24)-W(4)-Cs(4)	96.8(3)
O(8)-W(3)-O(11)	102.5(6)	O(12)-W(4)-Cs(3)	48.0(5)
O(10)-W(3)-O(11)	90.8(6)	O(14)-W(4)-Cs(3)	148.7(4)
O(8)-W(3)-O(9)	100.1(7)	O(13)-W(4)-Cs(3)	100.0(4)
O(10)-W(3)-O(9)	89.4(7)	O(11)-W(4)-Cs(3)	93.1(4)
O(11)-W(3)-O(9)	157.0(6)	O(2)-W(4)-Cs(3)	53.0(4)

O(24)-W(4)-Cs(3)	138.1(3)	O(18)-Nb(1)-O(10)#1	100.2(6)
Cs(4)-W(4)-Cs(3)	112.71(5)	O(19)-Nb(1)-O(10)#1	156.0(5)
O(15)-W(5)-O(16)	99.3(6)	O(19)#1-Nb(1)-O(10)#1	87.8(5)
O(15)-W(5)-O(17)	100.6(7)	O(18)-Nb(1)-O(10)	100.2(6)
O(16)-W(5)-O(17)	91.3(6)	O(19)-Nb(1)-O(10)	87.8(5)
O(15)-W(5)-O(13)	104.2(6)	O(19)#1-Nb(1)-O(10)	156.0(5)
O(16)-W(5)-O(13)	90.8(6)	O(10)#1-Nb(1)-O(10)	86.9(8)
O(17)-W(5)-O(13)	154.4(7)	O(18)-Nb(1)-O(23)	168.9(8)
O(15)-W(5)-O(7)	101.1(6)	O(19)-Nb(1)-O(23)	84.2(5)
O(16)-W(5)-O(7)	159.6(6)	O(19)#1-Nb(1)-O(23)	84.2(5)
O(17)-W(5)-O(7)	84.0(7)	O(10)#1-Nb(1)-O(23)	71.9(5)
O(13)-W(5)-O(7)	85.2(6)	O(10)-Nb(1)-O(23)	71.9(5)
O(15)-W(5)-O(24)	173.1(6)	O(18)-Nb(1)-Cs(1)#2	64.0(7)
O(16)-W(5)-O(24)	75.0(5)	O(19)-Nb(1)-Cs(1)#2	135.8(4)
O(17)-W(5)-O(24)	83.5(6)	O(19)#1-Nb(1)-Cs(1)#2	135.8(4)
O(13)-W(5)-O(24)	72.5(5)	O(10)#1-Nb(1)-Cs(1)#2	56.4(4)
O(7)-W(5)-O(24)	84.7(5)	O(10)-Nb(1)-Cs(1)#2	56.4(4)
O(15)-W(5)-Cs(5)	77.5(5)	O(23)-Nb(1)-Cs(1)#2	105.0(4)
O(16)-W(5)-Cs(5)	52.7(4)	O(18)-Nb(1)-Cs(4)#1	84.18(5)
O(17)-W(5)-Cs(5)	50.1(5)	O(19)-Nb(1)-Cs(4)#1	133.6(4)
O(13)-W(5)-Cs(5)	142.5(4)	O(19)#1-Nb(1)-Cs(4)#1	46.7(4)
O(7)-W(5)-Cs(5)	131.8(5)	O(10)#1-Nb(1)-Cs(4)#1	50.0(4)
O(24)-W(5)-Cs(5)	101.4(3)	O(10)-Nb(1)-Cs(4)#1	136.5(4)
O(15)-W(5)-Cs(2)#3	54.3(5)	O(23)-Nb(1)-Cs(4)#1	96.07(4)
O(16)-W(5)-Cs(2)#3	45.6(4)	Cs(1)#2-Nb(1)-Cs(4)#1	89.12(4)
O(17)-W(5)-Cs(2)#3	104.9(5)	O(18)-Nb(1)-Cs(4)	84.18(5)
O(13)-W(5)-Cs(2)#3	94.6(4)	O(19)-Nb(1)-Cs(4)	46.7(4)
O(7)-W(5)-Cs(2)#3	154.6(4)	O(19)#1-Nb(1)-Cs(4)	133.6(4)
O(24)-W(5)-Cs(2)#3	119.5(3)	O(10)#1-Nb(1)-Cs(4)	136.5(4)
Cs(5)-W(5)-Cs(2)#3	55.34(9)	O(10)-Nb(1)-Cs(4)	50.0(4)
O(15)-W(5)-Cs(1)	53.2(5)	O(23)-Nb(1)-Cs(4)	96.07(4)
O(16)-W(5)-Cs(1)	133.0(4)	Cs(1)#2-Nb(1)-Cs(4)	89.12(4)
O(17)-W(5)-Cs(1)	63.3(5)	Cs(4)#1-Nb(1)-Cs(4)	167.78(9)
O(13)-W(5)-Cs(1)	129.5(4)	O(19)-Nb(2)-O(20)	104.1(7)
