Electronic supporting information for

Heteroelements in polyoxometalates: a study on the influence of different group 15 elements on polyoxometalate formation

Jan-Christian Raabe[1], Froze Jameel[2], Matthias Stein[2], Jakob Albert[1] and Maximilian J. Poller*[1]

[1]Institute for Technical and Macromolecular Chemistry, Universität Hamburg, Bundesstraße 45, 20146 Hamburg, Germany

[2]Max Planck Institute for Dynamics of Complex Technical Systems, Molecular Simulations and Design Group, Sandtorstrasse 1, 39106, Magdeburg, Germany

*Corresponding Author

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1 Experimental Details

1.1 Chemicals

All chemicals were purchased from the following suppliers:

- Sodium tungstate dihydrate: VWR chemicals
- Nitric acid: was obtained from Merck as 65 % solution in water and was further diluted with deionized water to a concentration of 4 M.
- Phosphoric acid: was purchased as a 85 % solution in water from Grüssing, which was further diluted with demineralized water to a final concentration of 25 %.
- Arsenic(III) oxide: was purchased from Honeywell (ReagentPlus 99.0 %)
- Potassium hexahydroxoantimonate(V): Merck
- Hydrochloric acid: VWR chemicals as a 37 % solution in water
- Hydrogen peroxide: VWR chemicals as a 30 % solution in water
- Deionized water was always used as solvent

1.2 Synthetic procedures

Preparing the As(V) solution: Arsenic(III) oxide was added to a mixture of water (30 mL) and a 30 % solution of hydrogen peroxide in water (30 mL). It was refluxed for two hours, yielding an aqueous, colorless solution of arsenic(V) acid in water.

Preparing the Sb(V) solution: potassium hexahydroxo antimonate(V) was added to water (100 mL) and refluxed for one hour, yielding a colorless solution

General experimental procedure: Sodium tungstate dihydrate was dissolved in water (100 mL) or added to the respective As(V)/Sb(V) solution. The start volume of the reaction mixture was always 100 mL of an aqueous solution. For the experiments with the hetero elements N(V) and P(V) a 4 M solution of nitric acid or 25 % phosphoric acid solution in water was added to the tungstate solution. The pH value was adjusted to 5 or 1 using a 37 % solution of hydrochloric acid in water and the solution was concentrated under reduced pressure (85 °C, 200 to 0 mbar) to yield a white powder in the case of the experiments at pH 5 or a yellow powder in the experiments at pH 1 for N(V) and Sb(V). Purification of the POMs was done by our previous published nanofiltration process.[1,2]

Table S1 shows an overwiev of the precise weights of all precursor compounds:

Table S1: Precise weights of all precursor substances used in our experimental procedures.

No.	Precursor	pH 5 experiments			pH 1 experiments		
		Mass	Substance [mmol]	Equivalents	Mass	Amount of substance [mol]	Equivalents
1	$Na_2WO_4 \cdot 2\ H_2O$	5.0032 g	15.168	6.02	5.0012 g	15.162	6.02
	4 M HNO_3	0.63 mL	2.52	1.00	0.63 mL	2.52	1.00
2	$Na_2WO_4 \cdot 2\ H_2O$	5.0017 g	15.163	5.97	5.0040	15.170	5.98
	25 % H_3PO_4	0.9954 g	2.5394	1.00	0.9941	2.5361	1.00
3	$Na_2WO_4 \cdot 2\ H_2O$	5.0022 g	15.165	11.97	5.0027	15.166	12.00
	As_2O_3	0.2506 g	1.267	1.00	0.2499	1.236	1.00
4	$Na_2WO_4 \cdot 2\ H_2O$	5.0031 g	15.168	6.00	5.0012	15.162	6.00
	$K[Sb(OH)_6]$	0.6644 g	2.527	1.00	0.6643	2.527	1.00

All precisely measured pH values in our experiments are listed in Table S2:

Table S2: pH values in our experiments.

No.	pH 5 experiments		pH 1 experiments	
	pH value before adjustment	pH value after adjustment	pH value before adjustment	pH value after adjustment
1	7.790	5.040	7.866	1.018
2	7.926	5.066	7.884	0.998
3	5.829	4.984	5.495	0.953
4	9.900	5.180	9.124	1.007

1.3 Characterization

1.3.1 Compositional analysis

Elemental analysis (AAS/ICP-OES):

All samples were analyzed using an ICP-OES-spectrometer for elemental analysis (Fa. Spectro, type ARCOS) for W and P (method ICP-OES). Na, K and Sb were determined with AAS-F (Fa. Thermo, type Solaar S Series), method: F-AAS without HKL). Element As was measured with G-AAS. Nitrate was analyzed with IC.

- Compound $Na_8[W_{12}O_{40}]$ was dissolved in water (25 mL).
- Compound $Na_{12}[P_4W_{14}O_{58}]$ was dissolved in water (5 mL) and nitric acid (0.1 mL) was added. Then it was filled up to a final volume of 25 mL.
- The As(V) containing sample was dissolved in water (25 mL).
- Compound $Na_7[SbW_6O_{24}]$ was dissolved in water (25 mL).
- The oxides WO_3 and Sb_2O_5 were dissolved in aqua regia invers (5 mL) and hydrofluoric acid (1 mL) was added. Then it was filled up to a final volume of 50 mL.

In our experience, the above described method systematically results in slightly too low values for W, presumably due to partial precipitation of WO_3 during sample preparation.

Thermogravimetric analysis (TGA):

Approximately 20 mg of the sample was weighed into a quart crucible and the change in mass was measured at the following temperature program:

- Tare
- 1 minute waiting time
- Heating to 30 °C with heating rate of 10 K/min
- Stay at 30 °C for 15 minutes
- Heating to 350 °C with a heating rate of 10 K/min
- Stay at 350 °C for 30 minutes
- The sample was then cooled to room temperature

The starting temperature was below 30 °C. During the measurement, a nitrogen flow of 20 mL/min was passed through the instrument. The TGA data show three regions: hygroscopic water (water that comes from the air), lattice water (water from crystal association) and the mass consistency (pure POM without any moisture). The final data were exported as a x/y text document. Using Origin® 2019b the TGA data were plotted.

The results of the ICP-OES analysis for the different compounds are summarized below:

$Na_8[W_{12}O_{40}]$ (hetero element N(V) pH 5):

ICP-OES: Calculated for $Na_8[W_{12}O_{40}] \cdot 11\ H_2O$: 5.697 % Na, 0.000 % K, 68.339 % W. Found for $Na_8[W_{12}O_{40}] \cdot 9\ H_2O$: 6.67 % Na, 0.00 % K, 64.92 % W. Data normalized to tungsten. Na/K/W ratio: 9.9/0/12.

TGA: 6.413 % weight loss upon drying, this corresponds to 12 mol lattice water per mol of the POM.

WO_3 (hetero element N(V) pH 1):

ICP-OES: Calculated for WO_3: 79.297 % W. Found for WO_3: 46.23 % W. Nitrate was not determinable, because WO_3 is not soluble in pure water.

The W content deviates because the oxide is contaminated with nitrates.

$Na_{12}[P_4W_{14}O_{58}]$ (hetero element P(V) pH 5):

ICP-OES: Calculated for $Na_{12}[P_4W_{14}O_{58}] \cdot 16\ H_2O$: 16.585 % Na, 0.000 % K, 2.957 % P, 61.43 % W. Found for $Na_{12}[P_4W_{14}O_{58}] \cdot 16\ H_2O$: 0.294 % Na, 0.00986 % K, 2.03 % P, 58.9 % W. Data normalized to tungsten. Na/K/P/W ratio: 0.56/0.01/2.86/14.

