Electronic Supplementary Information

Cesium salts of niobo-tungstate isopolyanions with intermediate group V-group VI character

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List of Figures and Tables

Materials and Methods

Starting Materials

All reagents starting materials were purchased from VWR and used without further purification: $NbCl_5$ (99 %), $Na_2WO_4{\cdot}2H_2O$ (95 %), CsCl (99 %), KOH (85‑100 %), CsOH (99.9 %), hydrogen peroxide (30 wt%), isopropyl alcohol, and methanol. Literature procedures were used in the syntheses of $K_3[Nb(O_2)_4]$ and $Cs_3[Nb(O_2)_4]$[1] and their identities were confirmed by FTIR and UV-Vis spectroscopies.

X-Ray Crystallography

Diffraction intensities were collected at 150 K (CsNa**{Nb_4W_2}**) and 173 K (Cs and CsNa**{Nb_2W_4}**) on a Bruker Apex2 CCD diffractometer using Mo-Kα radiation, λ = 0.71073 Å. Space groups were determined based on systematic absences. Absorption corrections were applied by SADABS.[2] Structures were solved by direct methods and Fourier techniques and refined on F^2 using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms in solvent water molecules in CsNa**{Nb_4W_2}** were located and refined with isotropic thermal parameters, but with restrictions. An O-H distance of 1.0 Å was used in the refinement as a target for all O-H bonds. H atoms in Cs**{Nb_2W_4}** and CsNa**{Nb_2W_4}** were not found and not taken into consideration. Occupation factor refinements showed that in all investigated structures, W and Nb atoms share the same positions in the $(W/Nb)_6O_{19}$-unit, but the W/Nb ratio at different positions is varied. In CsNa**{Nb_4W_2}** and Cs**{Nb_2W_4},** the $(W/Nb)_6O_{19}$-unit is centro-symmetric and there are three W/Nb positions. Refinement shows that W and Nb atoms share these positions in ratios 0.498/0.502; 0.319/0.681; 0.235/0.765 (CsNa**{Nb_4W_2}**) and 0.871/0.129; 0.623/0377; 0.523/0.477 (Cs**{Nb_2W_4}**). These ratios provide formulae of $Cs_4Na_2Nb_{3.89}W_{2.11}O_{19}$ and $Cs_4Nb_{1.97}W_{4.03}O_{19}$, for the $(W/Nb)_6O_{19}$-units in CsNa**{Nb_4W_2}**, Cs**{Nb_2W_4}**, respectively. In CsNa**{Nb_2W_4}** the $(W/Nb)_6O_{19}$-unit C_3-symmetry with two symmetrically independent positions. Refinement shows that W and Nb atoms share both these positions with different ratios -- 0.756/0.244 and 0.532/0.468, providing a formula of $Cs_3NaNb_{2.14}W_{3.86}O_{19}$ for CsNa**{Nb_2W_4}**. Two Cs atoms in Cs**{Nb_2W_4}** and two Cs and one Na atoms in CsNa**{Nb_4W_2}** are located in a general positions. The Na atom in CsNa**{Nb_2W_4}** is located on a three-fold axis and the Cs atom is in a general position. In all structures Cs and Na atoms are joined by solvent water molecules. The CsNa**{Nb_2W_4}** structure is a racemic twin consisting of two blocks in the ratio 0.65/0.35. All calculations were performed by the Bruker SHELXTL (v. 6.10)[3] and SHELXL-2013 packages.[4]

Scanning Electron Microscopy (SEM) / Energy Dispersive X-ray Spectroscopy (EDX)

Micrographs and spectra of the crystalline materials were obtained from a Quanta 600F instrument (FEI).

Electrospray Ionization Mass Spectroscopy (ESI-MS)

Mass spectra were obtained from an Agilent 6230 ESI-MS system comprised of a Time-of-Flight (TOF) mass spectrometer coupled to an electrospray ioniser. 100 µL volumes of compound solutions (0.1 mM in H_2O) were first mixed with a water mobile phase and then infused into the ESI‑MS system at a flow rate of 0.5 mL min^{-1} using an Agilent 1260 Infinity quaternary pump. The solutions were nebulized with the aid of heated N_2 (325 ^oC) flowing at 8 L min^{-1} and a pressure of 35 psi (241 kPa). The voltages of the capillary, skimmer and RT octopole were set at 3500, 65 and 750 V respectively, while the voltage of the fragmentor was set at 100 V.

Fourier-Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded in attenuated reflectance mode (ATR) using a Nicolet™ iS™ 10 spectrometer (Thermo Scientific).

Ultraviolet-Visible Spectroscopy (UV-Vis)

Electronic absorption spectra were recorded on an Evolution™ 220 spectrophotometer (Thermo Scientific).

Thermogravimetric Analysis (TGA)

Crystalline samples (10-20 mg) were placed in alumina crucibles and the corresponding thermograms were recorded under air flow (100 mL min^{-1}) on a SDT Q600 instrument (TA).

pH measurements

The pH of the reaction mixtures was measured using an Orion™ VERSA STAR™ pH/ISE Benchtop Multiparameter Meter. The instrument was calibrated using standard solutions before each round of measurements.

Experimental Details

Crystallographic Data

Table S1: Summary of the crystallographic refinement data for CsNa**{Nb_4W_2}**, Cs**{Nb_2W_4}**, and CsNa**{Nb_2W_4}**.

	CsNa{Nb_4W_2}	Cs{Nb_2W_4}	CsNa{Nb_2W_4}
Empirical Formula	$Cs_4H_{24}Na_2O_{31}Nb_{3.89}W_{2.11}$	$Cs_4H_3O_{31}Nb_{1.97}W_{4.03}$	$Cs_3H_{20}O_{29}Nb_{2.14}W_{3.86}$
FW (g mol^{-1})	1846.70	1832.11	1814.67
T (K)	150(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Trigonal
Space group	$P2_1/n$	$P2_1/n$	R3
a (Å)	9.5760(3)	9.6119(8)	11.6472(15)
b (Å)	13.5844(4)	11.8087(10)	11.6472(15)
c (Å)	12.3503(4)	11.2532(9)	11.2532(9)
α (°)	90	90	90
β (°)	90.0790(12)	90.929(18)	90
γ (°)	90	90	120
V (Å^3)	1606.58(9)	1277.12(18)	2245.9(6)
Z	2	2	3
μ (mm^{-1})	13.446	24.655	19.280
***F*(000)**	1659	1582	2404
Crystal size (mm^3)	0.16 x 0.14 x 0.08	0.16 x 0.14 x 0.08	0.09 x 0.07 x 0.04
Reflections collected /unique [R(int)]	45150 / 9955 [0.0299]	42881 / 9627 [0.0744]	12477 / 2686 [0.0566]
GOF (F^2)	1.260	1.016	1.008
Final *R* indices [$I>2\sigma(I)$]	$R1^a$ = 0.0310, w*R*2 = 0.0917	$R1^a$ = 0.0468, w*R*2 = 0.0869	$R1^a$ = 0.0325, w*R*2 = 0.0520
***R* indices (all data)**	$R1^a$ = 0.0318, w*R*2 = 0.0921	$R1^a$ = 0.0897, w*R*2 = 0.1037	$R1^a$ = 0.0496, w*R*2 = 0.0563
Largest difference peak and hole (e Å^{-3})	2.644 and -1.995	5.933 and -4.251	1.211 and -1.167

$^a R1 = (\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$ $^b wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

Thermogravimetric Analysis

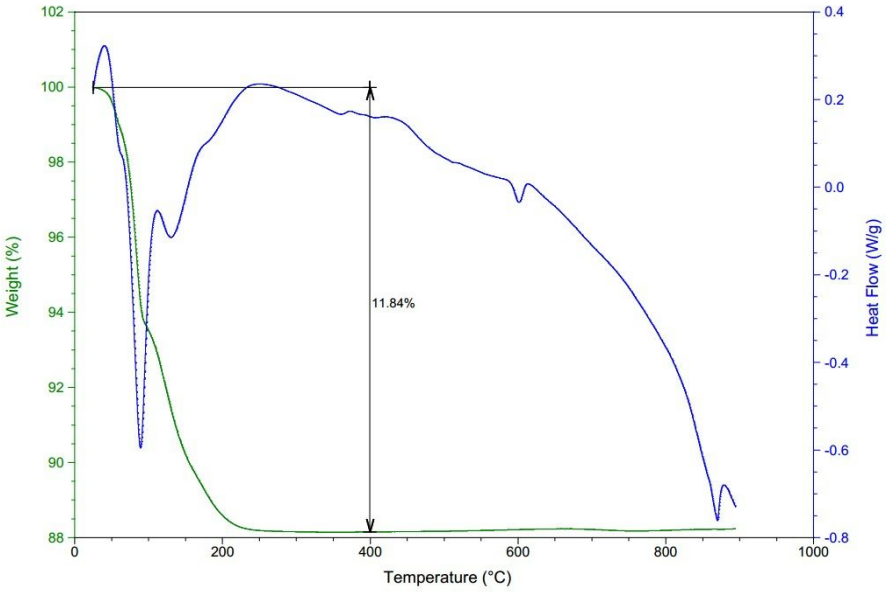


Figure S1: Thermogravimetric analysis for CsNa**{Nb_4W_2}** under air.

