

**Supplementary Materials: Neutral W(V) complexes featuring the  
W<sub>2</sub>O<sub>2</sub>(μ-O)<sub>2</sub> core and amino acids or EDTA derivatives as ligands:  
Synthesis and structural characterization**

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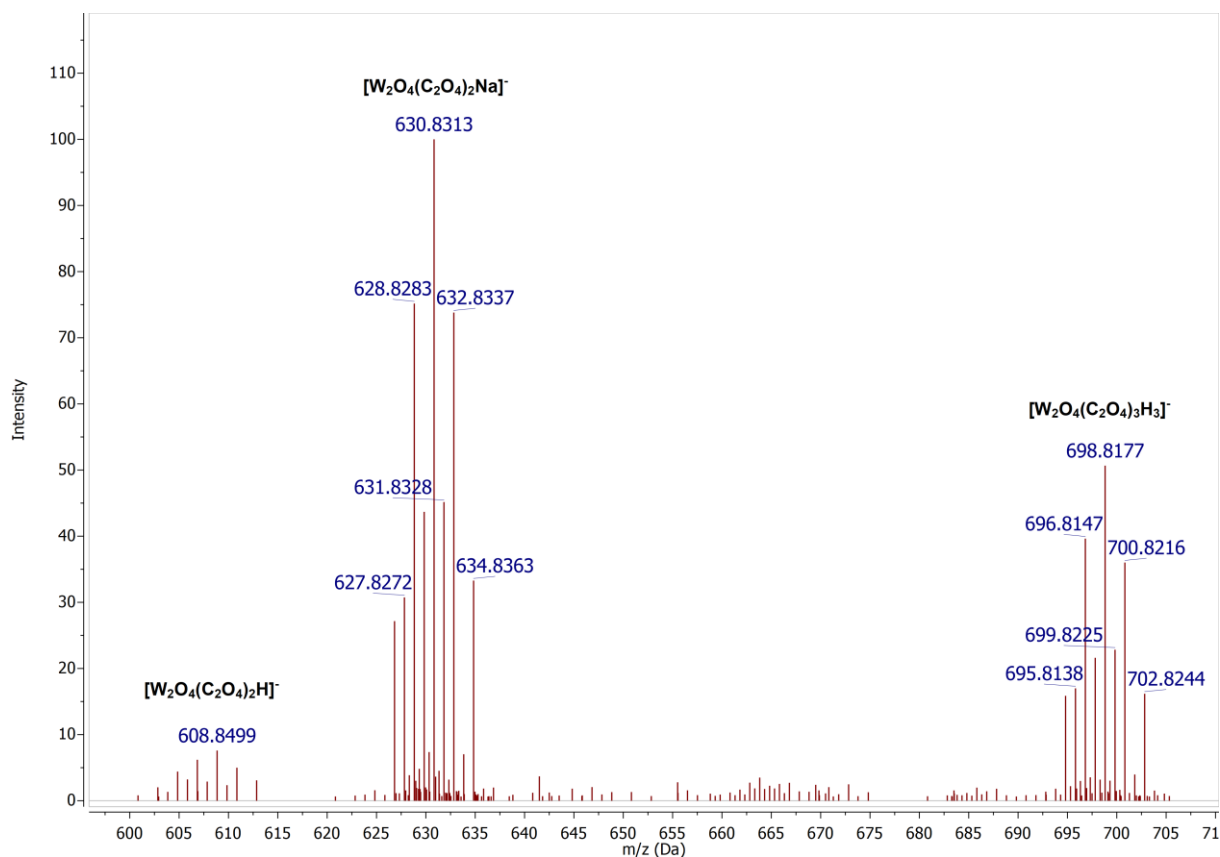
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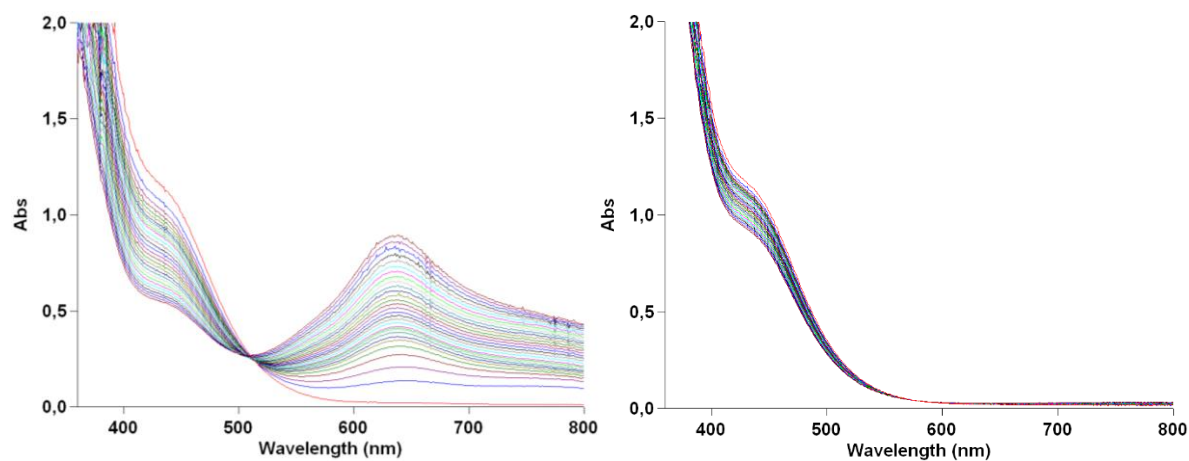
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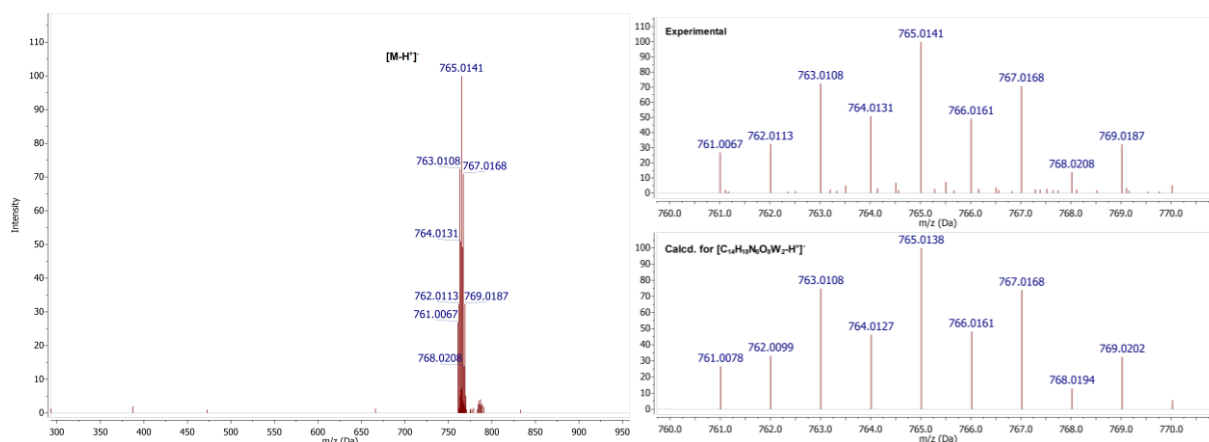
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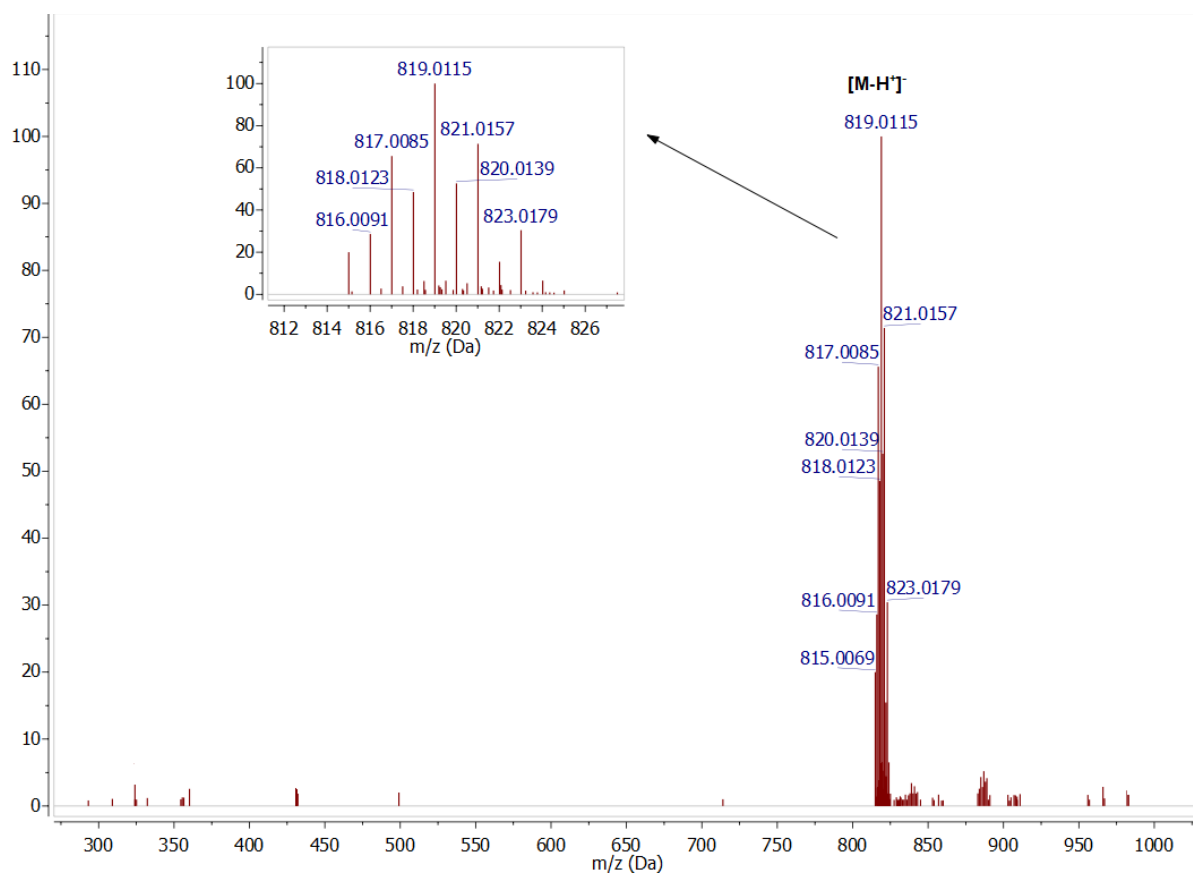
**Figure S1.** Main peaks observed in the ESI-HRMS (-) spectra of the oxalatotungstate(V) complex **P1**.