The phosphorus content differs due to the loss of PO_4^{3-} during nanofiltration.

TGA: 6.840 % weight loss upon drying, this corresponds to 16 mol lattice water per mol of the POM.

$Na_3[PW_{12}O_{40}]$ (hetero element P(V) pH 1):

ICP-OES: Calculated for $Na_3[PW_{12}O_{40}] \cdot 8\ H_2O$: 2.232 % Na, 0.000 % K, 1.002 % P, 71.391 % W. Found for $Na_3[PW_{12}O_{40}] \cdot 8\ H_2O$: 10.9 % Na, 0.000736 % K, 1.42 % P, 54.7 % W. Data normalized to tungsten. Na/K/P/W ratio: 19.0/0.0007/1.86/12.

The literature known POM $Na_3[PW_{12}O_{40}]$ was not further purified. Therefore, the Na content is increased, which also causes the contents of the other elements to deviate.

TGA: 4.524 % weight loss upon drying, this corresponds to 8 mol lattice water per mol of the POM.

$Na_9[AsW_9O_{34}]$ (hetero element As(V) pH 5):

ICP-OES: Calculated for $Na_9[AsW_9O_{34}] \cdot$ **$10\ H_2O$**: 7.777 % Na, 0.000 % K, 2.816 % As, 62.189 % W. Found for $Na_9[AsW_9O_{34}] \cdot$ **$10\ H_2O$**: 8.52 % Na, 0.00904 % K, 3.07 % As, 58.3 % W. Data normalized to tungsten. Na/K/As/W ratio: 10.5/0.00656/1.16/9.

TGA: 6.661 % weight loss upon drying, this corresponds to 10 mol lattice water per mol of the POM.

$Na_9[AsW_9O_{34}]$ (hetero element As(V) pH 1):

ICP-OES: Calculated for $Na_9[AsW_9O_{34}] \cdot 11\ H_2O$: 7.725 % Na, 0.000 % K, 2.797 % As, 61.771 % W. Found for $Na_9[AsW_9O_{34}] \cdot 11\ H_2O$: 6.62 % Na, 0.00584 % K, 2.51 % As, 59.3 % W. Data normalized to tungsten. Na/K/As/W ratio: 8.03/0.004/0.93/9.

TGA: 7.605 % weight loss upon drying, this corresponds to 11 mol lattice water per mol of the POM.

$Na_7[SbW_6O_{24}]$ (hetero element Sb(V) pH 5):

ICP-OES: Calculated for $Na_7[SbW_6O_{24}] \cdot 14\ H_2O$: 7.959 % Na, 0.000 % K, 6.022 % Sb, 54.554 % W. Found for $Na_7[SbW_6O_{24}] \cdot 14\ H_2O$: 8.45 % Na, 1.11 % K, 7.18 % Sb, 59.1 % W. Data normalized to tungsten. Na/K/Sb/W ratio: 6.86/0.53/1.10/6.

TGA: 12.12 % weight loss upon drying, this corresponds to 14 mol lattice water per mol of the POM.

WO_3/Sb_2O_5 (hetero element Sb(V) pH 1):

ICP-OES: Calculated for WO_3 and for Sb_2O_5: 79.297 % W, 75.273. Found for WO_3/Sb_2O_5: 42.65 % W, 13.0 % Sb.

The W/Sb content differs because the product was isolated as a mixture of WO_3 and Sb_2O_5.

The stoichiometry of all compounds was verified by ICP-OES analysis and the amount of hydration water was determined using thermogravimetric analysis (TGA) as shown in Table S3.

Table S3: ICP-OES elemental analysis and TGA results of the different synthesized compounds in this work.

Hetero element	Compound	Synthesized at pH value…	Element ratio[a]	Hydration water[b]
N(V)	$Na_8[W_{12}O_{40}]$	5	Na/K/NO_3^-/W 9.9/0/0/12	11
	WO_3	1	W: 46.23 %[c]	-
P(V)	$Na_{12}[P_4W_{14}O_{58}]$	5	Na/K/P/W 0.56/0.01/2.86[d]/14	16
	$Na_3[PW_{12}O_{40}]$	1	Na/K/P/W 19.0/0.0007/1.86/12[e]	8
As(V)	$Na_9[AsW_9O_{34}]$	5	Na/K/As/W 10.5/0.007/1.16/9	10
	$Na_9[AsW_9O_{34}]$	1	Na/K/As/W 8.03/0.004/0.93/9	11
Sb(V)	$Na_7[SbW_6O_{24}]$	5	Na/K/Sb/W 6.86/0.53/1.10/6	14
	WO_3/Sb_2O_5	1	Sb/W 2.76/6	-

[a]Element ratios were determined using ICP-OES analysis.
[b]Hydration water amount was determined by TGA.
[c]NO_3^- could not be determined because the sample was dissolved in an aqua regia/HF in the microwave. NO_3^- determination is only possible in a purely aqueous medium.
[d]The anion $[P_4W_{14}O_{58}]^{12-}$ appears to dissociate more strongly in aqueous solution (presumably due to greater instability compared to the other compounds), so that portions of the phosphorus are lost in subsequent purification steps. The identity of the compound was confirmed, especially with IR, Raman, and single crystal structure analysis.
[e]The anion $[PW_{12}O_{40}]^{3-}$ is already known in the literature and was therefore not further purified.

After our dialysis purification[1,2] for the anion $[P_4W_{14}O_{58}]^{12-}$, significant amounts of P were found in the permeate fraction (Table S4), explaining the lowered stoichiometry of 2.86. This indicates a stronger dissociation and thus higher instability of this anion in aqueous solution.

Table S4: Elemental analysis of the permeate fraction after purifying compound $Na_{12}[P_4W_{14}O_{58}]$.

Element	Na	K	P	W
Concentration [g/L]	1.345	0.00046	0.154	0.0551

1.3.2 Vibrational Spectroscopy

ATR-FT-IR spectroscopy:

All IR spectra were measured in attenuated total reflection (ATR) measurement mode on a QATR™-S single-reflection ATR (with a diamond prism) from Shimadzu. From the raw data obtained, the baseline was corrected, and the peaks were determined manually. The IR data were then exported as an x/y text document and plotted in Origin®2019b.

Raman spectroscopy:

All Raman spectra were measured on a SENTERRA Raman microscope from Bruker Optik GmbH. The aperture was set to 50 x 1000 µm. A 20 objective was used on the microscope. The excitation laser has a wavelength of 785 nm and the measurement range used was between 75 cm^{-1} and 1525 cm^{-1}. The integration time was 16 seconds, the number of scans was 8 and the Raman laser power was 10 mW. All data were exported as .dpt file and plotted in Origin®2019b.

1.3.3 Nuclear magnetic resonance (NMR) spectroscopy

All ^{31}P spectra were measured with a Time Domain Data Sizes (TD) of 32 K, the Number of Scans (NS) were set to 2k (= 2048), the Transmitter Frequency Offset for Channel F1 (O1) and the Spectral Width (SW) were -1 and 40 ppm. The Delay D1 was set to 1 s. NMR analysis was done using MestReNova®. All data were exported into .csv data and plotted in Origin®2019b.

The ^{31}P-NMR data of compound $Na_{12}[P_4W_{14}O_{58}]$ and $Na_3[PW_{12}O_{40}]$ are shown in Figure S1 and S2.