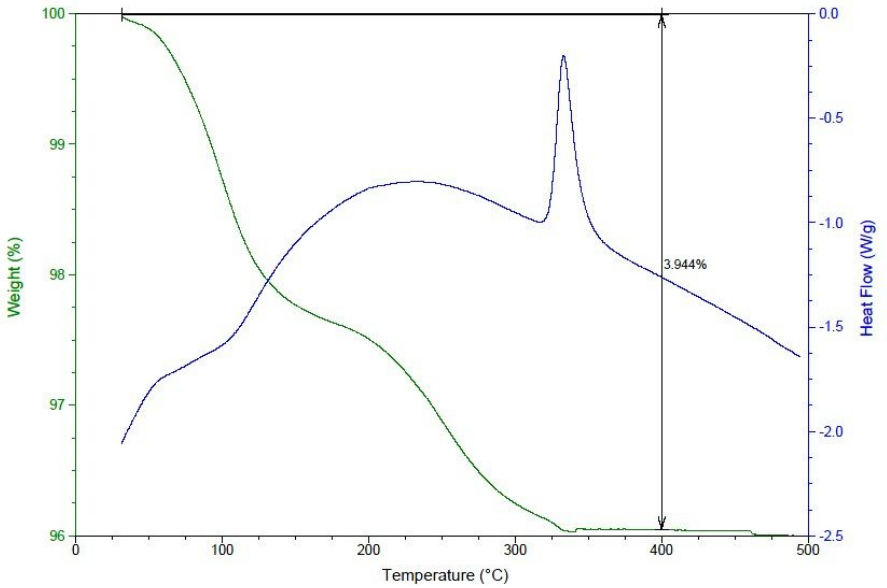


Figure S2: Thermogravimetric analysis for Cs**{Nb_2W_4}** under air.

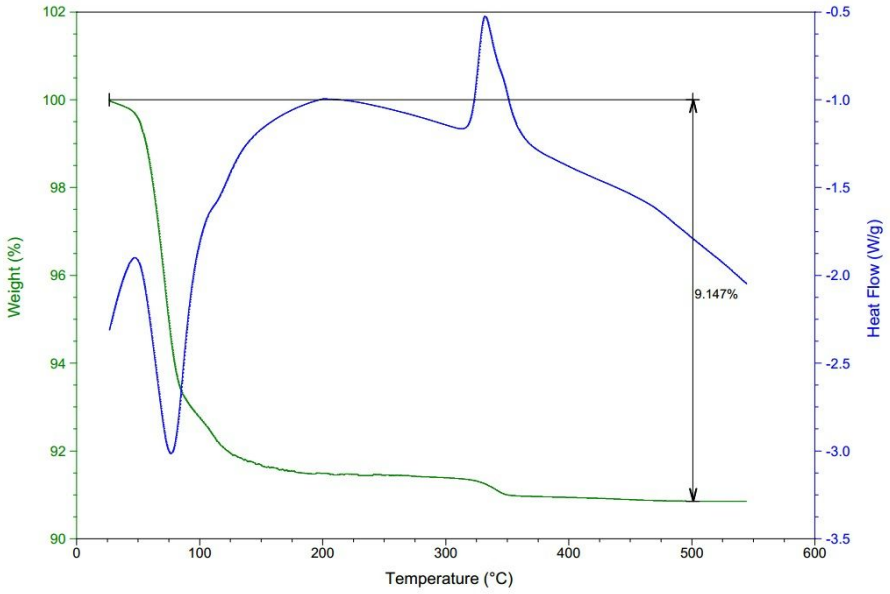


Figure S3: Thermogravimetric analysis for CsNa**{Nb_4W_2}** under air.

FTIR Spectra

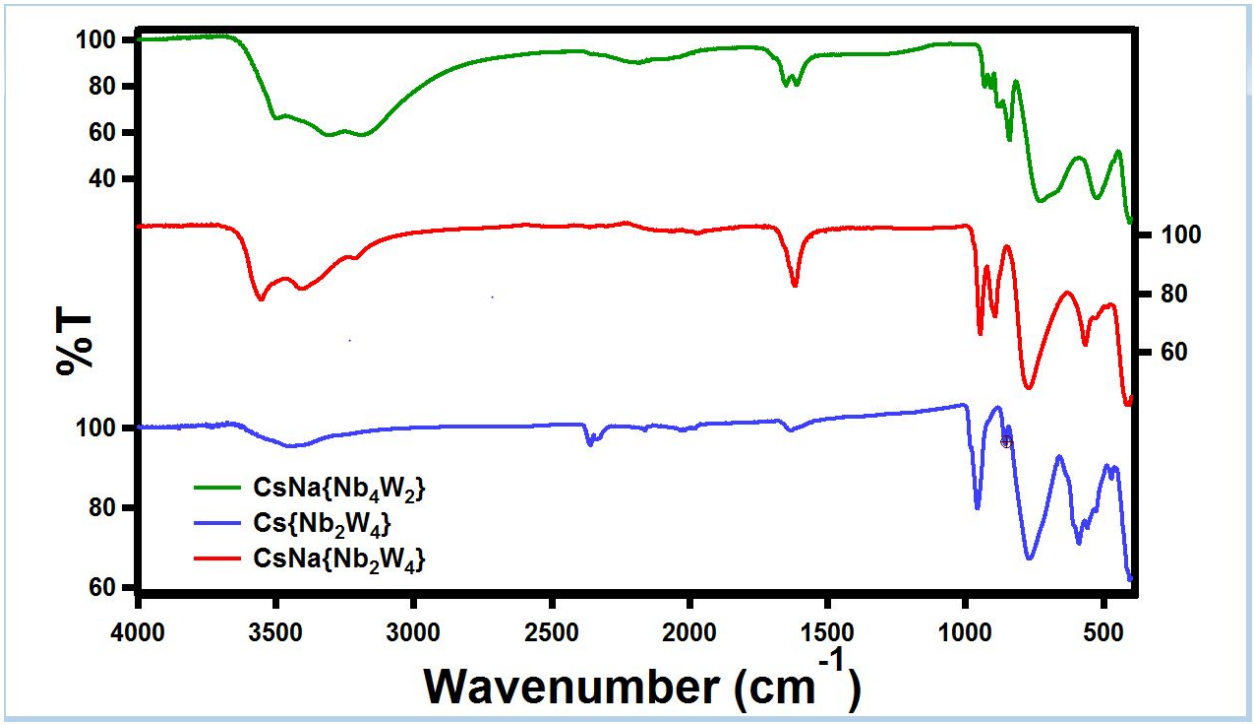


Figure S4: Full FTIR spectra of the studied species. The polyoxometalate fingerprint region is located at wavenumbers below 1000 cm^{-1}.

Group Theory Analysis

An irreducible representation of stretching modes for the terminal-oxo bonds in the **{Nb_4W_2}** ion is obtained. The *cis*- (C_{2v}) and *trans*- (D_{4h}) isomers are considered. The irreducible representations for **{Nb_2W_4}** are identical, albeit with tungsten and niobium interchanged.

Table S2: Solving for the irreducible representations of *cis*- and *trans*- isomers (C_{2v} and D_{4h}) considering symmetry operations on terminal-oxo bonds.

C_{2v}	E	$2C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$
W-O_t	2	0	2	0
Nb-O_t	4	0	2	2

$\Gamma_{W=O}$: $A_1 + B_1$ (both IR active)
$\Gamma_{Nb=O}$: $2A_1 + B_1 + B_2$ (all IR active)
Six IR-active modes.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
W-O_t	2	2	2	0	0	0	0	0	2	2
Nb-O_t	4	0	0	2	0	0	0	4	2	0

$\Gamma_{W=O}$: A_{1g} (inactive) + A_{2u} (IR active)
$\Gamma_{Nb=O}$: A_{1g} (inactive) + B_{1g} (inactive) + E_u (IR active)
Two IR-active modes.