O(7)-W(5)-Cs(1)	61.7(5)	O(19)-Nb(2)-O(21)	90.2(6)
O(24)-W(5)-Cs(1)	133.6(3)	O(20)-Nb(2)-O(21)	100.9(8)
Cs(5)-W(5)-Cs(1)	82.11(11)	O(19)-Nb(2)-O(14)	91.0(6)
Cs(2)#3-W(5)-Cs(1)	100.67(11)	O(20)-Nb(2)-O(14)	100.7(7)
O(15)-W(5)-Cs(2)	68.2(5)	O(21)-Nb(2)-O(14)	157.3(6)
O(16)-W(5)-Cs(2)	37.7(4)	O(19)-Nb(2)-O(16)	163.9(5)
O(17)-W(5)-Cs(2)	116.8(5)	O(20)-Nb(2)-O(16)	92.0(6)
O(13)-W(5)-Cs(2)	78.8(4)	O(21)-Nb(2)-O(16)	87.5(6)
O(7)-W(5)-Cs(2)	157.5(4)	O(14)-Nb(2)-O(16)	85.0(5)
O(24)-W(5)-Cs(2)	105.1(3)	O(19)-Nb(2)-O(24)	88.6(5)
Cs(5)-W(5)-Cs(2)	67.04(7)	O(20)-Nb(2)-O(24)	166.6(6)
Cs(1)-W(5)-Cs(2)	118.21(10)	O(21)-Nb(2)-O(24)	83.1(6)
O(18)-Nb(1)-O(19)	103.7(6)	O(14)-Nb(2)-O(24)	74.3(5)
O(18)-Nb(1)-O(19)#1	103.7(6)	O(16)-Nb(2)-O(24)	75.3(5)
O(19)-Nb(1)-O(19)#1	87.5(8)	O(19)-Nb(2)-Cs(4)	49.6(4)

O(20)-Nb(2)-Cs(4)	86.2(5)	O(12)#6-Cs(1)-O(15)#1	140.3(3)
O(21)-Nb(2)-Cs(4)	139.4(5)	O(10)#7-Cs(1)-O(15)#1	103.3(3)
O(14)-Nb(2)-Cs(4)	49.1(4)	O(10)#8-Cs(1)-O(15)#1	143.4(3)
O(16)-Nb(2)-Cs(4)	132.5(4)	O(6)-Cs(1)-O(15)#1	89.9(3)
O(24)-Nb(2)-Cs(4)	99.1(3)	O(15)-Cs(1)-O(15)#1	86.8(4)
O(19)-Nb(2)-Cs(5)	138.7(4)	OW7#4-Cs(1)-O(18)#8	49.0(11)
O(20)-Nb(2)-Cs(5)	78.5(5)	O(12)#5-Cs(1)-O(18)#8	94.8(3)
O(21)-Nb(2)-Cs(5)	49.7(5)	O(12)#6-Cs(1)-O(18)#8	94.8(3)
O(14)-Nb(2)-Cs(5)	129.6(4)	O(10)#7-Cs(1)-O(18)#8	49.0(3)
O(16)-Nb(2)-Cs(5)	45.0(4)	O(10)#8-Cs(1)-O(18)#8	49.0(3)
O(24)-Nb(2)-Cs(5)	94.9(3)	O(6)-Cs(1)-O(18)#8	172.5(4)
Cs(4)-Nb(2)-Cs(5)	164.11(6)	O(15)-Cs(1)-O(18)#8	95.5(3)
O(19)-Nb(2)-Cs(2)	149.0(4)	O(15)#1-Cs(1)-O(18)#8	95.5(3)
O(20)-Nb(2)-Cs(2)	55.2(6)	OW7#4-Cs(1)-O(7)#1	96.5(11)
O(21)-Nb(2)-Cs(2)	114.6(5)	O(12)#5-Cs(1)-O(7)#1	70.3(3)
O(14)-Nb(2)-Cs(2)	73.2(4)	O(12)#6-Cs(1)-O(7)#1	110.5(3)
O(16)-Nb(2)-Cs(2)	43.5(4)	O(10)#7-Cs(1)-O(7)#1	133.9(3)
O(24)-Nb(2)-Cs(2)	111.5(3)	O(10)#8-Cs(1)-O(7)#1	170.0(3)
Cs(4)-Nb(2)-Cs(2)	102.28(10)	O(6)-Cs(1)-O(7)#1	45.4(4)
Cs(5)-Nb(2)-Cs(2)	65.37(10)	O(15)-Cs(1)-O(7)#1	77.7(3)
O(24)#1-Si(1)-O(24)	109.9(9)	O(15)#1-Cs(1)-O(7)#1	46.2(3)
O(24)#1-Si(1)-O(23)	109.0(5)	O(18)#8-Cs(1)-O(7)#1	141.0(3)
O(24)-Si(1)-O(23)	109.0(5)	OW7#4-Cs(1)-O(7)	96.5(11)