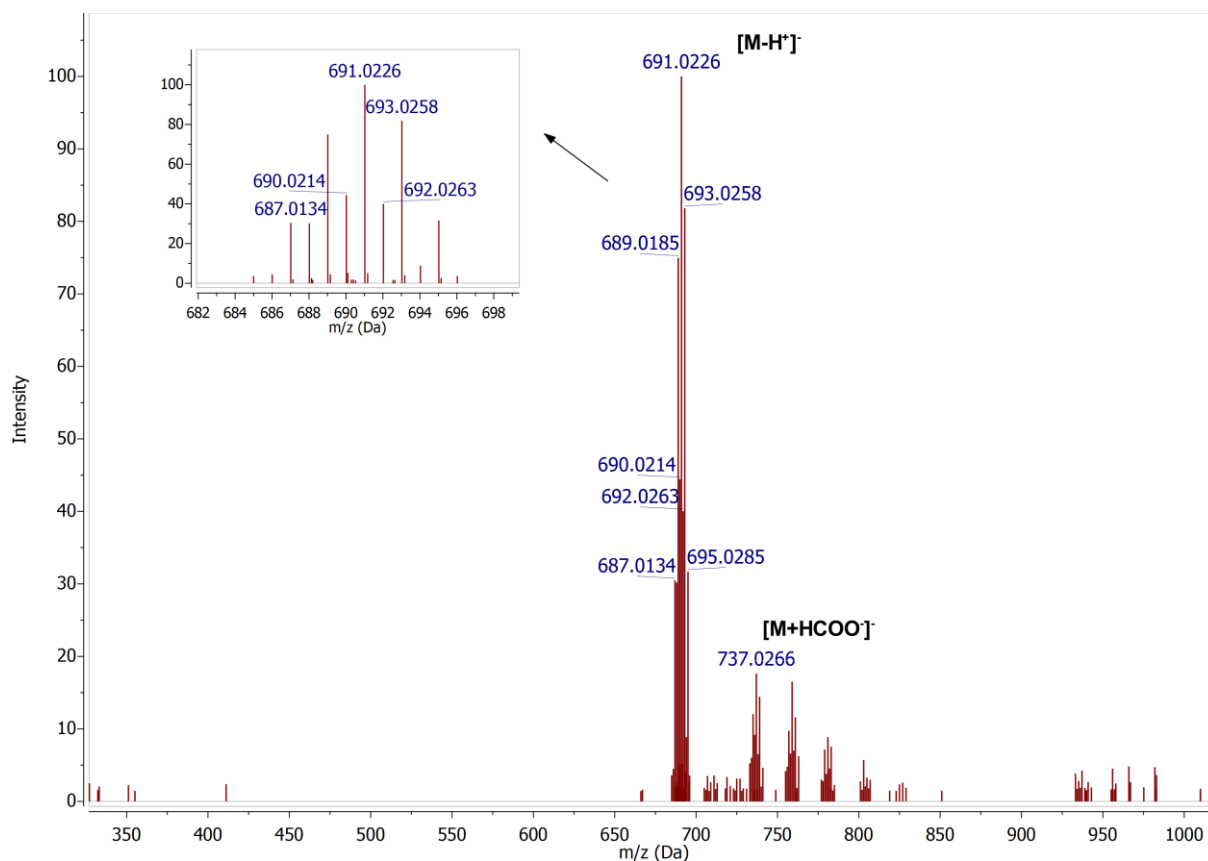
**Figure S2.** Stability of aqueous solutions of oxalatotungstate(V) complex **P1** followed by UV-Vis spectroscopy over 20 h of incubation at RT and under ambient atmosphere. Two different batches corresponding to  $\text{Na}_{2.2}[\text{W}_2\text{O}_4(\text{C}_2\text{O}_4)_{2.2}(\text{H}_2\text{O})_{3.5}]$  (left) and  $\text{Na}_{2.5}[\text{W}_2\text{O}_4(\text{C}_2\text{O}_4)_{2.5}(\text{H}_2\text{O})_{4.5}]$  (right) have been investigated. The composition of the batches was determined by elemental analysis; their identity was verified by MS and IR spectra.