Due to the existence of more than two terminal oxo stretching peaks in the 850-1000 cm^{-1} region of each IR spectrum (Figure 2, S4), the D_{4h} *trans*-isomer is ruled out.

Crystallographic Cesium Environments

Table S3: Cesium-oxygen distances in crystal structure of CsNa**{Nb_4W_2}** (Figure 7). Only bonds of lengths <3.6 Å are shown.

Atom 1	Atom 2	d (A)	Oxo type
Cs1	O8	3.1909	terminal oxo
	O5	3.2561	terminal oxo
	O10	3.3019	bridging oxo
	O3	3.3267	bridging oxo
	O4	3.3343	bridging oxo
	O14	3.0945	Cs-O-Na
	O13	3.1491	Cs-O-Na
	O11	3.1983	Cs-O-Na
	O12	3.2449	Cs-O-Na

Atom 1	Atom 2	d (A)	Oxo type
Cs2	O5	3.0268	terminal oxo
	O8	3.2385	terminal oxo
	O9	3.4379	terminal oxo
	O6	3.1165	bridging oxo
	O4	3.2222	bridging oxo
	O10	3.3516	bridging oxo
	O12	3.1452	Cs-O-Na
	O16	3.1966	Cs-O-Na
	O15	3.3793	Cs-O-Na
	O11	3.5572	Cs-O-Na

Table S4: Cesium-oxygen distances in crystal structure of Cs**{Nb_2W_4}** (Figure 8). Only bonds of lengths <3.6 Å are shown.

Atom 1	Atom 2	d (A)	Oxo type
Cs1	O10	3.0483	terminal oxo
	O8	3.2985	terminal oxo
	O9	3.3044	terminal oxo
	O7	3.2198	bridging oxo
	O6	3.3116	bridging oxo
	O2	3.4606	bridging oxo
	O1S	3.1921	Cs-O-Cs
	O2S	3.2108	Cs-O-Cs

Atom 1	Atom 2	d (A)	Oxo type
Cs2	O9	3.0401	terminal oxo
	O8	3.0606	terminal oxo
	O4	3.1549	bridging oxo
	O7	3.2095	bridging oxo
	O6	3.3083	bridging oxo
	O10	3.4973	bridging oxo
	O1S	3.5609	Cs-O-Cs
	O2S	3.0679	Cs-O-Cs

Table S5: Cesium-oxygen distances in crystal structure of CsNa**{Nb_2W_4}** (Figure 8). Only bonds of lengths <3.6 Å are shown.

Atom 1	Atom 2	d (A)	Oxo type
Cs1	O7	3.2600	terminal oxo
	O6	3.4433	terminal oxo
	O2	3.2849	bridging oxo
	O3	3.2898	bridging oxo
	O2S	3.0990	Cs-O-Na
	O4S	3.2114	Cs-O-Cs
	O1S	3.2281	Cs-O-Cs
	O3S	3.4806	Cs-O-Cs/Na

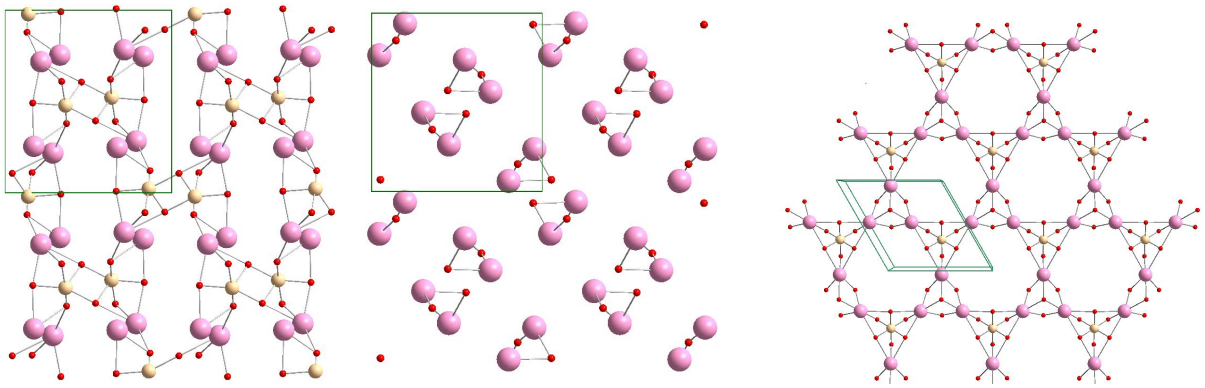
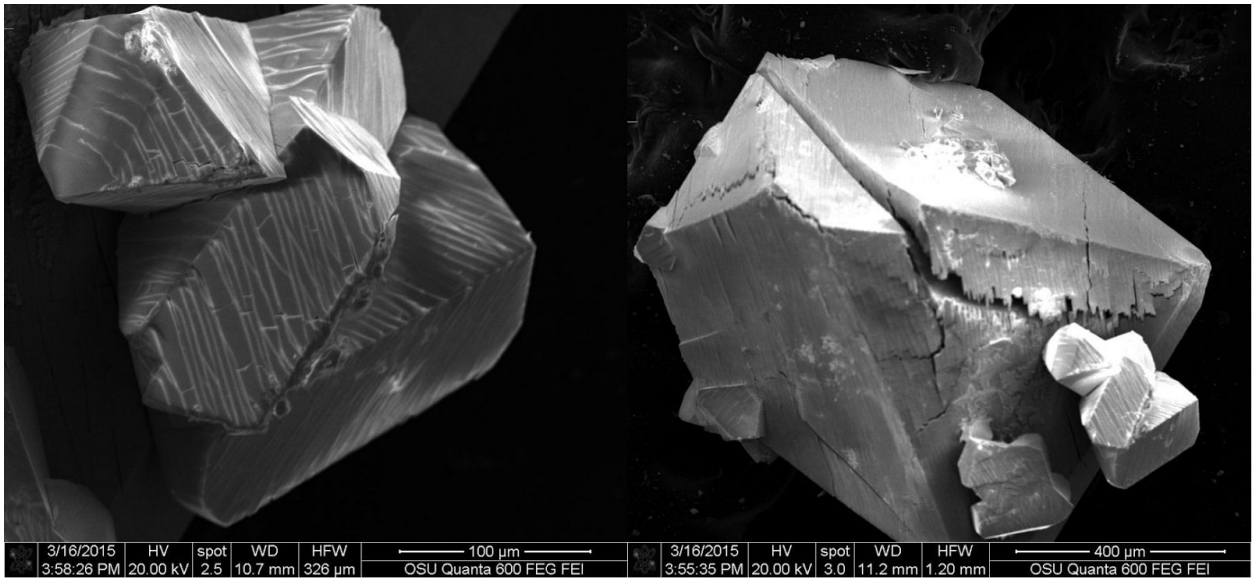


Figure S5: Representations of the crystal structures of CsNa**{Nb_4W_2}**, Cs**{Nb_2W_4}**, and CsNa**{Nb_2W_4},** highlighting the coordination environment of the cations of cation-only coordination environments of crystal structures. ***(Left)*** CsNa**{Nb_4W_2}** viewed along crystallographic *a*-axis, ***(Center)*** Cs**{Nb_2W_4}** viewed along crystallographic *a*-axis, ***(Right)*** CsNa**{Nb_2W_4}** viewed along crystallographic *c*-axis. Solvent water molecules act as bridges between Cs^+ (pink) and Na^+ (tan) counter-cations. Na^+ ions are coordinated solely by waters of hydration. Unit cell edges are shown in green.