O(24)#1-Si(1)-O(22)	109.7(6)	O(12)#5-Cs(1)-O(7)	110.5(3)
O(24)-Si(1)-O(22)	109.7(6)	O(12)#6-Cs(1)-O(7)	70.3(3)
O(23)-Si(1)-O(22)	109.5(9)	O(10)#7-Cs(1)-O(7)	170.0(3)
OW7#4-Cs(1)-O(12)#5	99.2(3)	O(10)#8-Cs(1)-O(7)	133.9(3)
OW7#4-Cs(1)-O(12)#6	99.2(3)	O(6)-Cs(1)-O(7)	45.4(4)
O(12)#5-Cs(1)-O(12)#6	161.4(5)	O(15)-Cs(1)-O(7)	46.2(3)
OW7#4-Cs(1)-O(10)#7	92.6(10)	O(15)#1-Cs(1)-O(7)	77.7(3)
O(12)#5-Cs(1)-O(10)#7	63.7(3)	O(18)#8-Cs(1)-O(7)	141.0(3)
O(12)#6-Cs(1)-O(10)#7	112.3(3)	O(7)#1-Cs(1)-O(7)	40.8(5)
OW7#4-Cs(1)-O(10)#8	92.6(10)	OW7#4-Cs(1)-O(17)	61.0(12)
O(12)#5-Cs(1)-O(10)#8	112.3(3)	O(12)#5-Cs(1)-O(17)	95.8(2)
O(12)#6-Cs(1)-O(10)#8	63.7(3)	O(12)#6-Cs(1)-O(17)	95.8(2)
O(10)#7-Cs(1)-O(10)#8	49.3(5)	O(10)#7-Cs(1)-O(17)	144.7(3)
OW7#4-Cs(1)-O(6)	138.5(12)	O(10)#8-Cs(1)-O(17)	144.7(3)
O(12)#5-Cs(1)-O(6)	84.2(3)	O(6)-Cs(1)-O(17)	77.5(4)
O(12)#6-Cs(1)-O(6)	84.2(3)	O(15)-Cs(1)-O(17)	44.8(2)
O(10)#7-Cs(1)-O(6)	124.6(4)	O(15)#1-Cs(1)-O(17)	44.8(2)
O(10)#8-Cs(1)-O(6)	124.6(4)	O(18)#8-Cs(1)-O(17)	110.0(4)
OW7#4-Cs(1)-O(15)	61.3(7)	O(7)#1-Cs(1)-O(17)	40.7(3)
O(12)#5-Cs(1)-O(15)	140.3(3)	O(7)-Cs(1)-O(17)	40.7(3)
O(12)#6-Cs(1)-O(15)	54.1(3)	Cs(2)#3-Cs(2)-OW8	161.5(23)
O(10)#7-Cs(1)-O(15)	143.4(3)	Cs(2)#3-Cs(2)-OW8#9	161.5(23)
O(10)#8-Cs(1)-O(15)	103.3(3)	OW8-Cs(2)-OW8#9	27.2(46)
O(6)-Cs(1)-O(15)	89.9(3)	Cs(2)#3-Cs(2)-O(16)#6	81.0(5)
OW7#4-Cs(1)-O(15)#1	61.3(7)	OW8-Cs(2)-O(16)#6	100.0(22)
O(12)#5-Cs(1)-O(15)#1	54.1(3)	OW8#9-Cs(2)-O(16)#6	117.2(22)

Cs(2)#3-Cs(2)-O(16)#3	81.0(5)	Cs(2)#3-Cs(2)-W(5)#6	95.5(3)
OW8-Cs(2)-O(16)#3	117.2(22)	OW8-Cs(2)-W(5)#6	79.6(23)
OW8#9-Cs(2)-O(16)#3	100.0(22)	OW8#9-Cs(2)-W(5)#6	102.7(23)
O(16)#6-Cs(2)-O(16)#3	74.4(5)	O(16)#6-Cs(2)-W(5)#6	25.5(2)
Cs(2)#3-Cs(2)-O(16)#9	72.9(4)	O(16)#3-Cs(2)-W(5)#6	97.4(3)
OW8-Cs(2)-O(16)#9	104.7(22)	O(16)#9-Cs(2)-W(5)#6	156.3(3)
OW8#9-Cs(2)-O(16)#9	88.8(22)	O(16)-Cs(2)-W(5)#6	85.3(2)
O(16)#6-Cs(2)-O(16)#9	153.9(3)	O(15)#6-Cs(2)-W(5)#6	23.6(2)
O(16)#3-Cs(2)-O(16)#9	101.0(4)	O(15)#3-Cs(2)-W(5)#6	128.6(3)
Cs(2)#3-Cs(2)-O(16)	72.9(4)	O(20)-Cs(2)-W(5)#6	118.37(12)
OW8-Cs(2)-O(16)	88.8(22)	Cs(5)#3-Cs(2)-W(5)#6	61.10(8)