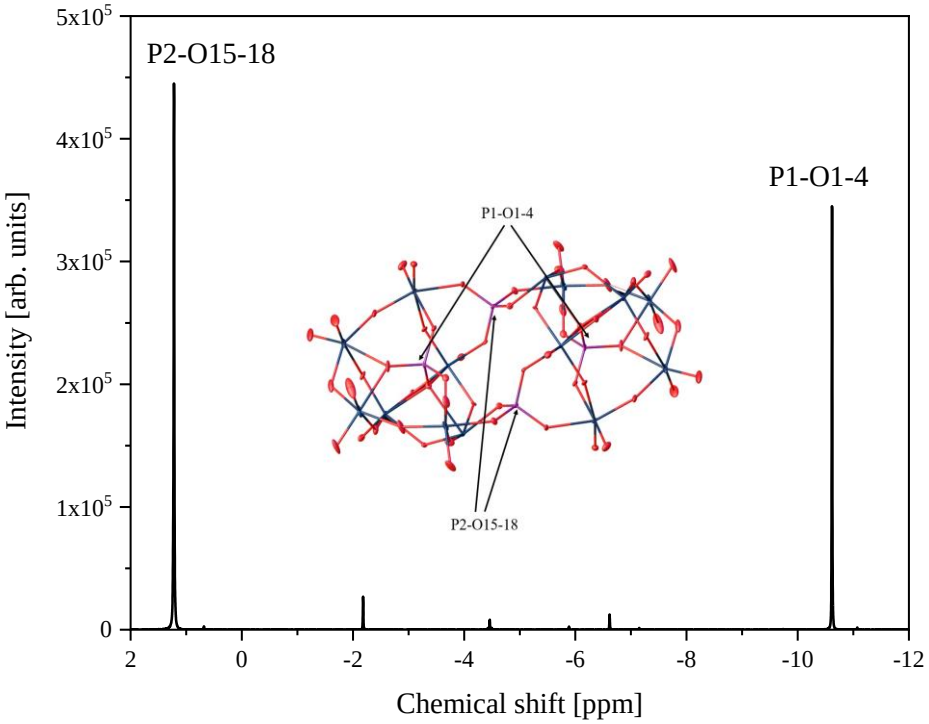

Figure S1: ^{31}P-NMR of $Na_{12}[P_4W_{14}O_{58}]$ in a mixture of 0.7 mL water (pH 5) and 0.07 mL acetone-*d*6. The spectrum was measured at 242.9 MHz, 85 % H_3PO_4 was used as external standard.

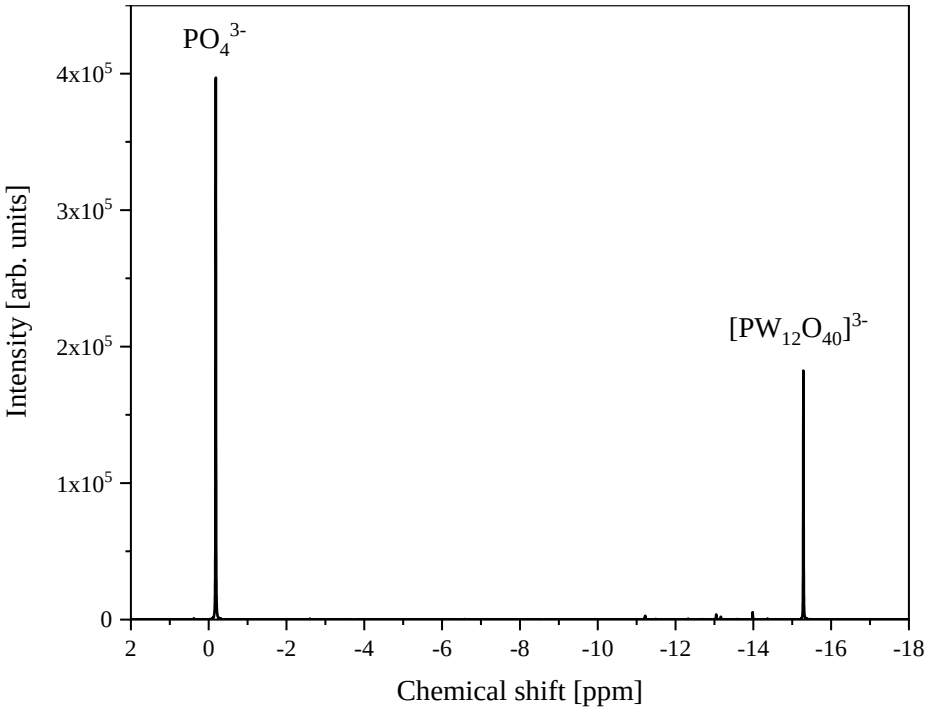

Figure S2: ^{31}P-NMR of $Na_3[PW_{12}O_{40}]$ in a mixture of 0.7 mL water (pH 5) and 0.07 mL acetone-*d*6. The spectrum was measured at 242.9 MHz, 85 % H_3PO_4 was used as external standard.

1.3.4 Ultraviolet visible spectroscopy (UV-Vis)

Stock solution: The respective POM (10 mg) was dissolved in deionized water (10 mL) → 1 g/L.

Spectra measurement: All UV-Vis spectra were measured with a Cary 60 UV-Vis spectrometer (Agilent Technologies) in a Quartz cuvette of 3 mL (QS). Measurements were done using the Cary WinUV software. Range: 200 nm and 800 nm. The extinction was measured in the slow measurement mode. Data were then exported as a .csv data set and plotted in Origin®2019b.

For measurement samples were prepared as follows: The stock solution (80 µL) was filled into the cuvette and water (2920 µL) was added to reach the final measuring volume of 3 mL.

The UV-Vis data of all compounds investigated in this work are shown in Figure S3 at a concentration of 26.7 mg/L. All spectra show the ligand-to-metal-charge-transfer bands (LMCT) of W(VI), which are listed in Table 5.[3,4] The LMCT positions were found in the range of 247 to 259 nm.

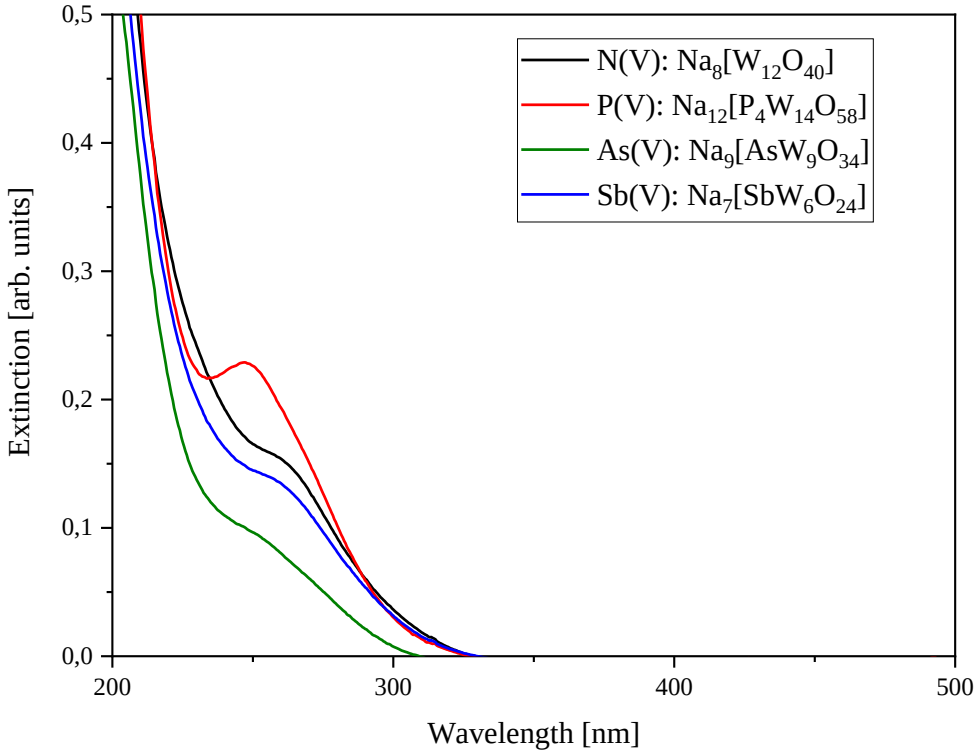

Figure S3: UV-Vis spectra of all POMs (synthesized at pH 5) investigated in this work.