SEM/EDX Micrographs and Spectra



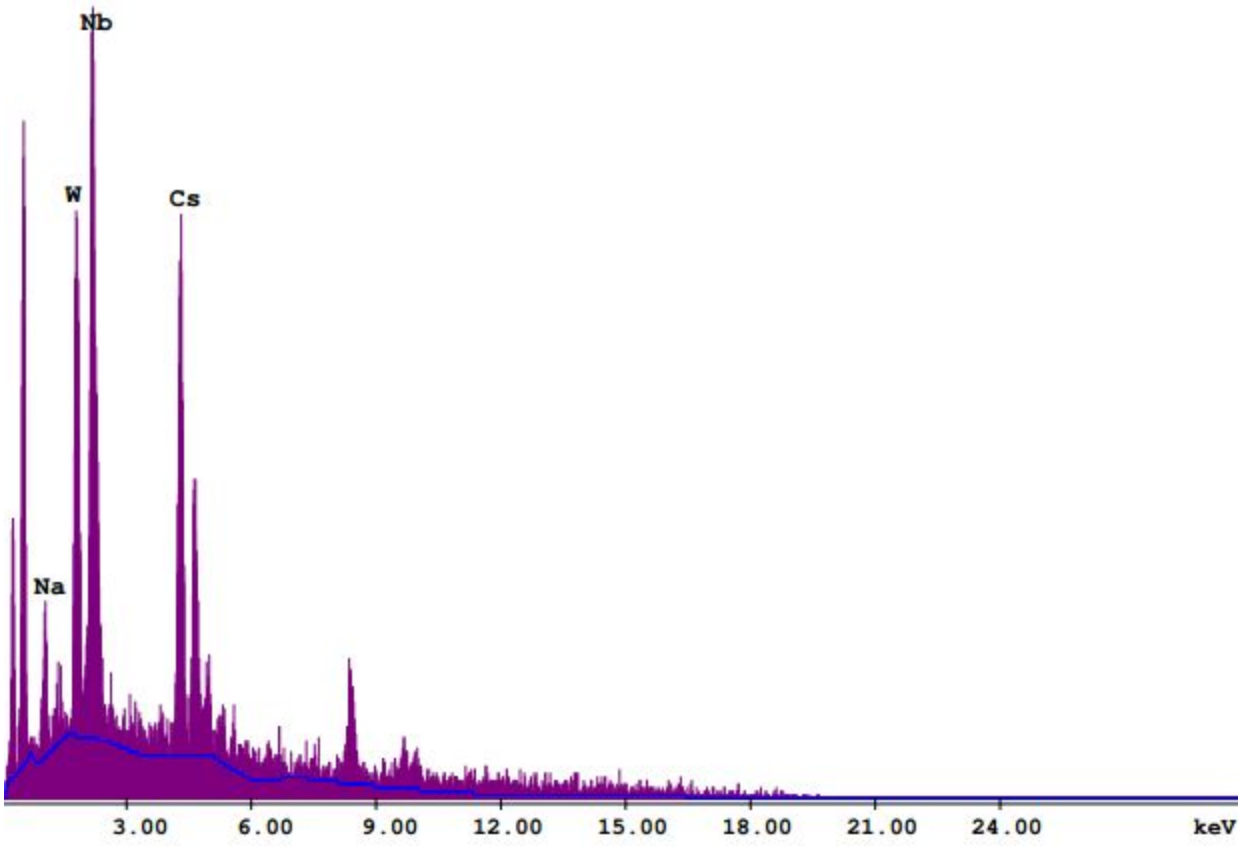


Figure S6: SEM micrographs and EDX spectrum for CsNa**{Nb_4W_2}**. Crystals are well-formed and block-like.

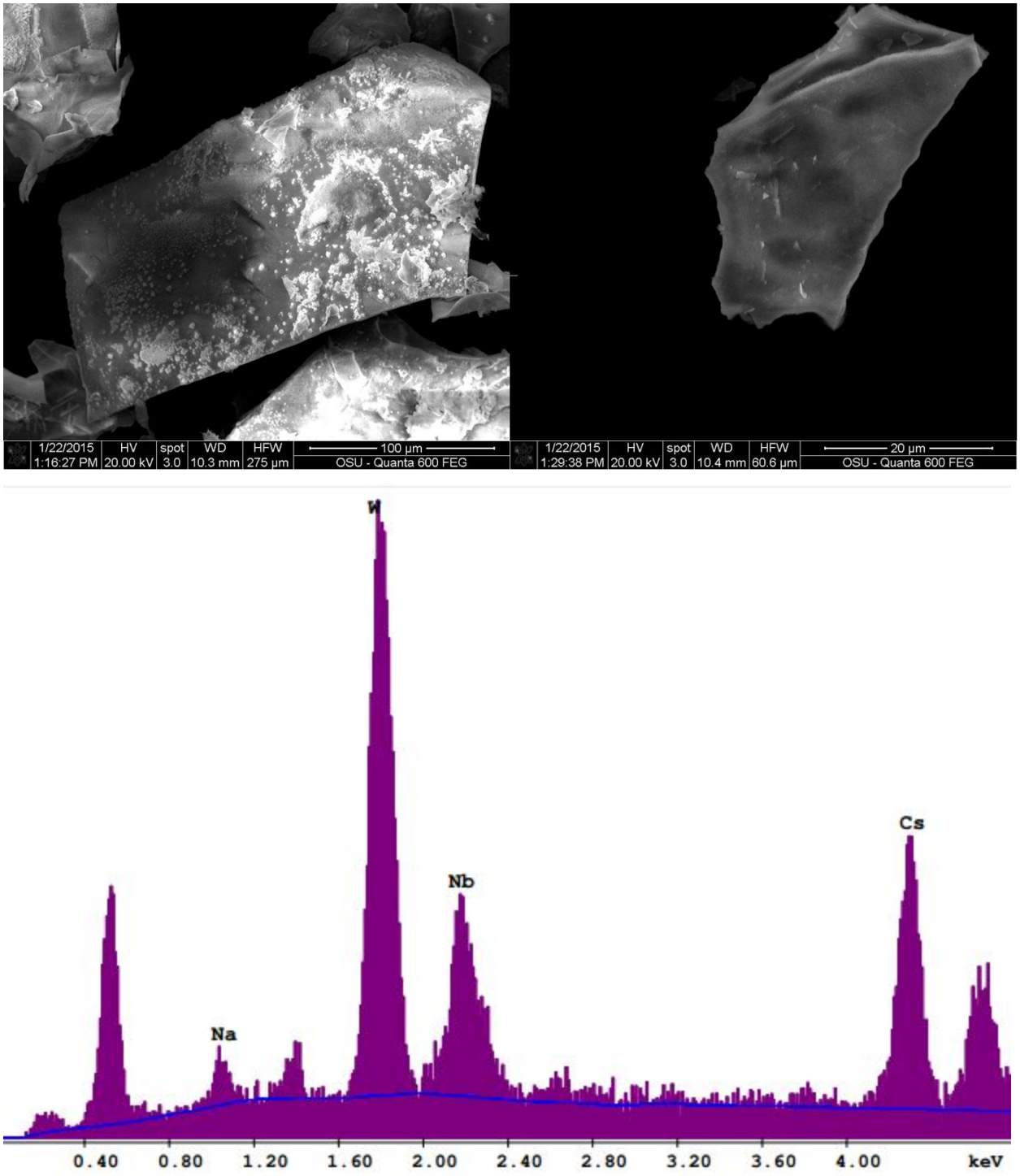


Figure S7: SEM micrographs and EDX spectrum for CsNa**{Nb_2W_4}**, indicating the existence of sodium in the lattice.