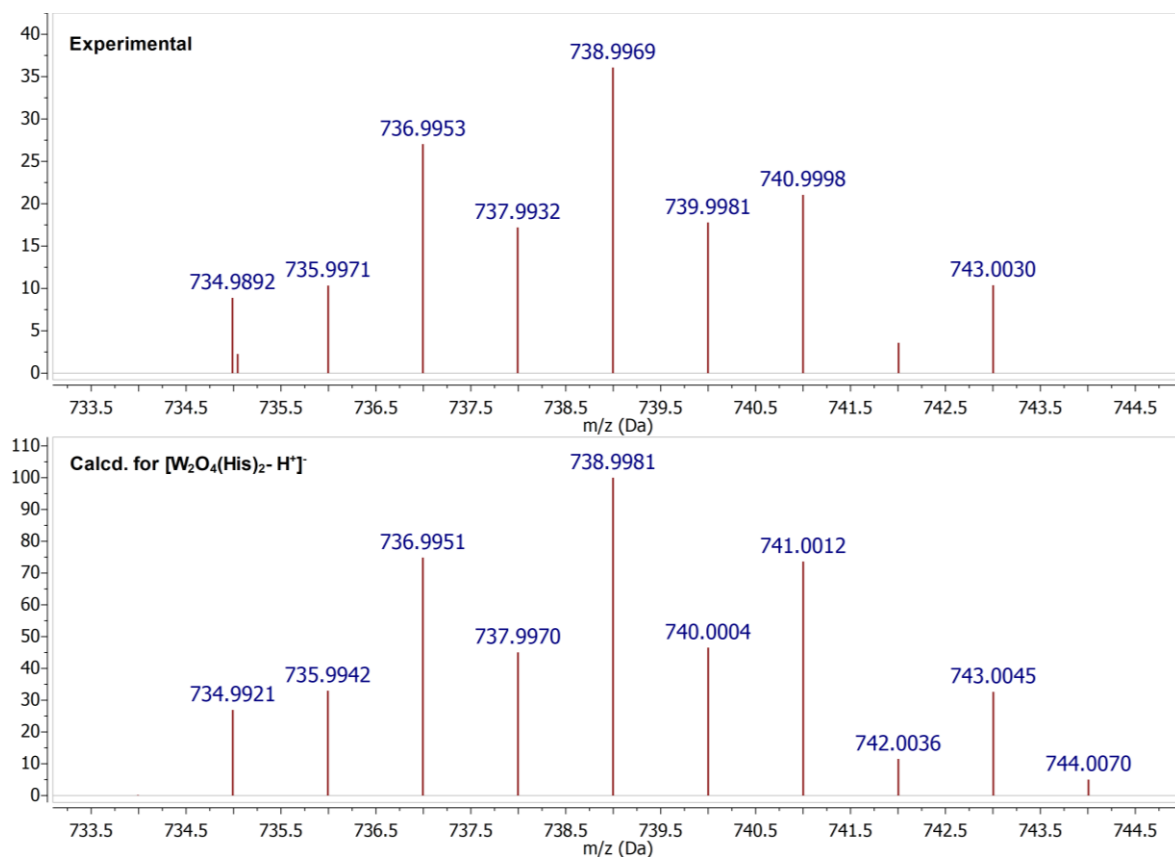
**Figure S3.** ESI-HRMS (-) spectra of  $[W_2O_4(L3)]$  (3). Experimental spectrum vs. simulated isotopic pattern for  $[C_{14}H_{18}N_6O_8W_2-H]^+$  is shown on the right side.



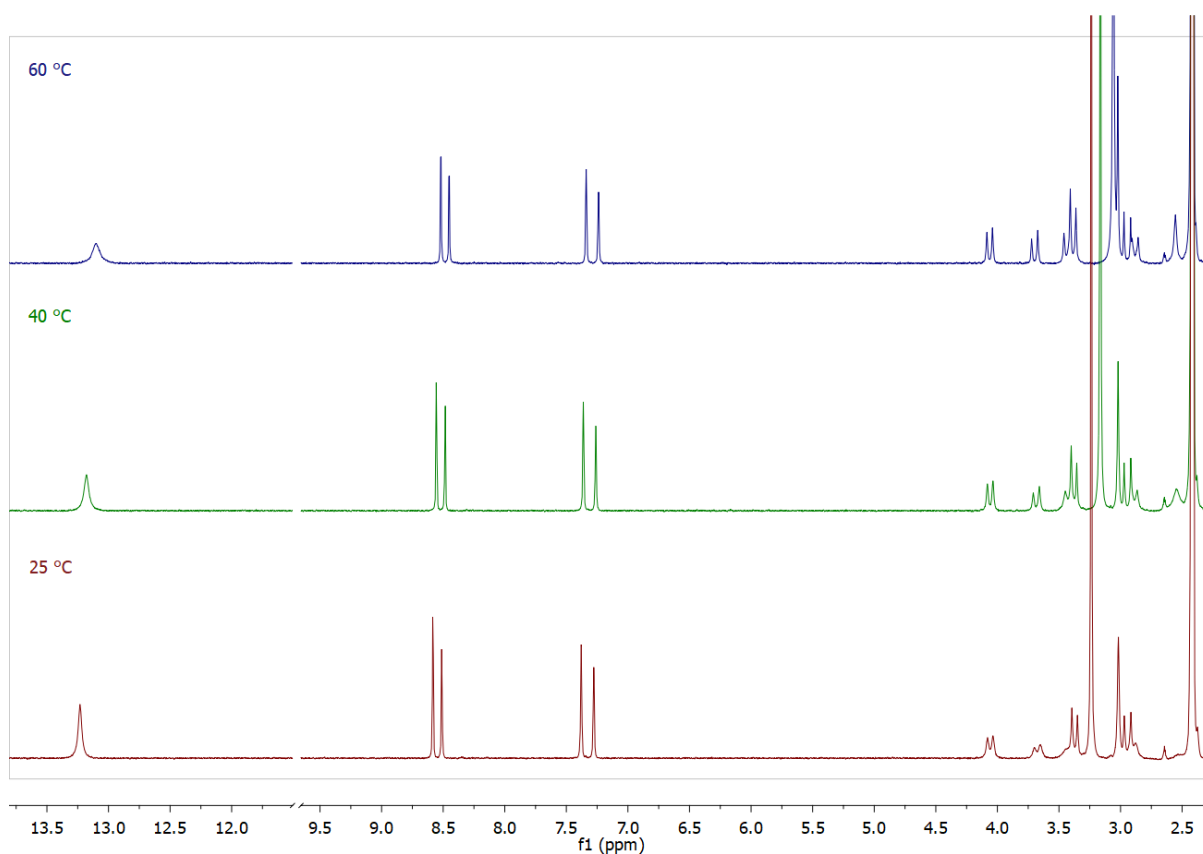
**Figure S4.** ESI-HRMS (-) spectra of  $[W_2O_4(L4)]$  (4).



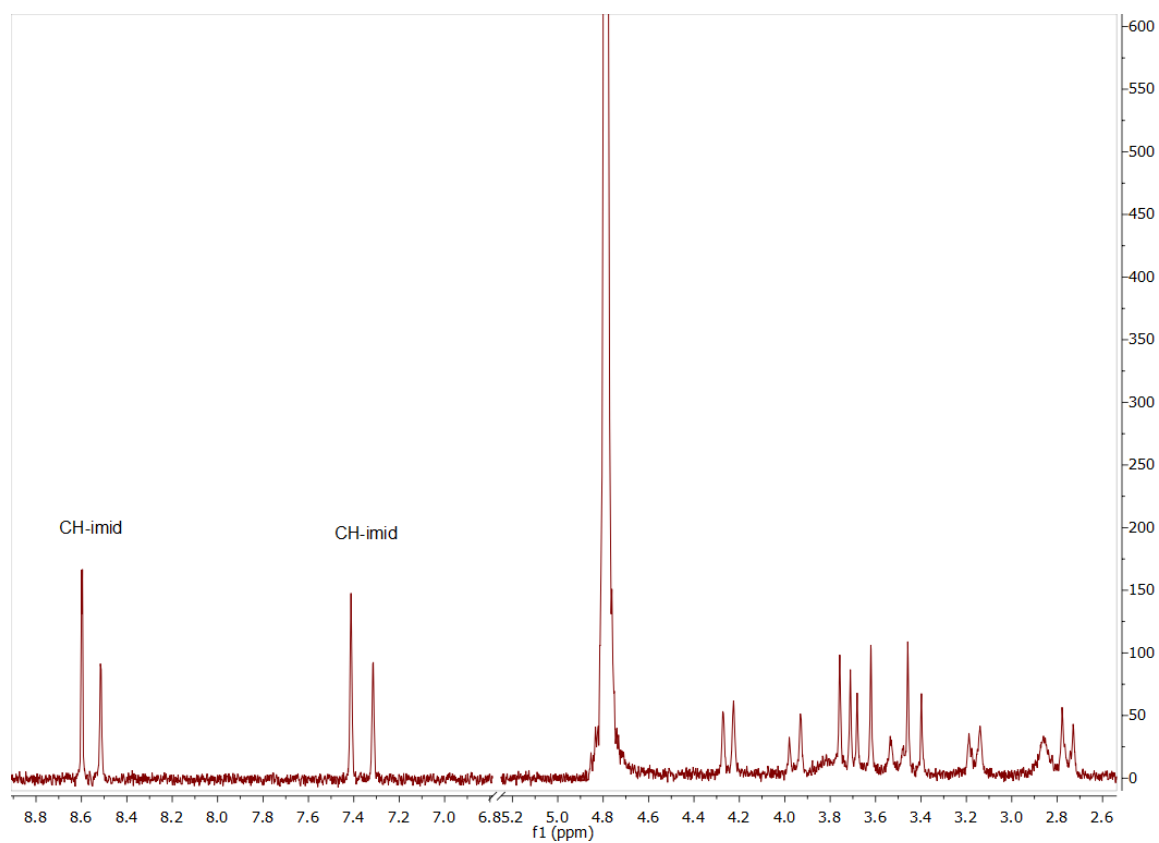
**Figure S5.** ESI-HRMS (-) spectra of  $[W_2O_4(L2)]$  (**2b**).