OW8#9-Cs(2)-O(16)	104.7(22)	OW5-Cs(3)-OW2	92.0(9)
O(16)#6-Cs(2)-O(16)	101.0(4)	OW5-Cs(3)-O(1)	89.4(8)
O(16)#3-Cs(2)-O(16)	153.9(3)	OW2-Cs(3)-O(1)	138.6(6)
O(16)#9-Cs(2)-O(16)	71.7(5)	OW5-Cs(3)-O(1)#10	65.3(8)
Cs(2)#3-Cs(2)-O(15)#6	111.7(3)	OW2-Cs(3)-O(1)#10	72.6(6)
OW8-Cs(2)-O(15)#6	58.9(23)	O(1)-Cs(3)-O(1)#10	70.5(4)
OW8#9-Cs(2)-O(15)#6	84.7(23)	OW5-Cs(3)-O(12)	129.8(7)
O(16)#6-Cs(2)-O(15)#6	48.9(3)	OW2-Cs(3)-O(12)	109.9(6)
O(16)#3-Cs(2)-O(15)#6	115.9(4)	O(1)-Cs(3)-O(12)	100.5(4)
O(16)#9-Cs(2)-O(15)#6	143.1(4)	O(1)#10-Cs(3)-O(12)	163.4(4)
O(16)-Cs(2)-O(15)#6	75.0(3)	OW5-Cs(3)-O(8)#11	169.1(8)
Cs(2)#3-Cs(2)-O(15)#3	111.7(3)	OW2-Cs(3)-O(8)#11	77.4(6)
OW8-Cs(2)-O(15)#3	84.7(23)	O(1)-Cs(3)-O(8)#11	97.1(4)
OW8#9-Cs(2)-O(15)#3	58.9(23)	O(1)#10-Cs(3)-O(8)#11	108.6(4)
O(16)#6-Cs(2)-O(15)#3	115.9(4)	O(12)-Cs(3)-O(8)#11	57.6(3)
O(16)#3-Cs(2)-O(15)#3	48.9(3)	OW5-Cs(3)-O(2)	110.6(8)
O(16)#9-Cs(2)-O(15)#3	75.0(3)	OW2-Cs(3)-O(2)	156.8(6)
O(16)-Cs(2)-O(15)#3	143.1(4)	O(1)-Cs(3)-O(2)	50.5(4)
O(15)#6-Cs(2)-O(15)#3	129.3(5)	O(1)#10-Cs(3)-O(2)	121.0(4)
Cs(2)#3-Cs(2)-O(20)	104.2(6)	O(12)-Cs(3)-O(2)	51.4(3)
OW8-Cs(2)-O(20)	63.9(21)	O(8)#11-Cs(3)-O(2)	80.3(3)
OW8#9-Cs(2)-O(20)	63.9(21)	OW5-Cs(3)-O(6)#12	66.1(8)
O(16)#6-Cs(2)-O(20)	142.7(2)	OW2-Cs(3)-O(6)#12	63.3(6)
O(16)#3-Cs(2)-O(20)	142.7(2)	O(1)-Cs(3)-O(6)#12	149.8(4)
O(16)#9-Cs(2)-O(20)	48.6(3)	O(1)#10-Cs(3)-O(6)#12	111.0(4)
O(16)-Cs(2)-O(20)	48.6(3)	O(12)-Cs(3)-O(6)#12	84.0(4)
O(15)#6-Cs(2)-O(20)	96.8(3)	O(8)#11-Cs(3)-O(6)#12	110.0(4)
O(15)#3-Cs(2)-O(20)	96.8(3)	O(2)-Cs(3)-O(6)#12	120.3(4)
Cs(2)#3-Cs(2)-Cs(5)#3	123.0(6)	OW5-Cs(3)-OW1	62.1(7)
OW8-Cs(2)-Cs(5)#3	70.3(21)	OW2-Cs(3)-OW1	141.5(5)
OW8#9-Cs(2)-Cs(5)#3	70.3(21)	O(1)-Cs(3)-OW1	73.1(3)
O(16)#6-Cs(2)-Cs(5)#3	55.3(3)	O(1)#10-Cs(3)-OW1	114.7(4)
O(16)#3-Cs(2)-Cs(5)#3	55.3(3)	O(12)-Cs(3)-OW1	74.0(4)
O(16)#9-Cs(2)-Cs(5)#3	142.5(2)	O(8)#11-Cs(3)-OW1	128.2(4)
O(16)-Cs(2)-Cs(5)#3	142.5(2)	O(2)-Cs(3)-OW1	53.9(3)
O(15)#6-Cs(2)-Cs(5)#3	67.6(3)	O(6)#12-Cs(3)-OW1	79.6(3)
O(15)#3-Cs(2)-Cs(5)#3	67.6(3)	OW5-Cs(3)-OW6	128.2(10)
O(20)-Cs(2)-Cs(5)#3	132.8(4)	OW2-Cs(3)-OW6	88.3(11)