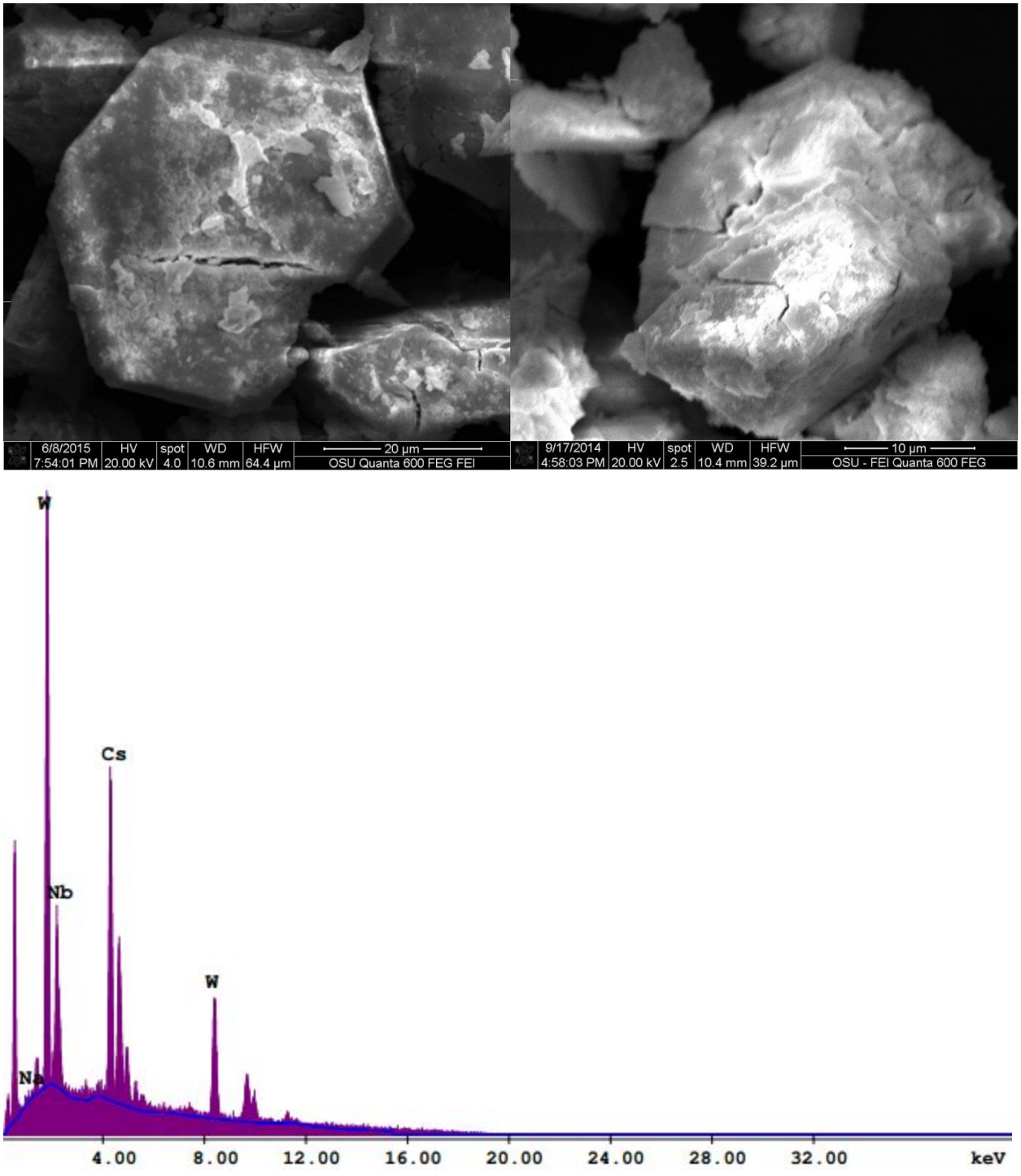


Figure S8: SEM micrographs and EDX spectrum for Cs**{Nb_2W_4}**, indicating the lack of Na^+ in the lattice. Crystals are hexagonal in shape.

ESI-MS Assignments

Table S6: List of the assignments on the ESI-MS spectra of CsNa**{Nb_4W_2}**, Cs**{Nb_2W_4}**, and CsNa**{Nb_2W_4}**

Compound	m/z observed	m/z calculated	Assignment	RA(%)
	248.948	248.939	$[HWO_4]^-$	59.1
	342.826	342.815	$[HNb_4W_2O_{18}]^{3-}$	100
	348.829	348.819	$[H_3Nb_4W_2O_{19}]^{3-}$	44.5
	354.160	354.158	$\{Cs_2[H_3Nb_2W_2O_{15}]\}^{3-}$	6.3
	372.839	372.833	$\{[H_3Nb_4W_2O_{19}](H_2O)_4\}^{3-}$	49.0
	389.765	389.753	$[Nb_4WO_{14}]^{2-}$	30.0
	397.763	397.762	$\{Cs_2[Nb_2WO_{10}]\}^{2-}$	7.8
CsNa**{Nb_4W_2}**	534.735	534.723	$\{Na[H_3Nb_4W_2O_{19}]\}^{2-}$	20.8
	542.733	542.732	$\{Cs_2Na[H_3Nb_2W_2O_{15}]\}^{2-}$	20.5
	589.694	589.681	$\{Cs[H_3Nb_4W_2O_{19}]\}^{2-}$	51.0
	597.692	597.690	$\{Cs_3[H_3Nb_2W_2O_{15}]\}^{2-}$	42.9
	634.712	634.707	$\{Cs[H_3Nb_4W_2O_{19}](H_2O)_5\}^{2-}$	3.8
	655.643	634.629	$\{Cs_2[H_2Nb_4W_2O_{19}]\}^{2-}$	5.5
	663.642	663.639	$\{Cs_4[H_2Nb_2W_2O_{15}]\}^{2-}$	10.3
	729.594	729.588	$\{Cs_5[HNb_2W_2O_{15}]\}^{2-}$	1.8
	248.938	248.939	$[HWO_4]^-$	3.96
	355.902	355.902	$[W_3O_{10}]^{2-}$	4.12
	372.828	372.828	$[Nb_2W_2O_{12}]^{2-}$	11.25
	408.844	408.844	$[HNb_2W_4O_{19}]^{3-}$	100
	613.768	613.768	$[H_2Nb_2W_4O_{19}]^{2-}$	3.63
CsNa**{Nb_2W_4}**	624.759	624.760	$\{Na[HNb_2W_4O_{19}]\}^{2-}$	15.2
	635.752	635.751	$\{Na_2[Nb_2W_4O_{19}]\}^{2-}$	2.99
	679.718	679.718	$\{Cs[HNb_2W_4O_{19}]\}^{2-}$	16.99
	690.709	690.709	$\{CsNa[Nb_2W_4O_{19}]\}^{2-}$	3.77
	745.666	745.667	$\{Cs_2[Nb_2W_4O_{19}]\}^{2-}$	2.37
	355.910	355.902	$[W_3O_{10}]^{2-}$	6.9
	372.835	372.828	$[Nb_2W_2O_{12}]^{2-}$	1.65
	408.851	408.844	$[HNb_2W_4O_{19}]^{3-}$	8.82
	488.803	488.796	$[Nb_2W_3O_{15}]^{2-}$	1.2
	496.801	496.905	$\{Cs_2[W_3O_{11}]\}^{2-}$	1.26
	530.731	530.745	$\{Cs_2[(OH)WO_4]\}^-$	1.1
	612.771	612.773	$\{Cs_2[W_4O_{14}]\}^{2-}$	2.87
Cs**{Nb_2W_4}**	621.273	621.778	$\{Cs_2[W_4O_{14}](H_2O)\}^{2-}$	
	628.767	628.763	$\{CsNa[HNbW_4O_{17}]\}^{2-}$	100
	640.765	640.785	$\{[H_2Nb_2W_4O_{19}](H_2O)_3\}^{2-}$	18.85
	679.729	679.718	$\{Cs[HNb_2W_4O_{19}]\}^{2-}$	2.62
	695.723	695.711	$\{Cs_4Na_2[W_3O_{13}](H_2O)_3\}^{2-}$	61.63
	706.714	706.734	$\{Cs[HNb_2W_4O_{19}](H_2O)_3\}^{2-}$	14.11
	753.675	753.678	$\{Cs[HNb_2W_4O_{19}](H_2O)_3\}^{2-}$	6.44

Bond Valence Sum Calculations

The bond-valence for each bond (BV) was calculated using equation (1)[5]

$$log(BV) = \frac{d_0 - d}{B} \quad (1)$$

where BV is the bond-valence for a particular bond, d is the bond length, while d_0 and B are empirical parameters. In each BVS analysis, Tytko et al.'s d_0 values for W and Nb (1.916 and 1.917, respectively)[5] were weighted by the ratios of each metal seen in each cluster. The values for B (0.9482 and 0.8592, respectively)[5] were treated similarly.

The BVS on each particular atom is obtained from equation (2)[5]

$$BVS = \sum_{i=1}^{k} BV_i \quad (2)$$

where *i* is the index of a bond between that atom and another atom and *k* is the coordination number of the atom for which BVS calculation is desired. All metal centers were assumed to be in their highest oxidation state, due to reduction not being feasible for these clusters.

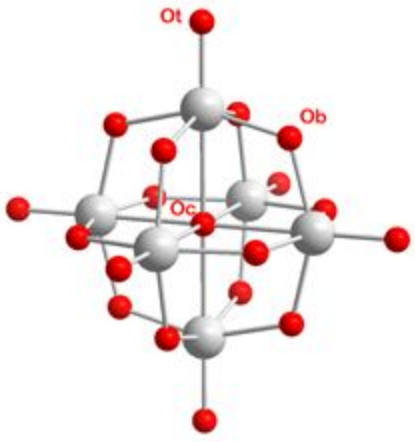


Fig S9: Representations of the molecular structures of hexametalate species. Color code: W/Nb, grey; O, red. Selected oxygen sites are labeled.