**Figure S6.** ESI-HRMS (-) spectra of  $[W_2O_4(His)_2]$  (**5**). Experimental spectrum vs. simulated isotopic pattern for  $[W_2O_4(His)_2-H]^+$  is shown.



**Figure S7.** Variable temperature  $^1\text{H}$  NMR spectra of  $[\text{W}_2\text{O}_4(\text{L3})]$  (**3**) in  $\text{DMSO-d}_6$  at  $25^\circ\text{C}$ ,  $40^\circ\text{C}$  and  $60^\circ\text{C}$ .



**Figure S8.**  $^1\text{H}$  NMR spectra of  $[\text{W}_2\text{O}_4(\text{L3})]$  (**3**) in  $\text{D}_2\text{O}$  at  $23^\circ\text{C}$ .



**Figure S9.**  $^1\text{H}$ - $^1\text{H}$  COSY of  $[\text{W}_2\text{O}_4(\text{L2})]$  (**2b**) in DMSO- $\text{d}_6$ .

## Crystal structure determination

All the measurements were performed using monochromatized Mo K $\alpha$  radiation at 100 K. The structures were solved by direct methods (SHELXS-97)<sup>1</sup> and refined by full-matrix least-squares techniques against  $F^2$  (SHELXL-2014/6).<sup>2</sup> The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. Crystal data, data collection parameters, and structure refinement details are given in Table S1 and S2, and in the deposited cif files.

**Crystal structure determination of 2a.** The H atoms of the NH<sub>2</sub> groups were localized at idealized geometries with approximately tetrahedral angles and N–H distances of 0.88 Å, and finally refined with common isotropic displacement parameters for the H atoms of the same group and the N–H distances fixed to 0.88 Å without any constraints to the bond angles. The positions of the H atoms of the water molecules were taken from a difference Fourier map, the O–H distances were fixed to 0.84 Å, and the H atoms were refined with common isotropic displacement parameters for the H atoms of the same molecule without any constraints to the bond angles. The H atoms of the CH<sub>2</sub> groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99 Å. The largest peaks in a final difference Fourier map (1.51 - 1.69 eÅ<sup>-3</sup>) were in the vicinity (0.74 - 1.19 Å) of the W atom. For 271 parameters final  $R$  indices of  $R_1 = 0.0557$  and  $wR^2 = 0.1199$  (GOF = 1.022) were obtained.

**Crystal structure determination of 3.** The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The H atoms H11 and H21 were put at the external bisectors of the C–N–C angles at a N–H distance of 0.88 Å but the individual isotropic displacement parameters were free to refine. The other H atoms of the imidazole rings were put at the external bisectors of the N–C–X angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the CH<sub>2</sub> groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99 Å. Since the positions of the H atoms of the water molecules could not be found in a difference Fourier map, their positions were calculated by examination of the observed intermolecular O...O distances. The O–H distances were fixed to 0.84 Å, the O...H distances within the water channel restrained to 2.0 Å, the H...H distances within the water molecules restrained to 1.44 Å, and one common isotropic displacement parameter was refined for the H atoms of the water molecules. The largest peak in a final difference Fourier map (1.67eÅ<sup>-3</sup>) was located between the two W atoms (1.25eÅ<sup>-3</sup> to W2, 1.31eÅ<sup>-3</sup> to W1), the 14 next largest peaks (1.03 - 1.38eÅ<sup>-3</sup>) were in the vicinity (0.73-1.14

Å) of the W atoms. For 327 parameters final *R* indices of  $R1 = 0.0313$  and  $wR^2 = 0.0724$  (GOF = 1.079) were obtained.

**Crystal Structure determination of 4.** The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The position of the H atom of the OH group was found by a structure-factor calculation performed without the hydrogen atom and choosing the torsion angle which maximizes the electron density. Finally, the O–H distance was fixed to 0.84 Å, and this H atom was refined with an individual isotropic displacement parameter without any constraints to the bond angles. The H atoms of the CH<sub>2</sub> groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99 Å. The H atoms of the pyridine ring were put at the external bisectors of the C–C–C angles at C–H distances of 0.95 Å and common isotropic displacement parameters were refined for these H atoms. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same solvent molecule and idealized geometries with tetrahedral angles, enabling rotations around the C–C bonds, and C–H distances of 0.98 Å. The largest peaks in a final difference Fourier map ( $1.30 - 1.35 \text{ e} \text{ Å}^{-3}$ ) were in the vicinity (0.88 - 0.95 Å) of the W atom. For 240 parameters final *R* indices of  $R1 = 0.0390$  and  $wR^2 = 0.0833$  (GOF = 1.022) were obtained.

**Crystal Structure determination of 5.** The absolute configuration was established by anomalous dispersion effects in the diffraction measurements on the crystal. The H atoms of the imidazole ring were put at the external bisectors of the X–C–N angles (X = C or N) at C–H distances of 0.95 Å and a common isotropic displacement parameter was refined for the three H atoms of this ring. The positions of the H atoms bonded to N were taken from a difference Fourier map, the N–H distances were fixed to 0.88 Å, and the H atoms of the NH<sub>2</sub> group were refined with a common isotropic displacement parameter without any constraints to the bond angles. The H atoms of the tertiary C–H groups were refined with a common isotropic displacement parameter and all X–C–H angles equal at a C–H distance of 1.00 Å. The H atoms of the CH<sub>2</sub> groups were refined with a common isotropic displacement parameter and idealized geometries with approx. tetrahedral angles and C–H distances of 0.99 Å. The positions of the H atoms of the water molecules were taken from a difference Fourier map, the O–H distances were fixed to 0.84 Å, and the H atoms of the fully occupied water molecule were refined with a common isotropic displacement parameter without any constraints to the bond angles. The H atom of the partly occupied water molecule lying at a two-fold rotation axis was refined with an isotropic displacement parameter fixed to 1.2 times  $U_{eq}$  of the O atom to which it is bonded to. The largest peaks in a final difference Fourier map ( $0.77 - 1.08 \text{ e} \text{ Å}^{-3}$ ) were in the vicinity (0.74 - 0.98 Å) of the W atom. For 165 parameters final *R* indices of  $R1 = 0.0240$  and  $wR^2 = 0.0534$  (GOF = 1.056) were obtained.