Table S5: LMCT positions for W(VI) of all POMs investigated in this work.

Hetero element involved	**N(V)**	**P(V)**	**As(V)**	**Sb(V)**
Compound	$Na_8[W_{12}O_{40}]$	$Na_{12}[P_4W_{14}O_{58}]$	$Na_9[AsW_9O_{34}]$	$Na_7[SbW_6O_{24}]$
LMCT band [nm]	259.0	247.0	247.0	255.0

Extinction coefficients: Extinction coefficients were determined using the software Cary concentrations. Five calibration standards were prepared from the stock solution (1 g/L) with a final volume of 3 mL for the cuvette:

- 20 µL stock solution + 2980 µL deionized water
- 40 µL stock solution + 2960 µL deionized water
- 50 µL stock solution + 2950 µL deionized water
- 60 µL stock solution + 2940 µL deionized water
- 80 µL stock solution + 2920 µL deionized water

Extinction coefficients were calculated according to equations 1 to 4:

Lambert-Beer's law (equation 1):

$$Abs = \varepsilon_\lambda \cdot d \cdot c \cdot M^{-1} \tag{1}$$

Abs: Absorption

ε_λ: extinction coefficient (wavelength λ dependant) [l mol^{-1} cm^{-1}]

d: Cuvette layer thickness (1 cm) [cm]

c: concentration [g/L]

M: molar mass [g/mol]

Calibration line (equation 2):

$$Abs = a \cdot c + b \tag{2}$$

a: slope

b: Axis intercept

Determining the extinction coefficient:

$$a = \varepsilon_\lambda \cdot d \cdot M^1 \tag{3}$$

$$\varepsilon_\lambda = \frac{a \cdot M}{d} \tag{4}$$

The LMCT peak maxima were analyzed according to the Lambert Beer's law and therefore the extinction coefficients were calculated and listed in Table S6.

Table S6: Extinction coefficients determined according to the Lambert Beer's law.

Hetero element involved	**N(V)**	**P(V)**	**As(V)**	**Sb(V)**
Compound	$Na_8[W_{12}O_{40}]$	$Na_{12}[P_4W_{14}O_{58}]$	$Na_9[AsW_9O_{34}]$	$Na_7[SbW_6O_{24}]$
Extinction coefficient [L mol^{-1} cm^{-1}]	$2.1576 \cdot 10^4$	$3.5899 \cdot 10^4$	$0.9380 \cdot 10^4$	$1.0151 \cdot 10^4$

As expected, the POM anion $[P_4W_{14}O_{58}]^{12-}$ shows the highest extinction coefficient due to the highest amount of W(VI) per molecule.

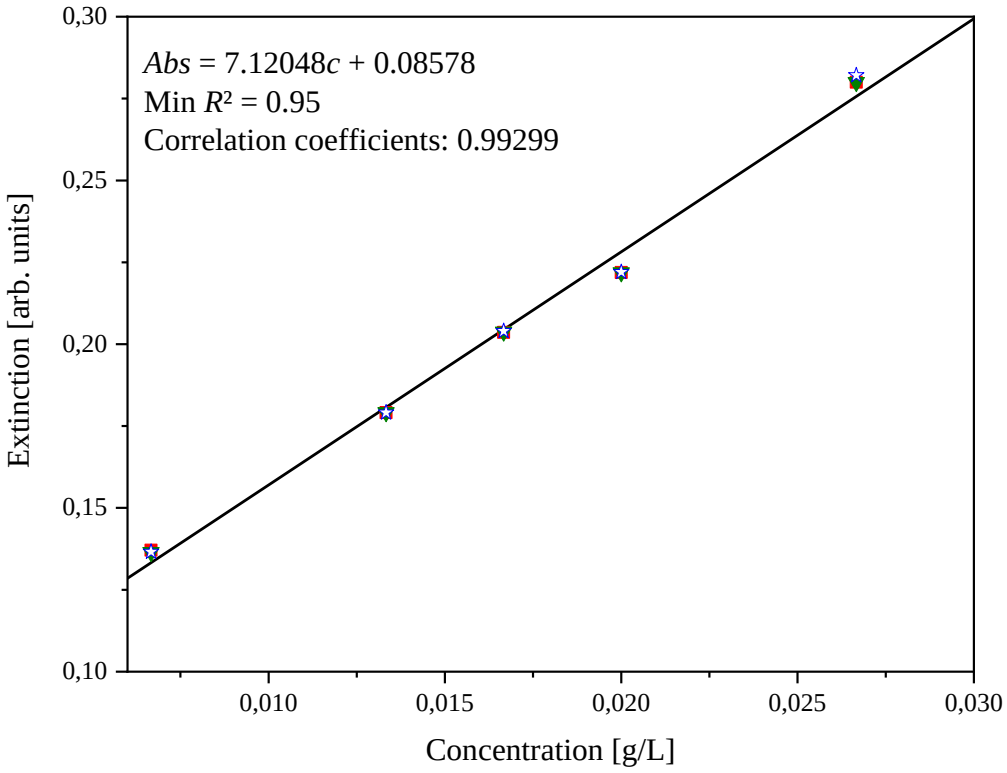

Figure S4: Calibration line for determining the extinction coefficient of the W(VI) LMCT for $[W_{12}O_{40}]^{8-}$.

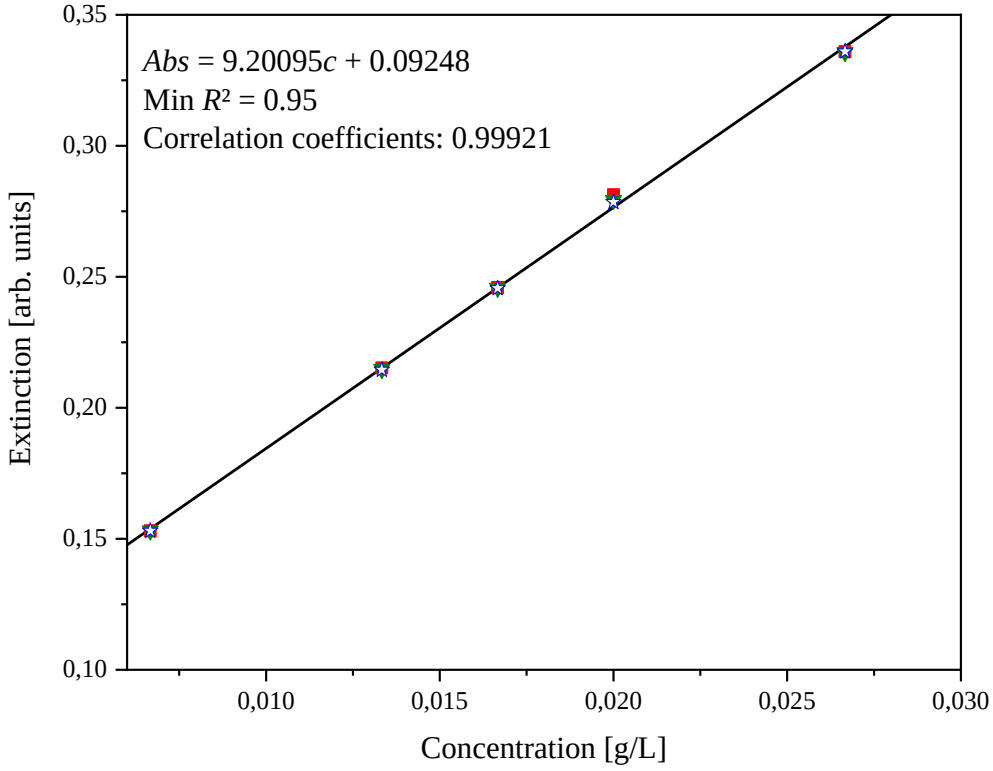

Figure S5: Calibration line for determining the extinction coefficient of the W(VI) LMCT for $[P_4W_{14}O_{58}]^{12-}$.