Table S7: Bond Valence Sum calculations for CsNa**{Nb_4W_2}**, including weighted values for B and d_0.

CsNa{Nb4W2}								
Parameters	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**
d0	1.916	{W6} (Tytko, Table 1)	1.916	{Nb6} (Tytko, Table 1)	1.917	{W6} (Tytko, Table 1)	1.916666667	Weighed Average (Tytko)
B	0.9482	W(VI) (Tytko, Table 1)	0.9482	Nb(V) (Tytko, Table 1)	0.8592	W(VI) (Tytko, Table 1)	0.888866667	
Oxo type	**Atom 1**	**Atom 2**	**d 1,2 [Å]**	**BV**	**BVS**	**Charge**	**Average charge**	**Stdev**
Ot (terminal)	O5	M1	1.7507	1.537	1.537	-0.463	-0.539	0.069
	O8	M2	1.7753	1.442	1.442	-0.558		
	O9	M3	1.7857	1.404	1.404	-0.596		
Ob (bridging)	O2	M1	1.9647	0.883	1.746	-0.254	-0.250	0.023
		M2	1.9735	0.863				
	O3	M1	1.9651	0.882	1.737	-0.263		
		M3	1.9771	0.855				
	O4	M3	1.9648	0.883	1.763	-0.237		
		M2	1.9657	0.881				
	O6	M2	1.9636	0.886	1.743	-0.257		
		M3	1.9758	0.858				
	O7	M1	1.9667	0.878	1.724	-0.276		
		M2	1.9814	0.846				
	O10	M1	1.9508	0.915	1.788	-0.212		
		M3	1.9691	0.873				
Oc (central)	O1	M1	2.348	0.327	1.969	-0.031	-0.031	
		M2	2.360	0.317				
		M3	2.333	0.340				

Table S8: Bond Valence Sum calculations for CsNa**{Nb_2W_4}**, including weighted values for B and d_0.

CsNa{Nb2W4}								
Parameters	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**
d0	1.916	{W6} (Tytko, Table 1)	1.916	{Nb6} (Tytko, Table 1)	1.917	{W6} (Tytko, Table 1)	1.916333333	Weighed Average (Tytko)
B	0.9482	W(VI) (Tytko, Table 1)	0.9482	Nb(V) (Tytko, Table 1)	0.8592	W(VI) (Tytko, Table 1)	0.918533333	
Oxo type	**Atom 1**	**Atom 2**	**d 1,2 [Å]**	**BV**	**BVS**	**Charge**	**Average charge**	**Stdev**
Ot (terminal)	O6	M1	1.752	1.510	1.510	-0.490	-0.478	0.017
	O7	M2	1.7456	1.534	1.534	-0.466		
Ob (bridging)	O2	M1	1.9191	0.993	1.822	-0.178	-0.188	0.018
		M2	1.9913	0.829				
	O3	M1	1.921	0.988	1.831	-0.169		
		M2	1.9848	0.842				
	O4	M1	1.9567	0.904	1.789	-0.211		
		M1	1.965	0.885				
	O5	M2	1.946	0.928	1.808	-0.192		
		M2	1.9674	0.880				
Oc (central)	O1	M1	2.3332	0.352	2.001	0.001	0.001	
		M1	2.3341	0.351				
		M1	2.3341	0.351				
		M2	2.3756	0.316				
		M2	2.3756	0.316				
		M2	2.3765	0.316				

Table S9: Bond Valence Sum calculations for Cs**{Nb_2W_4}**, including weighted values for B and d_0.

Cs{Nb2W4}								
Parameters	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**	**Value (Å)**	**Reference**
d0	1.916	{W6} (Tytko, Table 1)	1.916	{Nb6} (Tytko, Table 1)	1.917	{W6} (Tytko, Table 1)	1.916333333	Weighed Average (Tytko)
B	0.9482	W(VI) (Tytko, Table 1)	0.9482	Nb(V) (Tytko, Table 1)	0.8592	W(VI) (Tytko, Table 1)	0.918533333	
Oxo type	**Atom 1**	**Atom 2**	**d 1,2 [Ĺ]**	**BV**	**BVS**	**Charge**	**Average charge**	**Stdev**
Ot (terminal)	O8	M1	1.7256	1.613	1.613	-0.387	-0.446	0.065
	O9	M2	1.7377	1.565	1.565	-0.435		
	O10	M3	1.7588	1.484	1.484	-0.516		
Ob (bridging)	O2	M1	1.9153	1.003	1.881	-0.119	-0.156	0.066
		M2	1.9679	0.879				
	O3	M1	1.926	0.976	1.922	-0.078		
		M3	1.9387	0.945				
	O4	M3	1.9659	0.883	1.882	-0.118		
		M2	1.9167	0.999				
	O5	M1	1.9366	0.950	1.751	-0.249		
		M2	2.0049	0.801				
	O6	M2	1.9368	0.950	1.777	-0.223		
		M3	1.9922	0.827				
	O7	M1	1.9363	0.951	1.851	-0.149		
		M3	1.9584	0.900				
Oc (central)	O1	M1	2.3414	0.345	1.980	-0.020	-0.020	
		M2	2.3864	0.308				
		M3	2.3492	0.338				

Table S10: Nb/W ratios calculated from BVS calculations. Ratios depart somewhat from the ratios established from charge-balancing cations and EDX, due to the degree of disorder within the lattice.

Species	Nb calculated occupancy	W calculated occupancy
CsNa**{Nb_4W_2}**	4.259	1.741
CsNa**{Nb_2W_4}**	3.118	2.882
Cs**{Nb_2W_4}**	2.567	3.433

Computational Details

All species were fully optimized through first-principles calculations performed on the basis of density functional theory (DFT). The exchange and correlation terms were those in the generalized gradient approximation (GGA) PBE functional.[6-7] The calculations were performed using the Amsterdam Density Functional (ADF2014) package.[8-10] Full electron triple-ζ plus one polarization function basis sets (TZP) were used on all atoms including relativistic corrections through the scalar-relativistic zero-order regular approximation (ZORA).[11] Solvation effects were included using the conductor-like screening model (COSMO) in conjunction with the Allinger radii to create the dielectric cavity.[12-13] The lowest 10 singlet-singlet excitations were computed using time-dependent DFT calculations and PBE or B3LYP functionals.[14] Both the *cis*- and *trans*-isomers are considered for the mixed-metal species.

Table S11: Relative energies (electronic) of the *cis*- and *trans*-isomers of the studied species at PBE and B3LYP levels of theory. Energies in kcal•mol^{-1}

	cis-{Nb_4W_2}	*trans*-{Nb_4W_2}	*cis*-{Nb_2W_4}	*trans*-{Nb_2W_4}
PBE	0.00	1.64	0.00	0.75
B3LYP	0.00	1.78	0.00	0.69

Table S12: Excitation energies, oscillation strengths, and orbitals involved in electronic transitions at the PBE level of theory .

Species	Excitation Energy (eV)	Excitation Energy (nm)	Oscillation Strength	Main Transition	Weight Transition
$[W_4O_{19}]^{2-}$	3.6050	344.0	0.1242	HOMO → LUMO	0.9143
	3.6050	344.0	0.1242	HOMO → LUMO	0.9143
	3.6050	344.0	0.1242	HOMO → LUMO	0.9143
cis-$[W_4Nb_2O_{19}]^{4-}$	3.6772	337.2	0.1169	HOMO → LUMO HOMO-2 → LUMO+1	0.5782 0.3419
	3.6835	336.6	0.1294	HOMO-1 → LUMO+1	0.8863
	3.6940	335.7	0.1213	HOMO-2 → LUMO HOMO → LUMO+1	0.7133 0.1982
trans-$[W_4Nb_2O_{19}]^{4-}$	3.6788	337.1	0.1399	HOMO →LUMO HOMO → LUMO+1	0.8157 0.1646
	3.6788	337.1	0.1399	HOMO →LUMO HOMO → LUMO+1	0.8157 0.1646
	3.6837	336.6	0.1021	HOMO-1 → LUMO	0.8932
cis-$[Nb_4W_2O_{19}]^{6-}$	3.7189	333.4	0.1123	HOMO →LUMO+1 HOMO-1 →LUMO	0.7630 0.1722
	3.7222	333.1	0.1304	HOMO-2→ LUMO	0.9007
	3.7472	330.9	0.1149	HOMO-1 → LUMO+1	0.8048
trans-$[Nb_4W_2O_{19}]^{6-}$	3.7311	332.3	0.1130	HOMO-1 → LUMO HOMO-1 →LUMO+1	0.5172 0.4695
	3.7311	332.3	0.1130	HOMO-1 → LUMO HOMO-1 → LUMO+1	0.5172 0.4695
	3.7354	332.0	0.1580	HOMO → LUMO+1	0.9646
$[Nb_6O_{19}]^{8-}$	3.7875	327.4	0.1602	HOMO → LUMO	0.9553
	3.7875	327.4	0.1602	HOMO → LUMO	0.9553
	3.7875	327.4	0.1602	HOMO → LUMO	0.9553

Table S13: Excitation energies, oscillation strengths, and orbitals involved in electronic transitions at the B3LYP level of theory.