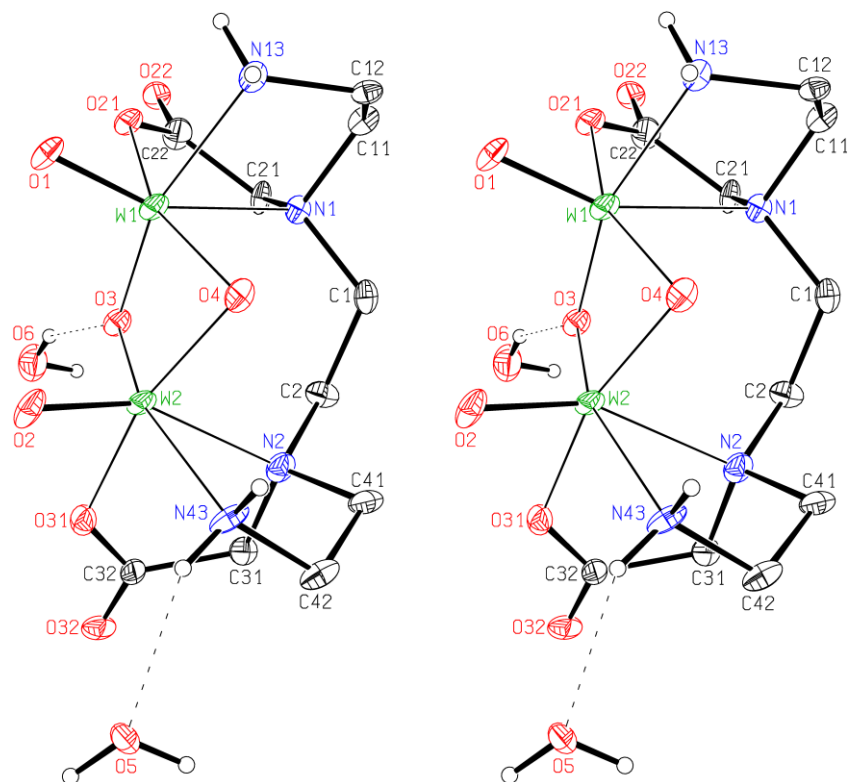


**Table S1** Crystallographic data and structure refinement for complexes **2a** and **3**.

Crystal Data	[W <sub>2</sub> O <sub>4</sub> (L2)] ( <b>2a</b> )	[W <sub>2</sub> O <sub>4</sub> (L3)] ( <b>3</b> )
Empirical formula	C <sub>10</sub> H <sub>20</sub> N <sub>4</sub> O <sub>8</sub> W <sub>2</sub> · 2H <sub>2</sub> O	C <sub>14</sub> H <sub>18</sub> N <sub>6</sub> O <sub>8</sub> W <sub>2</sub> · 3H <sub>2</sub> O
Formula weight	728.03	820.09
Crystal description	block, yellow	plate, orange
Crystal size	0.12 x 0.10 x 0.07 mm	0.21 x 0.12 x 0.05 mm
Crystal system, space group	monoclinic, P 2 <sub>1</sub> /n	orthorhombic, P n a 2 <sub>1</sub>
Unit cell dimensions:	a = 10.399(3) Å b = 11.196(3) Å c = 15.642(4) Å β = 108.591(16)°	a = 13.4293(14) Å b = 12.7387(13) Å c = 13.2657(14) Å
Volume	1726.1(8) Å <sup>3</sup>	2269.4(4) Å <sup>3</sup>
Z	4	4
Calculated density	2.802 Mg/m <sup>3</sup>	2.400 Mg/m <sup>3</sup>
F(000)	1360	1544
Linear absorption coefficient μ	13.379 mm <sup>-1</sup>	10.197 mm <sup>-1</sup>
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.485	1.000 and 0.349
Unit cell determination	2.28° < Θ < 26.45° 2092 reflections used at 100 K	2.20° < Θ < 30.53° 9937 reflections used at 100 K
<b>Data collection</b>		
Θ range for data collection	2.09 to 27.00°	2.20 to 30.0°
Reflections collected / unique	14763 / 3764	31035 / 6595
Significant unique reflections	2726 with I > 2σ (I)	5841 with I > 2σ (I)
R(int), R(sigma)	0.0858, 0.1050	0.0836, 0.0591
Completeness to Θ = 27.0°/30.0°	99.8%	100.0%
<b>Refinement</b>		
Data / parameters / restraints	3764 / 271 / 8	6595 / 327 / 13
Goodness-of-fit on F <sup>2</sup>	1.022	1.079
Final R indices [I > 2σ (I)]	R1 = 0.0557, wR2 = 0.1032	R1 = 0.0313, wR2 = 0.0681
R indices (all data)	R1 = 0.0916, wR2 = 0.1199	R1 = 0.0403, wR2 = 0.0724
Weighting scheme	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(aP) <sup>2</sup> +bP] where P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(aP) <sup>2</sup> +bP] where P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3
Weighting scheme parameters a,b	0.0399, 2.8221	0.0214, 1.1216
Largest Δ/σ in last cycle	0.002	0.003
Largest difference peak and hole	1.688 and -1.613e/Å <sup>3</sup>	1.670 and -1.837e /Å <sup>3</sup>
CCDC deposition number	2239128	2239129

**Table S2** Crystallographic data and structure refinement for complexes **4** and **5**.

Crystal Data	[W <sub>2</sub> O <sub>4</sub> (L4)] ( <b>4</b> )	[W <sub>2</sub> O <sub>4</sub> (His) <sub>2</sub> ] ( <b>5</b> )
Empirical formula	C <sub>18</sub> H <sub>20</sub> N <sub>4</sub> O <sub>10</sub> W <sub>2</sub> · 4C <sub>2</sub> H <sub>6</sub> OS	C <sub>12</sub> H <sub>16</sub> N <sub>6</sub> O <sub>8</sub> W <sub>2</sub> · 2.22H <sub>2</sub> O
Formula weight	1132.59	780.06
Crystal description	block, orange	block, orange
Crystal size	0.42 x 0.39 x 0.37 mm	0.18 x 0.16 x 0.13 mm
Crystal system, space group	tetragonal, I 4 <sub>1</sub>	trigonal, P 3 <sub>2</sub> 2 1
Unit cell dimensions:	a = 13.7049(6) Å b = 13.7049(6) Å c = 19.1476(18) Å	a = 9.4211(3) Å b = 9.4211(3) Å c = 18.2168(10) Å
Volume	3596.4(5) Å <sup>3</sup>	1400.25(12) Å <sup>3</sup>
Z	4	3
Calculated density	2.092 Mg/m <sup>3</sup>	2.775 Mg/m <sup>3</sup>
F(000)	2208	1092.6
Linear absorption coefficient μ	6.694 mm <sup>-1</sup>	12.384 mm <sup>-1</sup>
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.245	0.746 and 0.236
Unit cell determination	2.97° < Θ < 29.93° 9925 reflections used at 100 K	2.50° < Θ < 30.07° 9978 reflections used at 100 K
<b>Data collection</b>		
Θ range for data collection	1.83 to 30.00°	2.50 to 30.0°
Reflections collected / unique	27585 / 4902	29563 / 2719
Significant unique reflections	4393 with I > 2σ (I)	2657 with I > 2σ (I)
R(int), R(sigma)	0.0947, 0.0698	0.0995, 0.0431
Completeness to Θ = 30. 0°	99.9%	100.0%
<b>Refinement</b>		
Data / parameters / restraints	4902 / 240 / 2	2719 / 165 / 6
Goodness-of-fit on F <sup>2</sup>	1.022	1.056
Final R indices [I > 2σ (I)]	R1 = 0.0390, wR2 = 0.0818	R1 = 0.0240, wR2 = 0.0532
R indices (all data)	R1 = 0.0448, wR2 = 0.0833	R1 = 0.0247, wR2 = 0.0534
Weighting scheme	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(aP) <sup>2</sup> +bP] where P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	w = 1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(aP) <sup>2</sup> +bP] where P = (F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3
Weighting scheme parameters a,b	0.0400, 0.0000	0.0220, 0.4247
Largest Δ/σ in last cycle	0.001	0.002
Largest difference peak and hole	1.351 and -1.100e/Å <sup>3</sup>	1.078 and -1.389e /Å <sup>3</sup>
CCDC deposition number	2239130	2239131



**Figure S10.** Stereoscopic ORTEP plot of the asymmetric unit of **2a** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms of the NH<sub>2</sub> groups and of the water molecules are drawn with arbitrary radii, the other H atoms were omitted for clarity. Hydrogen bonds are indicated by dashed lines.