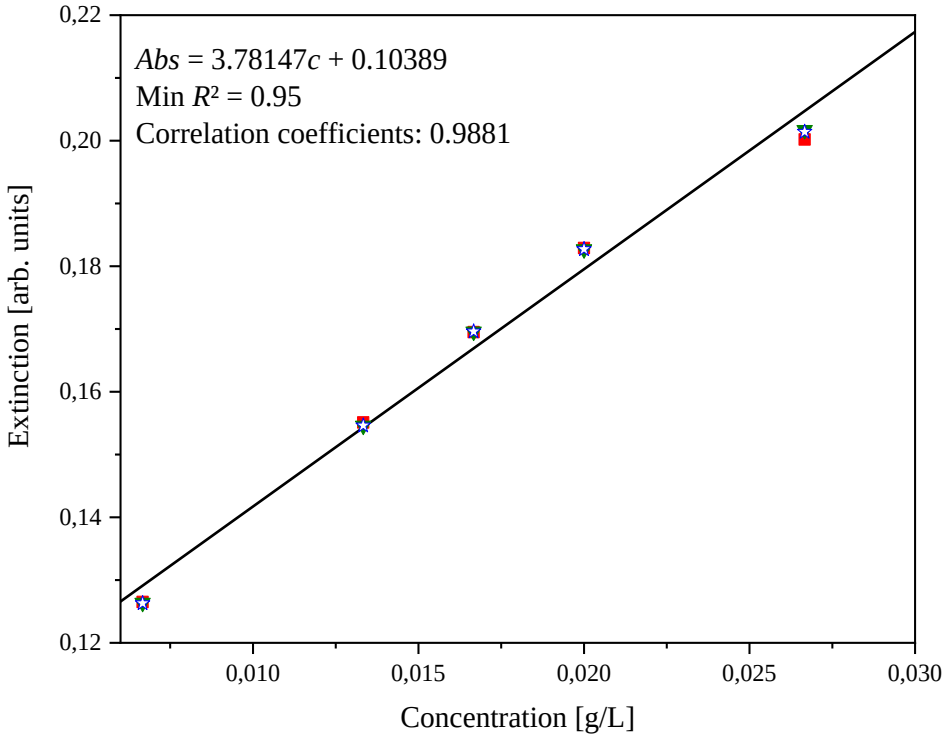

Figure S6: Calibration line for determining the extinction coefficient of the W(VI) LMCT for $[AsW_9O_{34}]^{9-}$.

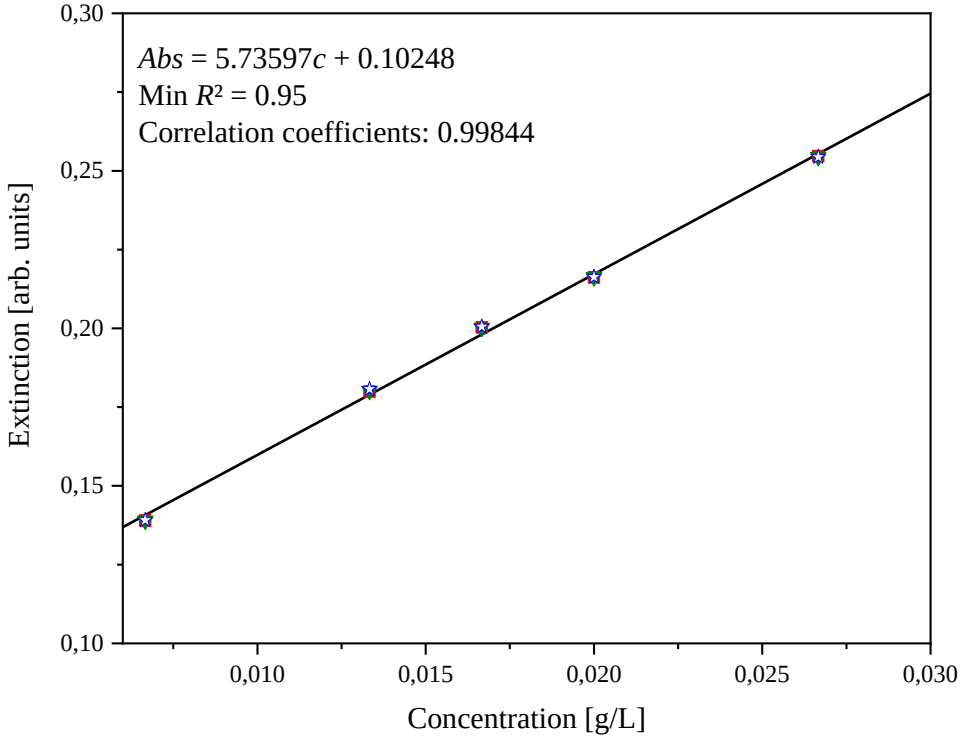

Figure S7: Calibration line for determining the extinction coefficient of the W(VI) LMCT for $[SbW_6O_{24}]^{7-}$.

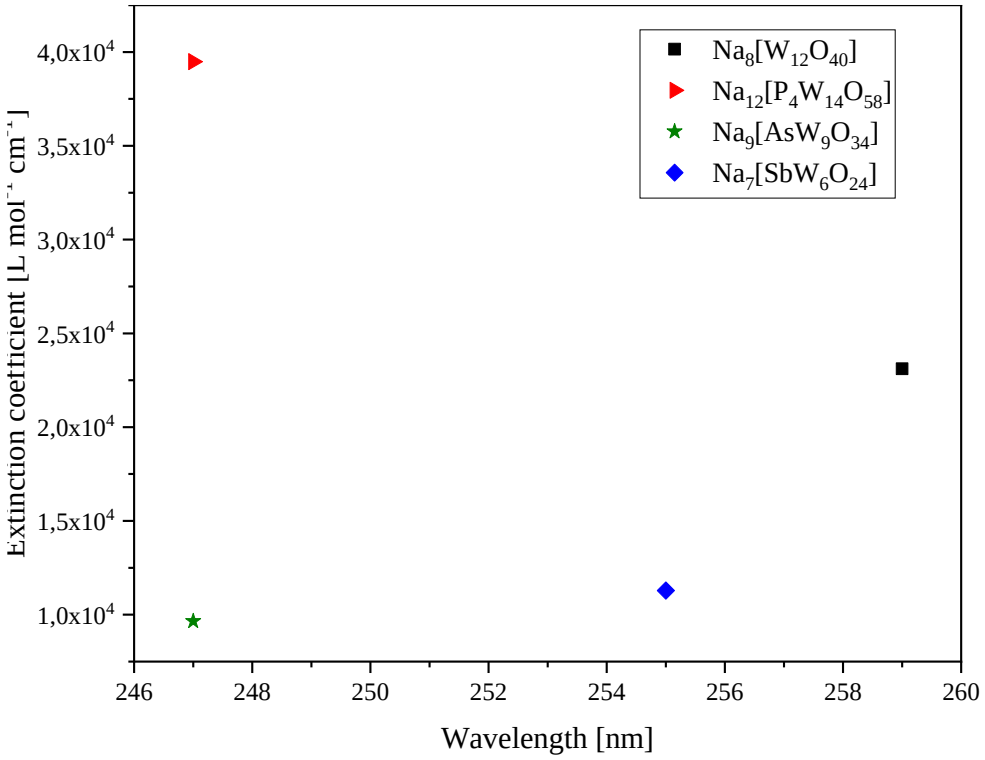

Figure S8: Plot of the extinction coefficient vs. wavelength for each POM.