Species	Excitation Energy (eV)	Excitation Energy (nm)	Oscillation Strength	Main Transition	Weight Transition
$[W_4O_{19}]^{2-}$	4.23501	292.8	0.2766	HOMO → LUMO	0.9753
	4.23501	292.8	0.2766	HOMO → LUMO	0.9753
	4.23501	292.8	0.2766	HOMO → LUMO	0.9753
cis-$[W_4Nb_2O_{19}]^{4-}$	4.33345	286.1	0.2134	HOMO-1 → LUMO+1 HOMO-2 → LUMO	0.7202 0.1077
	4.34805	285.2	0.2468	HOMO → LUMO HOMO-2 → LUMO+1	0.6006 0.3676
	4.35823	284.5	0.2619	HOMO-2 → LUMO HOMO → LUMO+1	0.7160 0.2223
trans-$[W_4Nb_2O_{19}]^{4-}$	4.36894	283.8	0.2648	HOMO-1 →LUMO HOMO-1 → LUMO+1	0.8360 0.1185
	4.36894	283.8	0.2648	HOMO-1 →LUMO HOMO-1 → LUMO+1	0.8360 0.1185
	4.34055	285.7	0.2731	HOMO → LUMO	0.9674
cis-$[Nb_4W_2O_{19}]^{6-}$	4.38697	282.7	0.2387	HOMO-1 →LUMO	0.9174
	4.43255	279.7	0.2295	HOMO→ LUMO+1 HOMO-2 → LUMO	0.7991 0.1591
	4.43610	279.5	0.1698	HOMO → LUMO	0.9174
trans-$[Nb_4W_2O_{19}]^{6-}$	4.44461	279.0	0.2418	HOMO-1 → LUMO+1 HOMO-1 →LUMO	0.5868 0.3736
	4.44461	279.0	0.2418	HOMO-1 → LUMO+1 HOMO-1 → LUMO	0.5868 0.3736
	4.48508	276.5	0.2750	HOMO → LUMO+1	0.9645
$[Nb_6O_{19}]^{8-}$	4.5405	273.1	0.31647	HOMO → LUMO	0.9622
	4.5405	273.1	0.31647	HOMO → LUMO	0.9622
	4.5405	273.1	0.31647	HOMO → LUMO	0.9622

Table S14: Decomposition of the frontier molecular orbitals in atomic orbitals at the B3LYP level of theory. Only atomic orbital contributions larger than 5% are shown.

$[W_6O_{19}]^{2-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-8.094 eV	HOMO	T1.g	91.50%	2 P:z	Oxygen
			10.50%	2 P:y	Oxygen
-3.218 eV	LUMO	E.u:1	66.42%	5 D:xy	Tungsten
			32.81%	2 P:z	Oxygen

cis-$[W_4Nb_2O_{19}]^{4-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-7.165 eV	HOMO-2	A2	45.56%	2 P:x	Oxygen
			28.03%	2 P:y	Oxygen
			14.61%	2 P:y	Oxygen
			5.81%	2 P:z	Oxygen
-7.145 eV	HOMO-1	B2	24.05%	2 P:z	Oxygen
			23.02%	2 P:y	Oxygen
			22.24%	2 P:y	Oxygen
			21.92%	2 P:z	Oxygen
			5.55%	2 P:z	Oxygen
-7.131 eV	HOMO	B1	26.31%	2 P:x	Oxygen
			24.00%	2 P:z	Oxygen
			18.76%	2 P:x	Oxygen
			17.88%	2 P:z	Oxygen
			6.80%	2 P:y	Oxygen
-2.120 eV	LUMO	B1	33.94%	5 D:z2	Tungsten
			11.39%	5 D:x2-y2	Tungsten
			9.51%	2 P:x	Oxygen
			8.96%	5 D:xy	Tungsten
			7.06%	2 P:z	Oxygen
			5.65%	2 P:x	Oxygen
			5.43%	5 D:xz	Tungsten
-2.089 eV	LUMO+1	A2	25.99%	5 D:xy	Tungsten
			22.34%	5 D:xz	Tungsten
			11.88%	4 D:xz	Niobium
			9.71%	4 D:xy	Niobium
			9.32%	2 P:z	Oxygen
			9.10%	2 P:y	Oxygen
-1.746 eV	LUMO+2	A1	49.47%	5 D:z2	Tungsten
			16.20%	5 D:x2-y2	Tungsten
			9.28%	2 P:z	Oxygen
			7.60%	2 P:y	Oxygen
			5.82%	2 P:y	Oxygen
			4.56%	2 P:z	Oxygen

trans-$[W_4Nb_2O_{19}]^{4-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-7.147 eV	HOMO-1	E1.g	45.68%	2 P:z	Oxygen
			44.22%	2 P:x	Oxygen
			7.56%	2 P:z	Oxygen
-7.138 eV	HOMO	A2.g	91.82%	2 P:y	Oxygen
			10.09%	2 P:x	Oxygen
-2.150 eV	LUMO	A1.u	64.84%	5 D:xz	Tungsten
			35.35%	2 P:y	Oxygen
-2.063 eV	LUMO+1	B1.u	43.89%	4 D:xy	Niobium
			30.16%	5 D:xz	Tungsten
			20.96%	2 P:z	Oxygen

cis-$[Nb_4W_2O_{19}]^{6-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-6.308 eV	HOMO-2	A2	44.59%	2 P:x	Oxygen
			26.38%	2 P:y	Oxygen
			15.68%	2 P:y	Oxygen
			5.32%	2 P:z	Oxygen
-6.288 eV	HOMO-1	B2	25.93%	2 P:z	Oxygen
			25.17%	2 P:y	Oxygen
			20.85%	2 P:z	Oxygen
			20.18%	2 P:y	Oxygen
			5.08%	2 P:z	Oxygen
-6.268 eV	HOMO B1		26.99%	2 P:x	Oxygen
			24.02%	2 P:z	Oxygen
			17.22%	2 P:z	Oxygen
			17.13%	2 P:x	Oxygen
			7.51%	2 P:y	Oxygen
-1.186 eV	LUMO	A2	26.70%	5 D:xy	Tungsten
			24.08%	5 D:xz	Tungsten
			10.78%	2 P:y	Oxygen
			10.29%	2 P:z	Oxygen
			9.27%	4 D:xz	Niobium
			7.83%	4 D:xy	Niobium
-1.089 eV	LUMO+1	B1	31.03%	4 D:z2	Niobium
			16.28%	5 D:xy	Tungsten
			10.50%	4 D:x2-y2	Niobium
			9.58%	2 P:x	Oxygen
			9.03%	5 D:xz	Tungsten
			6.61%	2 P:x	Oxygen
-0.761 eV	LUMO+2	B2	40.72%	5 D:z2	Tungsten
			16.82%	5 D:x2-y2	Tungsten
			10.46%	2 P:y	Oxygen
			8.72%	2 P:z	Oxygen
			7.53%	4 D:z2	Niobium

trans-$[Nb_4W_2O_{19}]^{6-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-6.284 eV	HOMO-1	E1.g	47.25%	2 P:z	Oxygen
			43.53%	2 P:x	Oxygen
			6.51%	2 P:x	Oxygen
-6.270 eV	HOMO	A2.g	87.36%	2 P:y	Oxygen
			16.02%	2 P:x	Oxygen
-1.216 eV	LUMO	B1.u	50.33%	5 D:xy	Tungsten
			17.20%	4 D:xz	Niobium
			17.11%	2 P:y	Oxygen
			15.41%	2 P:z	Oxygen
-1.035 eV	LUMO+1	A1.u	77.85%	4 D:xz	Niobium
			20.38%	2 P:y	Oxygen

$[Nb_6O_{19}]^{8-}$

Energy	Label	Sym.	%	Orb. Type	Atom Type
-5.506 eV	HOMO	T1.g	89.83%	2 P:y	Oxygen
			13.43%	2 P:x	Oxygen
-0.228 eV	LUMO	E.u	76.16%	4 D:xy	Niobium
			23.08%	2 P:z	Oxygen

Table S15: Cartesian coordinates (in Angstroms) of the studied species at the PBE level of theory.