**Table S3.** Selected bond lengths [Å] and angles [°] for **2a**.

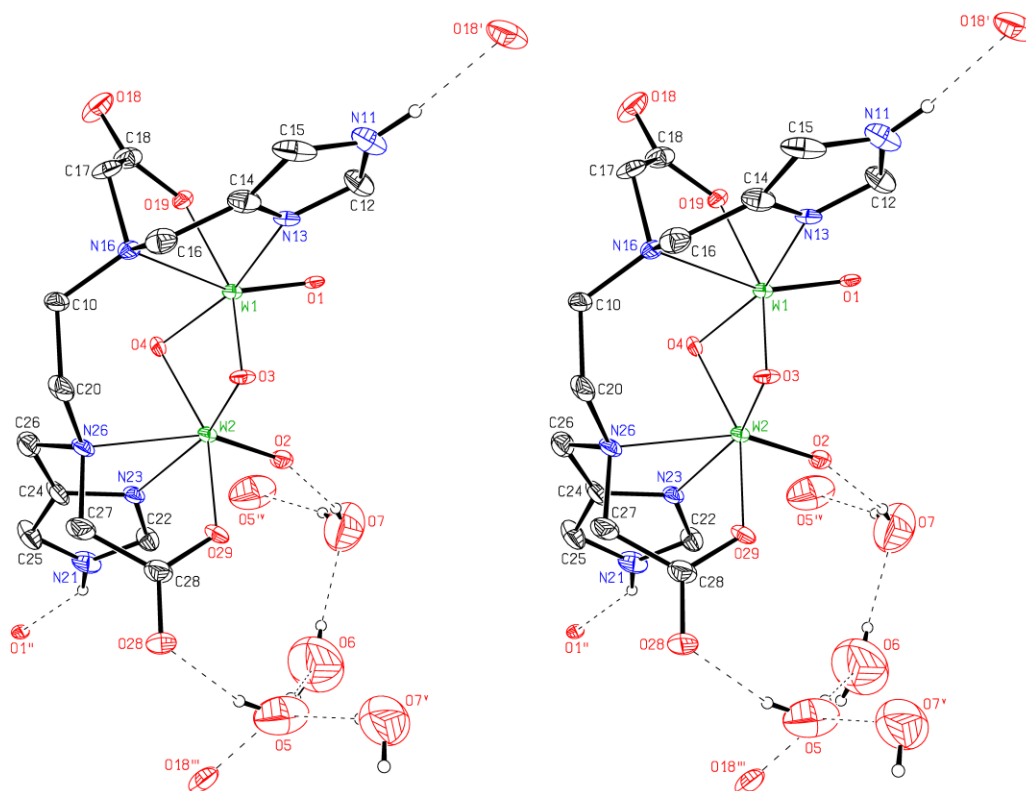
W1-O1	1.709(8)	O3-W2-N43	158.2(3)
W1-O3	1.950(9)	O4-W2-O31	162.8(3)
W1-O4	1.957(8)	W1-O3-W2	82.6(3)
W1-O21	2.119(8)	W1-O4-W2	81.8(3)
W1-N1	2.391(10)	C12-N13-W1	113.0(6)
W1-N13	2.185(6)	C22-O21-W1	123.3(8)
W2-O2	1.722(9)	C32-O31-W2	126.2(9)
W2-O3	1.938(8)	C42-N43-W2	116.9(5)
W2-O4	1.960(10)		
W2-O31	2.072(10)	W1-O3-W2-O4	-25.0(4)
W2-N2	2.418(11)	O3-W2-O4-W1	25.0(4)
W2-N43	2.224(5)	W2-O4-W1-O3	-24.8(3)
		O4-W1-O3-W2	25.1(3)
O3-W1-O4	92.0(4)	O1-W1-W2-O2	-2.0(5)
O1-W1-N1	157.6(4)	N13-W1-W2-O31	-162.3(4)
O3-W1-N13	158.7(3)	N13-W1-W2-N43	-0.5(5)
O4-W1-O21	155.4(4)	O21-W1-W2-O31	-10.3(5)
O3-W2-O4	92.3(4)	O21-W1-W2-N43	151.4(4)
O2-W2-N2	156.5(4)		

**Table S4.** Hydrogen bonds for **2a** [ $\text{\AA}$ ,  $^\circ$ ].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N13-H13...O1 <sup>i)</sup>	0.88	2.435(13)	3.200(9)	145.6(13)
N13-H14...O5 <sup>ii)</sup>	0.88	2.086(6)	2.932(6)	161.0(8)
N43-H43...O2 <sup>ii)</sup>	0.88	2.177(12)	3.049(11)	171(3)
N43-H44...O5	0.88	2.220(8)	2.942(6)	139.1(7)
O5-H51...O22 <sup>iii)</sup>	0.84	1.954(11)	2.710(11)	149.1(9)
O5-H52...O21 <sup>iv)</sup>	0.84	2.081(10)	2.878(9)	158.1(11)
O6-H61...O3	0.84	1.97(3)	2.760(10)	156(6)
O6-H62...O2 <sup>v)</sup>	0.84	2.32(2)	3.102(10)	155(4)

Symmetry transformations used to generate equivalent atoms:

i) 2-x, 1-y, 1-z ii) 1-x, 1-y, 1-z iii) 3/2-x, y-1/2, 3/2-z iv) x-1, y, z v) 3/2-x, y+1/2, 3/2-z



**Figure S11.** Stereoscopic ORTEP plot of **3** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level, the H atoms of the hydrogen bonds were plotted with arbitrary radii, the others were omitted for clarity. Hydrogen bonds are indicated by dashed lines.