1.3.5 Crystallography

The crystallographic data set comprising the anion $[W_{12}O_{40}]^{8-}$ (deposition number: 2293850) showed some problems during the refinement. Refining the model as $Na_8[W_{12}O_{40}]$ led to a residual electron density with a maximum and minimum peak of 5.6 and -11.5, respectively. This effect might be caused by several factors, including the difficulty to account correctly the absorption effect of the heavy atoms.[5] However, it turned out that the applied absorption correction scheme (either without face indexing, *i.e.*, empirical, or with face indexing, *i.e.*, numerical sphere, numerical Gaussian grid or analytical according to Clark & Reid[6]) had only a very minor influence on the residual electron/hole density values. Another attempt to fix the problem was the application of the new algorithm "NoSpherA2" as implemented in Olex2 where so-called "non-spherical form factors" are calculated on a quantum mechanical basis.[7–10] However, this approach did not lead to success, since the wavefunction could not be calculated because the self-consistent field calculation did not converge for unknown reasons. As the Fourier difference map showed a pronounced shashlik-like pattern with too little and too much electron density around the W atoms in alternating fashion (see Figure S9) a

corresponding attempt to model a disorder of the WO_6 octahedra was undertaken. Although this reduced drastically the electron density difference values with a maximum and minimum value of only 3.8 and -3.4, respectively, and the R_1 value could be reduced further down to 3.45 %, some other issues arose as, for instance, atoms with non-positive definite (NPD) values of the displacement parameters and unrealistic W-O bond lengths. Therefore, we believe that the structure altogether is better represented by the non-disordered model. The most important thing is, that due to the low R_1 value of 4.74 %, there is no doubt about the constitution of the $[W_{12}O_{40}]^{8-}$ anion and the identity of the paratungstate B, respectively.

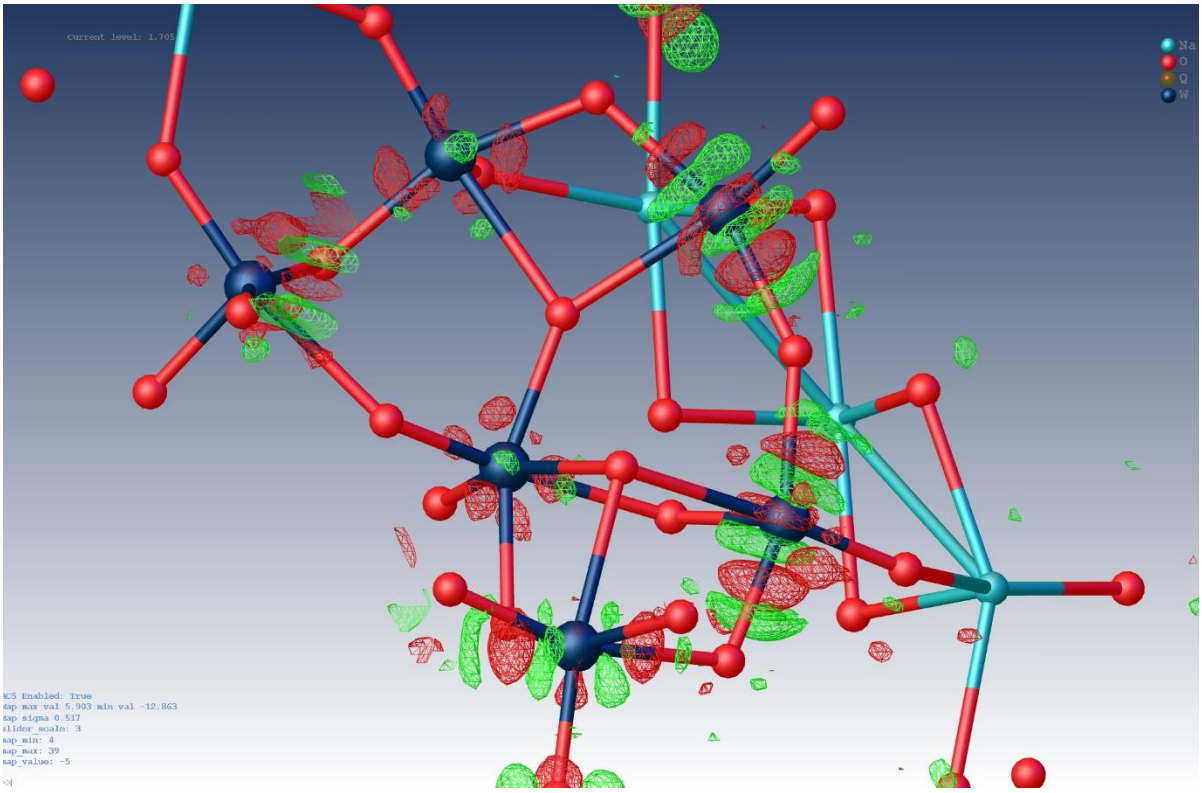

Figure S9: Fourier difference map of $Na_8[W_{12}O_{40}]$ showing a shashlik-like pattern of too high and too low electron density around the W atoms.

2 Computational data

2.1 General information

All DFT calculations were performed using TURBOMOLE V 7.5.1 2021.[11] Structures were optimized using the PBE0 hybrid functional[12] using an Ahlrichs' triple-ξ valence polarization (def2-TZVP) basis set for all atoms.[13] Geometry optimizations were carried out in gas phase with tight SCF convergence (10^{-8} h) criteria using a fine m4 grid. The resolution-of-identity approximation was applied using auxiliary def2-TZVP basis sets to approximate the Coulomb potentials. For each optimized structure, second derivatives were calculated with the same settings used for geometry optimizations. All optimized structures were characterized as minima by absence of any negative frequency. Zero point vibrational energies and thermodynamic corrections were calculated without any scaling factor. The molecular volume of the optimized structures was calculated using MoloVol. The thermodynamic corrections for all species were evaluated at 298 K and 1 bar within the rigid-rotor harmonic-oscillator approximation. The implicit COSMO[14] (Conductor like Solvation MOdel) was used to incorporate solvation effects.

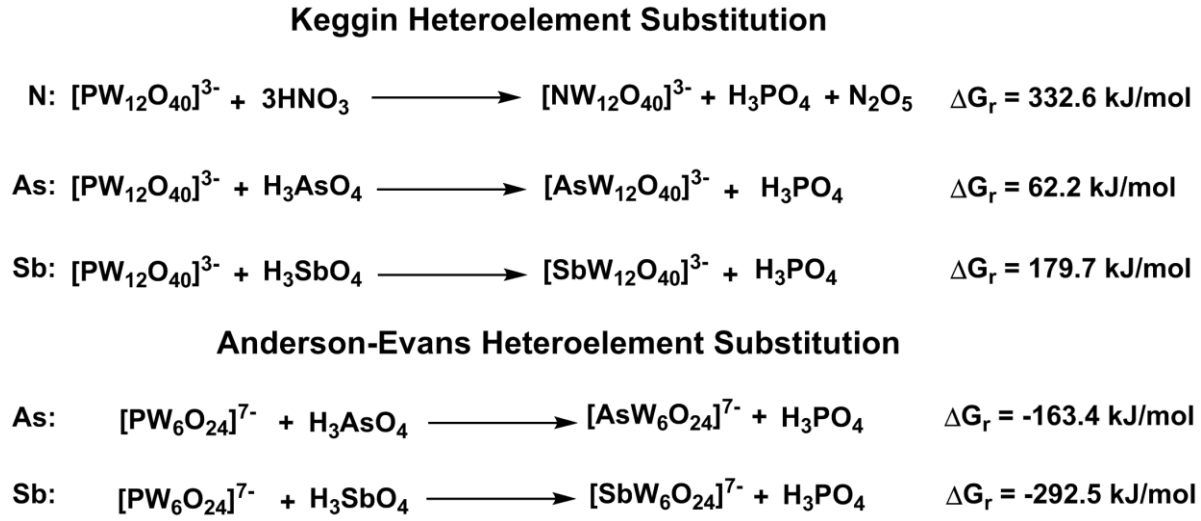

Figure S10: The Gibbs energies of formation from isodesmic reactions of the Keggin and Anderson-Evans complexes with their respective acids.