O(1)-Cs(3)-OW6	59.6(10)	O(14)-Cs(4)-O(11)	49.5(3)
O(1)#10-Cs(3)-OW6	65.5(8)	OW3-Cs(4)-O(11)	124.1(7)
O(12)-Cs(3)-OW6	98.0(7)	OW3#13-Cs(4)-O(11)	130.3(7)
O(8)#11-Cs(3)-OW6	50.3(8)	O(19)-Cs(4)-O(11)	59.1(3)
O(2)-Cs(3)-OW6	82.0(10)	O(19)#11-Cs(4)-O(11)	132.3(3)
O(6)#12-Cs(3)-OW6	150.0(10)	O(11)#11-Cs(4)-O(11)	81.5(4)
OW1-Cs(3)-OW6	129.8(10)	O(14)#11-Cs(4)-O(10)#11	184.3(3)
OW5-Cs(3)-W(1)	101.8(7)	O(14)-Cs(4)-O(10)#11	90.8(3)
OW2-Cs(3)-W(1)	154.6(5)	OW3-Cs(4)-O(10)#11	152.2(7)
O(1)-Cs(3)-W(1)	23.3(3)	OW3#13-Cs(4)-O(10)#11	86.0(6)
O(1)#10-Cs(3)-W(1)	93.7(3)	O(19)-Cs(4)-O(10)#11	137.9(3)
O(12)-Cs(3)-W(1)	77.4(3)	O(19)#11-Cs(4)-O(10)#11	150.6(3)
O(8)#11-Cs(3)-W(1)	87.4(2)	O(11)#11-Cs(4)-O(10)#11	148.4(3)
O(2)-Cs(3)-W(1)	27.3(2)	O(11)-Cs(4)-O(10)#11	83.6(3)
O(6)#12-Cs(3)-W(1)	141.9(3)	O(14)#11-Cs(4)-O(10)	90.8(3)
OW1-Cs(3)-W(1)	63.48(4)	O(14)-Cs(4)-O(10)	84.3(3)
OW6-Cs(3)-W(1)	66.4(10)	OW3-Cs(4)-O(10)	86.0(6)
OW5-Cs(3)-W(4)	125.6(7)	OW3#13-Cs(4)-O(10)	152.2(7)
OW2-Cs(3)-W(4)	131.5(6)	O(19)-Cs(4)-O(10)	50.6(3)
O(1)-Cs(3)-W(4)	77.6(3)	O(19)#11-Cs(4)-O(10)	137.9(3)
O(1)#10-Cs(3)-W(4)	146.4(3)	O(11)#11-Cs(4)-O(10)	83.6(3)
O(12)-Cs(3)-W(4)	23.2(3)	O(11)-Cs(4)-O(10)	48.4(3)
O(8)#11-Cs(3)-W(4)	64.6(2)	O(10)#11-Cs(4)-O(10)	118.5(5)
O(6)#12-Cs(3)-W(4)	101.9(3)	O(14)#11-Cs(4)-Nb(2)	155.7(2)
OW1-Cs(3)-W(4)	63.6(3)	OW3-Cs(4)-Nb(2)	78.9(7)
OW6-Cs(3)-W(4)	89.5(8)	OW3#13-Cs(4)-Nb(2)	84.2(7)
W(1)-Cs(3)-W(4)	54.30(3)	O(19)#11-Cs(4)-Nb(2)	149.2(2)
O(14)#11-Cs(4)-O(14)	170.4(5)	O(11)#11-Cs(4)-Nb(2)	141.4(2)
O(14)#11-Cs(4)-OW3	82.3(7)	O(11)-Cs(4)-Nb(2)	59.9(2)
O(14)-Cs(4)-OW3	105.5(7)	O(10)#11-Cs(4)-Nb(2)	119.0(2)
O(14)#11-Cs(4)-OW3#13	105.5(7)	O(10)-Cs(4)-Nb(2)	72.7(2)
O(14)-Cs(4)-OW3#13	82.3(7)	O(14)-Cs(4)-Nb(2)#11	155.7(2)
OW3-Cs(4)-OW3#13	74.3(11)	OW3-Cs(4)-Nb(2)#11	84.2(7)
O(14)#11-Cs(4)-O(19)	130.4(3)	OW3#13-Cs(4)-Nb(2)#11	78.9(7)
O(14)-Cs(4)-O(19)	50.9(3)	O(19)-Cs(4)-Nb(2)#11	149.2(2)
OW3-Cs(4)-O(19)	67.2(7)	O(11)#11-Cs(4)-Nb(2)#11	59.9(2)
OW3#13-Cs(4)-O(19)	102.7(7)	O(11)-Cs(4)-Nb(2)#11	141.4(2)
O(14)#11-Cs(4)-O(19)#11	150.9(3)	O(10)#11-Cs(4)-Nb(2)#11	72.7(2)