**Table S5.** Selected bond lengths [Å] and angles [°] for **3**.

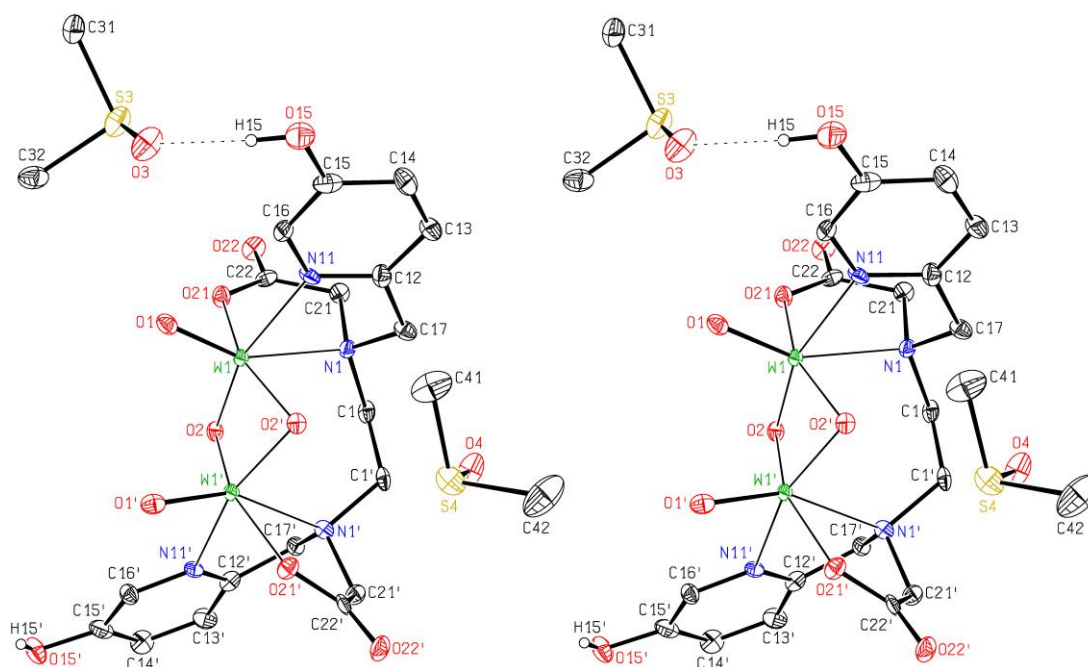
W1-O1	1.712(6)	W2-O2	1.735(6)
W1-O3	1.932(5)	W2-O3	1.941(6)
W1-O4	1.946(6)	W2-O4	1.946(6)
W1-O19	2.081(6)	W2-O29	2.066(6)
W1-N13	2.171(8)	W2-N23	2.156(8)
W1-N16	2.389(7)	W2-N26	2.412(8)
C18-O18	1.233(11)	C28-O28	1.240(12)
C18-O19	1.303(11)	C28-O29	1.267(12)
O1-W1-N16	155.4(3)	O2-W2-N26	157.7(3)
O3-W1-O19	156.9(3)	O4-W2-O29	155.5(3)
O4-W1-N13	160.8(3)	O3-W2-N23	157.8(3)
O1-W1-O3	109.6(3)	O2-W2-O4	110.6(3)
O1-W1-O4	111.0(3)	O2-W2-O3	111.3(3)
O1-W1-O19	93.2(3)	O2-W2-O29	92.9(3)
O1-W1-N13	87.9(3)	O2-W2-N23	90.3(3)
O3-W1-O4	92.1(3)	O3-W2-O4	91.8(2)
W1-O3-W2	82.6(2)	W2-O4-W1	82.1(2)
C12-N13-C14	106.8(8)	C22-N23-C24	107.7(8)
C12-N13-W1	133.9(7)	C22-N23-W2	132.0(7)
C14-N13-W1	119.2(6)	C24-N23-W2	120.2(6)
C18-O19-W1	124.3(6)	C28-O29-W2	124.1(6)
O1-W1-W2-O2	-1.4(5)	N13-W1-O3-W2	-173.6(5)
O3-W1-O4-W2	-25.3(4)	O19-W1-O4-W2	177.3(4)
W1-O4-W2-O3	25.1(4)	N23-W2-O4-W1	-176.9(4)
O4-W2-O3-W1	-25.3(4)	O29-W2-O3-W1	179.1(5)
W2-O3-W1-O4	25.3(4)		

**Table S6.** Hydrogen bonds for **3** [Å, °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N11-H11...O18 <sup>i)</sup>	0.88	1.89	2.765(11)	171.2
N21-H21...O1 <sup>ii)</sup>	0.88	2.00	2.769(10)	146.0
O5-H51...O28	0.84	2.056(11)	2.858(11)	159.4(10)
O5-H56...O6	0.84	2.040(8)	2.879(7)	177(7)
O6-H61...O18 <sup>iii)</sup>	0.84	2.365(12)	3.145(11)	154.7(13)
O6-H67...O7	0.84	2.031(9)	2.853(8)	166.0(12)
O7-H71...O2	0.84	2.142(12)	2.959(8)	164(3)
O7-H75...O5 <sup>iv)</sup>	0.84	2.023(7)	2.843(7)	164.9(14)

Symmetry transformations used to generate equivalent atoms:

<sup>i)</sup> 1-x, -y, z+1/2    <sup>ii)</sup> 1/2-x, y+1/2, z-1/2    <sup>iii)</sup> x, y+1, z    <sup>iv)</sup> x-1/2, 3/2-y, z



**Figure S12.** Stereoscopic ORTEP plot of complex **4** and the two DMSO molecules of the asymmetric unit showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms of the OH groups are drawn with arbitrary radii, the other H atoms were omitted for clarity. The hydrogen bond is indicated by a dashed line.

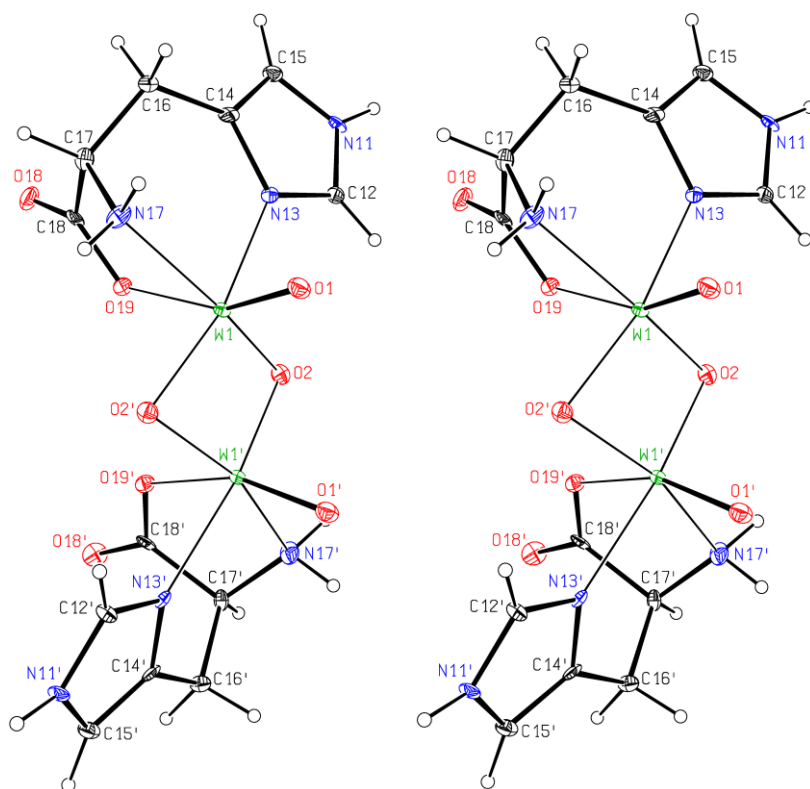
**Table S7.** Selected bond lengths [Å] and angles [°] for **4**.

W1-O1	1.716(8)
W1-O2	1.946(6)
W1-O2 <sup>i)</sup>	1.960(6)
W1-O21	2.086(7)
W1-N11	2.212(8)
W1-N1	2.362(8)
W1-O2-W1 <sup>i)</sup>	81.9(2)
O2-W1-O2 <sup>i)</sup>	92.8(3)
O1-W1-N1	154.6(3)
O2-W1-N11	159.4(3)
O2 <sup>i)</sup> -W1-O21	156.9(3)
C16-N11-C12	117.8(8)
C12-N11-W1	120.6(6)
C16-N11-W1	120.6(6)
C22-O21-W1	125.3(6)
O2 <sup>i)</sup> -W1-O2-W1 <sup>i)</sup>	24.1(5)
O2-W1-O2 <sup>i)</sup> -W1 <sup>i)</sup>	-24.3(5)
O1-W1-W1 <sup>i)</sup> -O1 <sup>i)</sup>	0.9(11)
N11-W1-W1 <sup>i)</sup> -O21 <sup>i)</sup>	-4.0(10)
N11-W1-W1 <sup>i)</sup> -N11 <sup>i)</sup>	-158.6(7)
O21-W1-W1 <sup>i)</sup> -O21 <sup>i)</sup>	150.6(7)

Symmetry transformation used to generate equivalent atoms: <sup>i)</sup> -x, 1-y, z

**Table S8.** Hydrogen bonds for **4** [Å, °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O15-H15...O3	0.84	1.781(11)	2.616(11)	172.6(3)



**Figure S13.** Stereoscopic ORTEP plot of complex **5** showing the atomic numbering scheme. The probability ellipsoids are drawn at the 50% probability level. The H atoms are drawn with arbitrary radii.