2.2 Cartesian coordinates

Cartesian coordinates of the optimized structures in Å

$[NW_{12}O_{40}]^{3-}$

O	0.0828607	1.2718738	-3.6874977
O	1.9090346	3.3026590	-0.5793297
O	-0.0702244	5.2934969	-0.0172464
O	0.7594919	-3.4953634	1.7905944
O	2.1020083	-0.1178495	2.8850769
O	3.5571844	-0.1061275	-0.3224547
W	-1.5610863	1.7300634	-2.7529147
O	-0.1403746	-1.4150532	3.3047504
W	1.4505968	-0.0683339	-3.3407307
O	2.4102472	1.2277792	-2.2664785
O	-2.4070272	-2.8117048	-3.9572162
O	-1.1992073	-0.0778373	0.7045928
W	1.6305185	1.7543414	2.7000795
O	-2.7206629	1.2505901	2.4965996
W	-1.5592069	-0.0932155	3.2916163
O	0.7290356	-1.2269595	0.3264326
O	2.3914395	-1.3938660	-2.2855004
O	-0.2574342	-0.0696717	-1.3679853
O	-0.1210995	1.2068305	3.3218640
O	-2.8349956	-1.8161490	-1.2940173
O	2.2992216	-2.7246336	4.0822709
O	2.3352074	2.4669614	4.1211675
W	3.1016968	1.7664894	-0.5381587
O	-0.6144932	-3.1369512	-1.7300733
O	3.0610654	1.9547432	1.3967842
W	0.0330338	-3.7270042	0.0003287
O	-4.5532481	-2.8309000	0.7695888
O	2.3486861	-0.0646067	-4.8293179
W	0.0879328	3.5632223	0.0530029
O	4.5933382	-2.7078862	-0.9776954
O	4.6327901	2.4879746	-0.9394493
W	-3.1044817	1.7178383	0.6470592
O	-2.3629193	2.7450256	-3.9159121
O	-0.1505893	-5.4536191	-0.0933302
O	3.0299180	-2.1831098	1.3665182
O	-1.6527000	3.0035141	0.6999533
O	-2.1900036	-0.0410772	-3.2596477
W	-1.5880930	-1.8284108	-2.7790914
O	1.8574339	-3.4853553	-0.6287880
W	3.0737137	-1.9684843	-0.5654808
O	0.0631184	-1.3837660	-3.7064528
O	-2.0939648	-0.0999576	4.9462957
O	-2.8086973	1.7152633	-1.2687218
O	-3.8919511	-0.0550936	0.5015462
O	-4.5129127	2.7250879	0.8112031
O	0.8103679	3.2956131	1.8394081
O	-2.7415896	-1.4064968	2.4779626
W	1.6029341	-1.9800536	2.6733685
O	0.7457962	1.0482286	0.3430006
O	-0.5666615	3.0065889	-1.6859051
O	-1.6979822	-3.1488963	0.6569127
N	0.0062092	-0.0817100	0.0019885
W	-3.1304302	-1.8417582	0.6210101

$[PW_{12}O_{40}]^{3-}$

O	0.0771320	1.2620087	-3.7004608
O	1.9172699	3.3137574	-0.5640737
O	-0.1375929	5.1685010	-0.0429903
O	0.7764572	-3.5053256	1.7855021
O	2.0357197	-0.1160201	2.7095065
O	3.3812266	-0.1049282	-0.2517354
W	-1.5176554	1.6689207	-2.7197447
O	-0.1638670	-1.3904775	3.1217433
W	1.3933575	-0.0681712	-3.2932843
O	2.2653519	1.2048424	-2.1682458
O	-2.3695528	-2.7996558	-3.8148797
O	-1.3183344	-0.0769550	0.7735681
W	1.6073969	1.7426162	2.6231786
O	-2.7384238	1.2387780	2.5008883
W	-1.5610064	-0.0923859	3.2156795
O	0.7987269	-1.3398184	0.3570135
O	2.2469096	-1.3695827	-2.1870758
O	-0.2848815	-0.0683501	-1.5025788
O	-0.1443182	1.1852548	3.1403468
O	-2.7145879	-1.6781221	-1.2388733
O	2.2210259	-2.6117137	4.0315396
O	2.2583163	2.3578327	4.0677096
W	3.0285137	1.7541911	-0.5068849
O	-0.5345745	-2.9807899	-1.6685544
O	3.0595934	1.9740510	1.3959262
W	0.0633367	-3.6560671	0.0142086
O	-4.4232760	-2.8164544	0.7116066
O	2.3522337	-0.0649470	-4.6968751
W	0.1173580	3.4914734	0.0661439
O	4.5061028	-2.5920304	-0.9997451
O	4.5434189	2.3747815	-0.9643588
W	-3.0512542	1.6558081	0.6578610
O	-2.3264566	2.7278063	-3.7752033
O	-0.2164199	-5.3273678	-0.1192698
O	3.0280064	-2.2024360	1.3656429
O	-1.5546271	2.8400009	0.7187381
O	-2.1734149	-0.0412104	-3.2811810
W	-1.5441393	-1.7688941	-2.7445368
O	1.8657502	-3.4959222	-0.6137878
W	3.0007556	-1.9548185	-0.5336142
O	0.0573300	-1.3726765	-3.7190414
O	-1.9856886	-0.1010446	4.8614644
O	-2.6898317	1.5741528	-1.2155541

O	-3.9006332	-0.0556804	0.5224667
O	-4.3816914	2.7096191	0.7507529
O	0.8278539	3.3046360	1.8350184
O	-2.7581809	-1.3953544	2.4818713
W	1.5791276	-1.9664957	2.5961544
O	0.8175047	1.1598609	0.3752015
O	-0.4898691	2.8491915	-1.6263874
O	-1.5987443	-2.9891826	0.6766918
P	0.0031587	-0.0812813	0.0007304
W	-3.0770676	-1.7816420	0.6333617