O(14)-Cs(4)-O(19)#11	130.4(3)	O(10)-Cs(4)-Nb(2)#11	119.0(2)
OW3-Cs(4)-O(19)#11	102.7(7)	Nb(2)-Cs(4)-Nb(2)#11	158.77(9)
OW3#13-Cs(4)-O(19)#11	67.2(7)	OW7-Cs(5)-OW7#4	55.8(25)
O(19)-Cs(4)-O(19)#11	167.9(5)	OW7-Cs(5)-O(17)	126.7(13)
O(14)#11-Cs(4)-O(11)#11	149.5(3)	OW7#4-Cs(5)-O(17)	71.0(13)
O(14)-Cs(4)-O(11)#11	121.5(3)	OW7-Cs(5)-O(17)#4	71.0(13)
OW3-Cs(4)-O(11)#11	130.3(7)	OW7#4-Cs(5)-O(17)#4	126.7(13)
OW3#13-Cs(4)-O(11)#11	124.1(7)	O(17)-Cs(5)-O(17)#4	162.3(7)
O(19)-Cs(4)-O(11)#11	132.3(3)	OW7-Cs(5)-O(16)#1	132.8(6)
O(19)#11-Cs(4)-O(11)#11	159.1(3)	OW7#4-Cs(5)-O(16)#1	98.0(9)
O(14)#11-Cs(4)-O(11)	121.5(3)	O(17)-Cs(5)-O(16)#1	50.0(3)

O(17)#4-Cs(5)-O(16)#1	120.0(3)	O(17)#4-Cs(5)-Cs(2)#3	90.95(4)
OW7-Cs(5)-O(16)	132.8(6)	O(16)#1-Cs(5)-Cs(2)#3	135.9(3)
OW7#4-Cs(5)-O(16)	98.0(9)	O(16)-Cs(5)-Cs(2)#3	51.8(2)
O(17)-Cs(5)-O(16)	50.0(3)	O(16)#4-Cs(5)-Cs(2)#3	135.9(3)
O(17)#4-Cs(5)-O(16)	120.0(3)	O(16)#9-Cs(5)-Cs(2)#3	51.8(2)
O(16)#1-Cs(5)-O(16)	84.5(5)	O(21)-Cs(5)-Cs(2)#3	95.56(14)
OW7-Cs(5)-O(16)#4	98.0(9)	O(21)#4-Cs(5)-Cs(2)#3	95.56(14)
OW7#4-Cs(5)-O(16)#4	132.8(6)	Cs(2)#14-Cs(5)-Cs(2)#3	167.7(3)
O(17)-Cs(5)-O(16)#4	120.0(3)	W(1)-O(1)-Cs(3)	110.1(7)
O(17)#4-Cs(5)-O(16)#4	50.0(3)	W(1)-O(1)-Cs(3)#10	139.9(7)
O(16)#1-Cs(5)-O(16)#4	70.7(5)	Cs(3)-O(1)-Cs(3)#10	109.5(4)
O(16)-Cs(5)-O(16)#4	124.9(5)	W(1)-O(2)-W(4)	151.2(7)
OW7-Cs(5)-O(16)#9	98.0(9)	W(1)-O(2)-Cs(3)	98.2(5)
OW7#4-Cs(5)-O(16)#9	132.8(6)	W(4)-O(2)-Cs(3)	98.7(5)
O(17)-Cs(5)-O(16)#9	120.0(3)	W(1)-O(3)-W(2)	121.2(6)
O(17)#4-Cs(5)-O(16)#9	50.0(3)	W(1)#1-O(4)-W(1)	121.3(10)
O(16)#1-Cs(5)-O(16)#9	124.9(5)	W(1)-O(5)-W(3)	150.3(7)
O(16)-Cs(5)-O(16)#9	70.7(5)	W(2)-O(6)-Cs(1)	105.4(8)
O(16)#4-Cs(5)-O(16)#9	84.5(5)	W(2)-O(6)-Cs(3)#5	125.1(3)
OW7-Cs(5)-O(21)	177.6(13)	Cs(1)-O(6)-Cs(3)#5	86.5(4)
OW7#4-Cs(5)-O(21)	126.6(13)	W(2)-O(6)-Cs(3)#6	125.1(3)
O(17)-Cs(5)-O(21)	55.6(4)	Cs(1)-O(6)-Cs(3)#6	86.5(4)
O(17)#4-Cs(5)-O(21)	106.7(5)	Cs(3)#5-O(6)-Cs(3)#6	108.7(5)
O(16)#1-Cs(5)-O(21)	48.2(3)	W(2)-O(7)-W(5)	150.7(8)
O(16)-Cs(5)-O(21)	48.2(3)	W(2)-O(7)-Cs(1)	89.2(6)
O(16)#4-Cs(5)-O(21)	80.3(3)	W(5)-O(7)-Cs(1)	90.5(5)