**Table S9.** Selected bond lengths [Å] and angles [°] for **5**.

W1-O1	1.737(4)	O1-W1-W1 <sup>i)</sup> -O1 <sup>i)</sup>	-6.2(2)
W1-O2	1.946(4)	O1-W1-W1 <sup>i)</sup> -O19 <sup>i)</sup>	177.79(17)
W1-O19	2.139(4)	O2-W1-W1 <sup>i)</sup> -O2 <sup>i)</sup>	-157.2(3)
W1-N13	2.184(5)	O2-W1-W1 <sup>i)</sup> -N13 <sup>i)</sup>	-158.9(3)
W1-N17	2.227(3)	O2-W1-W1 <sup>i)</sup> -N17 <sup>i)</sup>	-6.2(3)
C18-O18	1.221(8)	O19-W1-W1 <sup>i)</sup> -O1 <sup>i)</sup>	177.8(2)
C18-O19	1.294(7)	O19-W1-W1 <sup>i)</sup> -O19 <sup>i)</sup>	1.8(2)
		N13-W1-W1 <sup>i)</sup> -O2	-1.7(3)
W1-O2-W1 <sup>i)</sup>	82.04(16)	N13-W1-W1 <sup>i)</sup> -O2 <sup>i)</sup>	-158.9(3)
O2-W1-O2 <sup>i)</sup>	95.40(17)	N13-W1-W1 <sup>i)</sup> -N13 <sup>i)</sup>	-160.6(3)
O1-W1-O19	158.50(18)	N13-W1-W1 <sup>i)</sup> -N17 <sup>i)</sup>	-7.9(3)
O2 <sup>i)</sup> -W1-N13	164.27(18)	N17-W1-W1 <sup>i)</sup> -O2	151.0(2)
O2-W1-N17	158.41(17)	N17-W1-W1 <sup>i)</sup> -O2 <sup>i)</sup>	-6.2(3)
N13-W1-N17	86.12(15)	N17-W1-W1 <sup>i)</sup> -N13 <sup>i)</sup>	-7.9(3)
C12-N13-C14	106.1(5)	N17-W1-W1 <sup>i)</sup> -N17 <sup>i)</sup>	144.8(2)
C12-N13-W1	125.6(4)	O2 <sup>i)</sup> -W1-W1 <sup>i)</sup> -O2	157.2(3)
C14-N13-W1	127.7(4)		
C18-O19-W1	121.8(4)		

Symmetry transformation used to generate equivalent atoms:

<sup>i)</sup> -x, y-x, 5/3-z

**Table S10.** Hydrogen bonds for **5** [Å, °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N11-H11...O1 <sup>i)</sup>	0.88	2.051(14)	2.810(6)	144.0(18)
N17-H171...O3 <sup>ii)</sup>	0.88	2.52(3)	3.029(5)	117(3)
N17-H171...O4 <sup>iii)</sup>	0.88	2.523(8)	3.362(4)	159.8(19)
N17-H172...O18 <sup>iv)</sup>	0.88	2.48(3)	3.053(6)	123(3)
N17-H172...O3	0.88	2.58(2)	3.311(6)	141(2)
O3-H32...O1	0.84	2.376(16)	2.921(6)	123.1(15)
O3-H31...O18 <sup>v)</sup>	0.84	2.166(18)	2.983(6)	164(6)

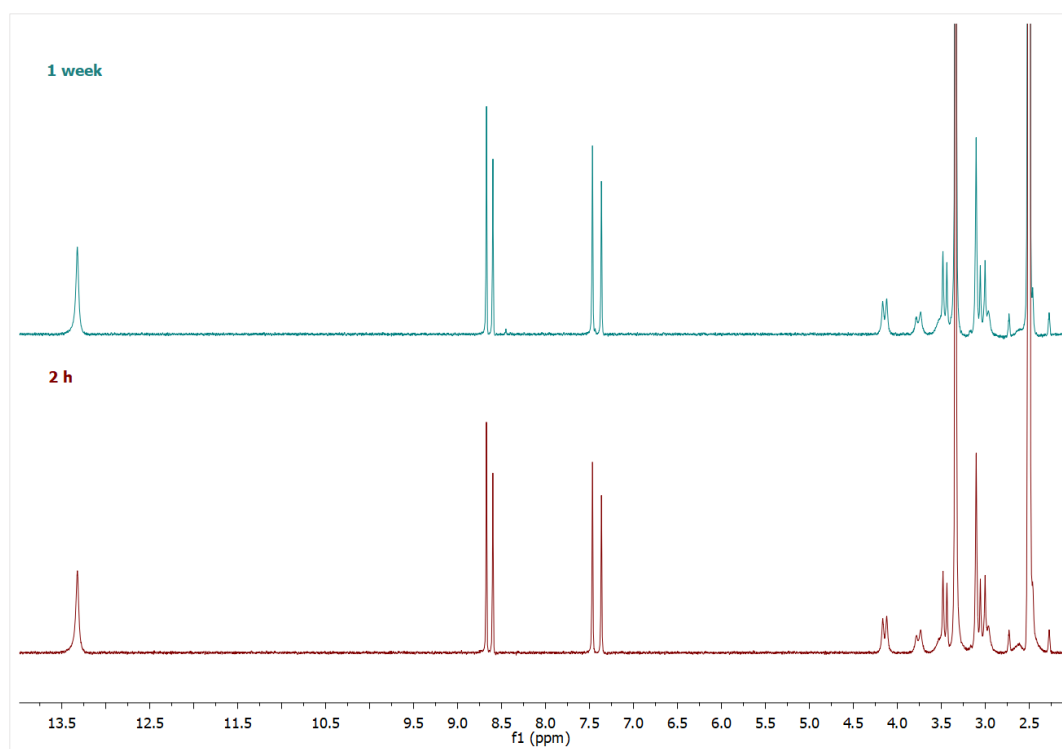
Symmetry transformations used to generate equivalent atoms:

<sup>i)</sup> -y, x-y, z-1/3    <sup>ii)</sup> 1-x, y-x+1, 5/3-z    <sup>iii)</sup> y-x+1, 1-x, z+1/3

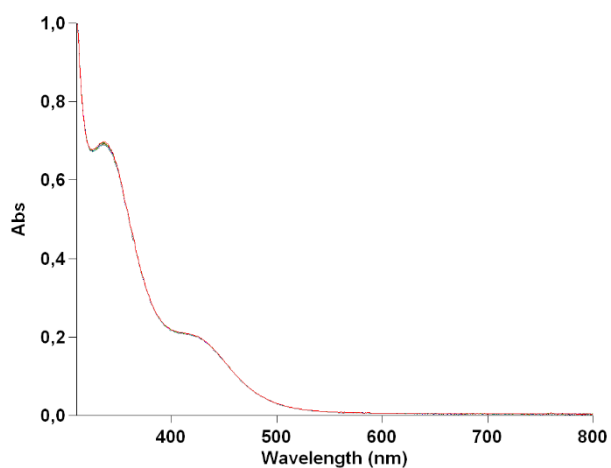
<sup>iv)</sup> 1-x, y-x, 5/3-z    <sup>v)</sup> x-y+1, 1-y, 4/3-z



### Stability of complex 3



**Figure S14.**  $^1\text{H}$  NMR spectra of  $[\text{W}_2\text{O}_4(\text{L3})]$  (**3**) in  $\text{DMSO-d}_6$  after 2 h (bottom) and 1 week of incubation at RT.



**Figure S15.** Stability of complex **3** (0.5 mM) dissolved in phosphate buffer (20 mM, pH 7.4) as followed by UV-Vis spectroscopy over 20 h of incubation at RT and under ambient atmosphere.

## References

- (1) Sheldrick, G. M. A Short History of SHELX. *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64* (1), 112–122. <https://doi.org/10.1107/S0108767307043930>.
- (2) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71* (1), 3–8. <https://doi.org/10.1107/S2053229614024218>.