{W_6}

W	0.000000	0.000000	2.355123
W	0.000000	0.000000	-2.355123
W	0.000000	2.355123	0.000000
W	0.000000	-2.355123	0.000000
W	-2.355123	0.000000	0.000000
W	2.355123	0.000000	0.000000
O	0.000000	-4.080386	0.000000
O	0.000000	0.000000	4.080386
O	0.000000	0.000000	-4.080386
O	-1.886654	1.886654	0.000000
O	1.886654	-1.886654	0.000000
O	-4.080386	0.000000	0.000000
O	4.080386	0.000000	0.000000
O	-1.886654	0.000000	1.886654
O	1.886654	0.000000	-1.886654
O	0.000000	-1.886654	1.886654
O	0.000000	1.886654	-1.886654
O	1.886654	1.886654	0.000000
O	-1.886654	-1.886654	0.000000
O	1.886654	0.000000	1.886654
O	-1.886654	0.000000	-1.886654
O	0.000000	0.000000	0.000000
O	0.000000	1.886654	1.886654
O	0.000000	-1.886654	-1.886654
O	0.000000	4.080386	0.000000

trans-{Nb_2W_4}

Nb	0.000000	0.000000	2.416639
Nb	0.000000	0.000000	-2.416639
W	0.000000	2.352806	0.000000
W	0.000000	-2.352806	0.000000
W	-2.352806	0.000000	0.000000
W	2.352806	0.000000	0.000000
O	0.000000	-4.096229	0.000000
O	0.000000	0.000000	4.196871
O	0.000000	0.000000	-4.196871
O	-1.902037	1.902037	0.000000
O	1.902037	-1.902037	0.000000
O	-4.096229	0.000000	0.000000
O	4.096229	0.000000	0.000000
O	-1.960479	0.000000	1.883258
O	1.960479	0.000000	-1.883258

O 0.000000 -1.960479 1.883258
O 0.000000 1.960479 -1.883258
O 1.902037 1.902037 0.000000
O -1.902037 -1.902037 0.000000
O 1.960479 0.000000 1.883258
O -1.960479 0.000000 -1.883258
O 0.000000 0.000000 0.000000
O 0.000000 1.960479 1.883258
O 0.000000 -1.960479 -1.883258
O 0.000000 4.096229 0.000000

cis-{Nb_2W_4}

Nb 0.000000 1.694815 1.923468
W 0.000000 -1.671093 -1.457627
Nb 0.000000 -1.694815 1.923468
W 0.000000 1.671093 -1.457627
W 2.354204 0.000000 0.216240
W -2.354204 0.000000 0.216240
O 0.000000 2.863663 -2.733834
O 0.000000 2.986216 3.142488
O 0.000000 -2.863663 -2.733834
O 1.971224 -1.348003 1.505637
O -1.894146 1.330320 -1.171994
O 4.096093 0.000000 0.135000
O -4.096093 0.000000 0.135000
O 1.971224 1.348003 1.505637
O -1.894146 -1.330320 -1.171994
O 0.000000 2.717815 0.126684
O 0.000000 -2.717815 0.126684
O -1.971224 -1.348003 1.505637
O 1.894146 1.330320 -1.171994
O -1.971224 1.348003 1.505637
O 1.894146 -1.330320 -1.171994
O 0.000000 0.000000 0.152865
O 0.000000 0.000000 2.956136
O 0.000000 0.000000 -2.492999
O 0.000000 -2.986216 3.142488

trans-{Nb_4W_2}

W 0.000000 0.000000 2.362161
W 0.000000 0.000000 -2.362161
Nb 0.000000 2.402829 0.000000
Nb 0.000000 -2.402829 0.000000
Nb -2.402829 0.000000 0.000000
Nb 2.402829 0.000000 0.000000
O 0.000000 -4.206746 0.000000
O 0.000000 0.000000 4.124843
O 0.000000 0.000000 -4.124843
O -1.962202 1.962202 0.000000
O 1.962202 -1.962202 0.000000
O -4.206746 0.000000 0.000000
O 4.206746 0.000000 0.000000
O -1.898992 0.000000 1.982496
O 1.898992 0.000000 -1.982496
O 0.000000 -1.898992 1.982496
O 0.000000 1.898992 -1.982496
O 1.962202 1.962202 0.000000
O -1.962202 -1.962202 0.000000
O 1.898992 0.000000 1.982496
O -1.898992 0.000000 -1.982496

O 0.000000 0.000000 0.000000
O 0.000000 1.898992 1.982496
O 0.000000 -1.898992 -1.982496
O 0.000000 4.206746 0.000000

cis-{Nb_4W_2}

W 0.000000 1.673172 -1.430255
Nb 0.000000 -1.689276 1.949279
W 0.000000 -1.673172 -1.430255
Nb 0.000000 1.689276 1.949279
Nb -2.403319 0.000000 0.257780
Nb 2.403319 0.000000 0.257780
O 0.000000 3.004573 3.176978
O 0.000000 2.875545 -2.723957
O 0.000000 -3.004573 3.176978
O -1.893927 -1.383222 -1.196061
O 1.969373 1.407973 1.595090
O -4.205623 0.000000 0.171729
O 4.205623 0.000000 0.171729
O -1.893927 1.383222 -1.196061
O 1.969373 -1.407973 1.595090
O 0.000000 2.743532 0.150972
O 0.000000 -2.743532 0.150972
O 1.893927 -1.383222 -1.196061
O -1.969373 1.407973 1.595090
O 1.893927 1.383222 -1.196061
O -1.969373 -1.407973 1.595090
O 0.000000 0.000000 0.175949
O 0.000000 0.000000 -2.488733
O 0.000000 0.000000 3.016610
O 0.000000 -2.875545 -2.723957

{Nb_6}

Nb 0.000000 0.000000 2.397272
Nb 0.000000 0.000000 -2.397272
Nb 0.000000 2.397272 0.000000
Nb 0.000000 -2.397272 0.000000
Nb -2.397272 0.000000 0.000000
Nb 2.397272 0.000000 0.000000
O 0.000000 -4.224520 0.000000
O 0.000000 0.000000 4.224520
O 0.000000 0.000000 -4.224520
O -1.979758 1.979758 0.000000
O 1.979758 -1.979758 0.000000
O -4.224520 0.000000 0.000000
O 4.224520 0.000000 0.000000
O -1.979758 0.000000 1.979758
O 1.979758 0.000000 -1.979758
O 0.000000 -1.979758 1.979758
O 0.000000 1.979758 -1.979758
O 1.979758 1.979758 0.000000
O -1.979758 -1.979758 0.000000
O 1.979758 0.000000 1.979758
O -1.979758 0.000000 -1.979758
O 0.000000 0.000000 0.000000
O 0.000000 1.979758 1.979758
O 0.000000 -1.979758 -1.979758
O 0.000000 4.224520 0.000000

Calculated IR Spectra

Table S16: Terminal metal-oxo frequecies for the studied species. Frequencies in cm^{-1} and intensities in km/mole.

Species	Frequency	Intensity	Assignment
$[W_6O_{19}]$	940	822	Terminal W=O
trans-$[W_4Nb_2O_{19}]$	902	798	Terminal W=O
	839	874	Terminal Nb=O
cis-$[W_4Nb_2O_{19}]$	902	810	Terminal W=O cis to Nb centers
	898	224	Mixture Terminal Nb=O and W=O
	897	426	Terminal W=O trans to Nb centers
	855	536	Symmetric Terminal Nb=O
	844	436	Asymmetric Terminal Nb=O
trans-$[Nb_4W_2O_{19}]$	862	763	Terminal W=O
	800	789	Terminal Nb=O
cis-$[Nb_4W_2O_{19}]$	875	168	Symmetric Terminal W=O
	857	391	Asymmetric Terminal W=O
	824	463	Mixture Terminal Nb=O and W=O
	804	403	Terminal Nb=O trans to W centers
	800	765	Terminal Nb=O cis to W centers
	798	113	Terminal Nb=O
$[Nb_6O_{19}]$	762	649	Terminal Nb=O

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