O(16)#9-Cs(5)-O(21)	80.3(3)	W(3)-O(8)-Cs(3)#11	140.0(6)
OW7-Cs(5)-O(21)#4	126.6(13)	W(3)#1-O(9)-W(3)	122.4(10)
OW7#4-Cs(5)-O(21)#4	177.6(13)	W(3)#1-O(9)-Cs(1)#2	96.7(6)
O(17)-Cs(5)-O(21)#4	106.7(5)	W(3)-O(9)-Cs(1)#2	96.7(6)
O(17)#4-Cs(5)-O(21)#4	55.6(4)	W(3)-O(10)-Nb(1)	121.4(7)
O(16)#1-Cs(5)-O(21)#4	80.3(3)	W(3)-O(10)-Cs(4)	104.4(5)
O(16)-Cs(5)-O(21)#4	80.3(3)	Nb(1)-O(10)-Cs(4)	102.2(5)
O(16)#4-Cs(5)-O(21)#4	48.2(3)	W(3)-O(10)-Cs(1)#2	115.0(6)
O(16)#9-Cs(5)-O(21)#4	48.2(3)	Nb(1)-O(10)-Cs(1)#2	93.3(5)
O(21)-Cs(5)-O(21)#4	51.0(6)	Cs(4)-O(10)-Cs(1)#2	120.6(4)
OW7-Cs(5)-Cs(2)#14	84.6(2)	W(3)-O(11)-W(4)	152.7(8)
OW7#4-Cs(5)-Cs(2)#14	84.6(2)	W(3)-O(11)-Cs(4)	105.1(5)
O(17)-Cs(5)-Cs(2)#14	90.95(4)	W(4)-O(11)-Cs(4)	101.1(5)
O(17)#4-Cs(5)-Cs(2)#14	90.95(4)	W(4)-O(12)-Cs(1)#12	158.4(7)
O(16)#1-Cs(5)-Cs(2)#14	51.8(2)	W(4)-O(12)-Cs(3)	108.8(6)
O(16)-Cs(5)-Cs(2)#14	135.9(3)	Cs(1)#12-O(12)-Cs(3)	90.4(4)
O(16)#4-Cs(5)-Cs(2)#14	51.8(2)	W(4)-O(13)-W(5)	123.8(7)
O(16)#9-Cs(5)-Cs(2)#14	135.9(3)	W(4)-O(14)-Nb(2)	120.3(7)
O(21)-Cs(5)-Cs(2)#14	95.56(14)	W(4)-O(14)-Cs(4)	105.5(5)
O(21)#4-Cs(5)-Cs(2)#14	95.56(14)	Nb(2)-O(14)-Cs(4)	102.6(5)
OW7-Cs(5)-Cs(2)#3	84.6(2)	W(5)-O(15)-Cs(2)#3	102.1(6)
OW7#4-Cs(5)-Cs(2)#3	84.6(2)	W(5)-O(15)-Cs(1)	104.0(6)
O(17)-Cs(5)-Cs(2)#3	90.95(4)	Cs(2)#3-O(15)-Cs(1)	137.0(4)

W(5)-O(16)-Nb(2)	118.0(6)	Si(1)-O(22)-W(2)	125.0(9)
W(5)-O(16)-Cs(2)#3	108.8(5)	Si(1)-O(22)-W(1)#1	123.6(6)
Nb(2)-O(16)-Cs(2)#3	131.6(6)	W(2)-O(22)-W(1)#1	92.1(5)
W(5)-O(16)-Cs(2)	121.4(5)	Si(1)-O(22)-W(1)	123.6(6)
Nb(2)-O(16)-Cs(2)	110.5(5)	W(2)-O(22)-W(1)	92.1(5)
W(5)-O(16)-Cs(5)	100.0(5)	W(1)#1-O(22)-W(1)	90.7(6)
Nb(2)-O(16)-Cs(5)	108.5(5)	Si(1)-O(23)-W(3)#1	125.1(5)
Cs(2)#3-O(16)-Cs(5)	72.9(3)	Si(1)-O(23)-W(3)	125.1(5)
Cs(2)-O(16)-Cs(5)	93.7(3)	W(3)#1-O(23)-W(3)	91.7(6)
W(5)#1-O(17)-W(5)	155.1(11)	Si(1)-O(23)-Nb(1)	124.0(9)
W(5)#1-O(17)-Cs(5)	102.2(5)	W(3)#1-O(23)-Nb(1)	90.3(5)
W(5)-O(17)-Cs(5)	102.2(5)	W(3)-O(23)-Nb(1)	90.3(5)
W(5)#1-O(17)-Cs(1)	89.7(5)	Si(1)-O(24)-Nb(2)	125.1(7)
W(5)-O(17)-Cs(1)	89.7(5)	Si(1)-O(24)-W(4)	124.9(7)
Cs(5)-O(17)-Cs(1)	102.5(5)	Nb(2)-O(24)-W(4)	92.2(4)
Nb(1)-O(18)-Cs(1)#2	90.4(8)	Si(1)-O(24)-W(5)	123.3(6)
Nb(2)-O(19)-Nb(1)	147.1(8)	Nb(2)-O(24)-W(5)	91.7(4)
Nb(2)-O(19)-Cs(4)	104.2(5)	W(4)-O(24)-W(5)	89.6(4)
Nb(1)-O(19)-Cs(4)	106.3(5)	Cs(3)#6-OW1-Cs(3)	145.7(6)
Nb(2)-O(20)-Nb(2)#9	139.6(12)	Cs(3)-OW2-Cs(3)#15	124.5(10)
Nb(2)-O(20)-Cs(2)	99.3(6)	Cs(4)-OW3-Cs(4)#13	105.7(11)
Nb(2)#9-O(20)-Cs(2)	99.3(6)	OW6#11-OW6-Cs(3)	145.6(76)
Nb(2)#1-O(21)-Nb(2)	148.8(9)	Cs(5)-OW7-Cs(1)#4	125.6(21)
Nb(2)#1-O(21)-Cs(5)	105.3(5)	OW8#9-OW8-Cs(2)	76.4(23)
Nb(2)-O(21)-Cs(5)	105.3(5)		

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z+1/2 #2 x,y+1,z #3 -x,-y,-z+1 #4 -x,y,-z+1/2

#5 x,-y,z-1/2 #6 x,-y,-z+1 #7 x,y-1,-z+1/2

#8 x,y-1,z #9 -x,y,z #10 -x+1/2,-y+1/2,-z+1

#11 x,-y+1,-z+1 #12 x,-y,z+1/2 #13 -x,-y+1,-z+1

#14 -x,-y,z-1/2 #15 x,y,-z+3/2

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *syn*-Cs₈H₂3•18H₂O. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
W(1)	6(1)	34(1)	26(1)	0(1)	-2(1)	-1(1)
W(2)	11(1)	27(1)	30(1)	0	0	4(1)
W(3)	17(1)	24(1)	26(1)	-3(1)	-1(1)	-5(1)
W(4)	11(1)	30(1)	19(1)	0(1)	-1(1)	-2(1)
W(5)	13(1)	23(1)	22(1)	2(1)	0(1)	-2(1)
Nb(1)	14(1)	18(1)	27(2)	0	0	1(1)
Nb(2)	6(1)	26(1)	21(1)	-1(1)	1(1)	1(1)
Si(1)	2(3)	10(3)	16(4)	0	0	1(3)
Cs(1)	138(4)	40(2)	45(2)	0	0	-24(2)
Cs(2)	28(3)	141(8)	93(6)	81(5)	0	0
Cs(3)	30(1)	95(2)	42(1)	6(1)	-3(1)	-2(1)
Cs(4)	35(2)	44(2)	45(2)	-18(1)	0	0
Cs(5)	25(4)	64(5)	67(5)	0	0	0
O(1)	21(9)	70(11)	25(9)	8(8)	-12(7)	0(8)
O(2)	9(7)	33(8)	40(9)	17(7)	-10(6)	-3(6)
O(3)	5(7)	35(8)	34(9)	2(7)	-1(6)	12(6)
O(5)	15(8)	32(8)	28(8)	-14(6)	12(6)	-18(6)
O(7)	21(9)	44(9)	44(10)	23(8)	2(7)	2(8)
O(8)	19(8)	36(8)	19(8)	-11(6)	-6(6)	-10(6)
O(9)	49(15)	29(11)	11(10)	0	0	1(10)
O(10)	29(9)	25(8)	31(9)	1(6)	-1(7)	-3(7)
O(11)	6(7)	38(8)	26(8)	-2(7)	1(6)	-8(6)
O(12)	30(9)	31(8)	26(9)	0(7)	8(7)	-7(7)
O(14)	21(8)	23(7)	32(9)	4(6)	4(6)	1(6)
O(15)	28(9)	24(8)	45(10)	15(7)	-12(7)	-7(7)
O(16)	13(7)	31(8)	23(8)	3(6)	2(6)	-4(6)
O(17)	17(11)	23(10)	23(11)	0	0	13(9)
O(18)	18(12)	41(13)	53(16)	0	0	22(10)
O(19)	12(7)	21(7)	41(9)	3(6)	-5(6)	-3(6)
O(20)	3(10)	28(11)	46(14)	0(10)	0	0
O(23)	3(9)	16(9)	18(10)	0	0	2(7)