$[AsW_{12}O_{40}]^{3-}$

O	0.0740751	1.2692053	-3.7368183
O	1.9363986	3.3451042	-0.5627859
O	-0.1563571	5.1686420	-0.0514677
O	0.7898208	-3.5372470	1.7989742
O	2.0268631	-0.1157625	2.6759745
O	3.3494499	-0.1048966	-0.2359695
W	-1.5167277	1.6631645	-2.7325358
O	-0.1690297	-1.3879819	3.0871136
W	1.3841337	-0.0680088	-3.3036284
O	2.2347806	1.2026259	-2.1489173
O	-2.3761620	-2.8143399	-3.8017444
O	-1.4297282	-0.0764622	0.8387233
W	1.6139678	1.7542745	2.6201319
O	-2.7674250	1.2459557	2.5222642
W	-1.5748371	-0.0922301	3.2155284
O	0.8656434	-1.4459747	0.3872307
O	2.2162128	-1.3671368	-2.1676202
O	-0.3089893	-0.0672337	-1.6293703
O	-0.1495403	1.1832829	3.1056358
O	-2.6939212	-1.6508468	-1.2295063
O	2.2154593	-2.5980737	4.0454203
O	2.2524238	2.3436720	4.0815403
W	3.0298700	1.7655387	-0.4995437
O	-0.5174156	-2.9507187	-1.6582220
O	3.0847362	1.9983797	1.4076144
W	0.0747346	-3.6616819	0.0194812
O	-4.4173324	-2.8317118	0.6971602
O	2.3715054	-0.0652236	-4.6879195
W	0.1288674	3.4969734	0.0713113
O	4.5123565	-2.5766144	-1.0136436
O	4.5494814	2.3592967	-0.9781393
W	-3.0599566	1.6500883	0.6664170
O	-2.3329354	2.7423316	-3.7622130
O	-0.2353577	-5.3269439	-0.1278341
O	3.0527038	-2.2272247	1.3769255
O	-1.5360625	2.8099371	0.7245915
O	-2.1882704	-0.0407946	-3.3151385
W	-1.5430673	-1.7627996	-2.7571022
O	1.8845248	-3.5277558	-0.6129083
W	3.0019115	-1.9665098	-0.5265209
O	0.0540812	-1.3791693	-3.7555658
O	-1.9675110	-0.1010707	4.8696889
O	-2.6696264	1.5465241	-1.2066975
O	-3.9359086	-0.0554878	0.5339522
O	-4.3753389	2.7251658	0.7365214
O	0.8414889	3.3357609	1.8487181
O	-2.7872209	-1.4022883	2.5031780
W	1.5854763	-1.9784323	2.5929809
O	0.8863988	1.2642258	0.4069936
O	-0.4734810	2.8191753	-1.6167067
O	-1.5797052	-2.9593624	0.6831434
As	0.0031930	-0.0812895	0.0008475
W	-3.0858068	-1.7757672	0.6420367

$[SbW_{12}O_{40}]^{3-}$

O	0.0705833	1.2817442	-3.7903349
O	1.9650403	3.3924733	-0.5638499
O	-0.1834458	5.1656738	-0.0643435
O	0.8074559	-3.5852251	1.8202570
O	2.0119532	-0.1153896	2.6204307
O	3.2979099	-0.1045882	-0.2106976
W	-1.5141377	1.6523410	-2.7509049
O	-0.1780032	-1.3838162	3.0301256
W	1.3680823	-0.0680469	-3.3178123
O	2.1854379	1.1989516	-2.1178269
O	-2.3847167	-2.8344224	-3.7798720
O	-1.5660517	-0.0759788	0.9186266
W	1.6229486	1.7716871	2.6125440
O	-2.8096645	1.2588486	2.5554073
W	-1.5964900	-0.0918805	3.2131289
O	0.9478822	-1.5759441	0.4241065
O	2.1665718	-1.3634221	-2.1361345
O	-0.3394387	-0.0657872	-1.7847651
O	-0.1584544	1.1800597	3.0484126
O	-2.6602241	-1.6065474	-1.2141031
O	2.2047421	-2.5754467	4.0636510
O	2.2417955	2.3199592	4.0993526
W	3.0299337	1.7830356	-0.4874218
O	-0.4895705	-2.9021007	-1.6415631
O	3.1236769	2.0326657	1.4254455
W	0.0935535	-3.6683542	0.0273746
O	-4.4046348	-2.8528971	0.6757373
O	2.3979268	-0.0658903	-4.6720343
W	0.1478637	3.5032421	0.0796005
O	4.5187870	-2.5529469	-1.0323090
O	4.5557877	2.3360189	-0.9972127
W	-3.0713309	1.6392161	0.6802050
O	-2.3411793	2.7624750	-3.7398768

O	-0.2628857	-5.3233043	-0.1410288
O	3.0912175	-2.2623664	1.3945242
O	-1.5054769	2.7607650	0.7339704
O	-2.2131912	-0.0402430	-3.3651237
W	-1.5406035	-1.7514732	-2.7753443
O	1.9123371	-3.5755944	-0.6142363
W	3.0016584	-1.9839734	-0.5141210
O	0.0503741	-1.3911423	-3.8092353
O	-1.9394348	-0.1009983	4.8792923
O	-2.6366033	1.5012654	-1.1921028
O	-3.9888804	-0.0551341	0.5486922
O	-4.3623322	2.7465990	0.7153737
O	0.8598293	3.3832578	1.8706547
O	-2.8298119	-1.4148816	2.5363330
W	1.5938263	-1.9963393	2.5853295
O	0.9705856	1.3925890	0.4456796
O	-0.4465166	2.7703659	-1.6009741
O	-1.5482510	-2.9107077	0.6936150
Sb	0.0032607	-0.0811744	0.0007145
W	-3.0968468	-1.7649337	0.6562241

$[PW_6O_{24}]^{7-}$

W	-2.5642135	1.8624505	0.5788947
W	-1.1661264	0.2528285	2.9937854
W	1.4026744	-1.6043733	2.4146774
P	0.0000025	0.0000032	-0.0000007
O	0.4862797	1.0788202	-1.3119471
O	-1.6256614	0.2269160	-0.6511742
O	-0.4603788	1.2852405	1.1224108
O	-2.7799127	0.5536540	1.9809031
O	-2.6682600	3.3334332	1.5525228
O	-1.8205720	2.7827351	-0.9444943
O	-4.2240308	1.6717523	0.0035534
O	0.6902517	-0.0975132	3.3866840
O	-1.9046384	-0.9961274	4.0025504
O	-1.2297680	1.6733150	4.0431469
O	3.0275070	-1.4002444	3.0781576
O	0.7488619	-2.9102939	3.4100881
W	2.5642029	-1.8624562	-0.5788990
W	1.1661212	-0.2528254	-2.9937827
W	-1.4026793	1.6043687	-2.4146789
O	-0.4862777	-1.0788179	1.3119487
O	1.6256639	-0.2269128	0.6511760
O	0.4603807	-1.2852384	-1.1224090
O	2.7799142	-0.5536623	-1.9809081
O	2.6682705	-3.3334360	-1.5525178
O	1.8205646	-2.7827345	0.9444913
O	4.2240331	-1.6717451	-0.0035439
O	-0.6902541	0.0975072	-3.3866785
O	1.9046332	0.9961308	-4.0025451
O	1.2297673	-1.6733165	-4.0431586
O	-3.0275034	1.4002503	-3.0781668
O	-0.7488522	2.9102916	-3.4100859

$[AsW_6O_{24}]^{7-}$

W	-2.6072618	1.8933051	0.5883779
W	-1.1854723	0.2571272	3.0435140
W	1.4264009	-1.6310755	2.4552163
As	-0.0000024	-0.0000008	-0.0000023
O	0.4985775	1.1284192	-1.4157871
O	-1.7230644	0.2742504	-0.6928073
O	-0.5178673	1.3498238	1.1990688
O	-2.7898350	0.5875205	2.0091586
O	-2.7090798	3.3797698	1.5369462
O	-1.8629577	2.7860395	-0.9612160
O	-4.2738828	1.6918663	0.0393533
O	0.6766661	-0.1264079	3.4189719
O	-1.9506556	-0.9808849	4.0444663
O	-1.2249319	1.6669646	4.1069984
O	3.0389675	-1.4114646	3.1412645
O	0.7877288	-2.9562059	3.4332953
W	2.6072593	-1.8933045	-0.5883816
W	1.1854731	-0.2571189	-3.0435108
W	-1.4264035	1.6310732	-2.4552126
O	-0.4985798	-1.1284223	1.4157870
O	1.7230621	-0.2742532	0.6928058
O	0.5178654	-1.3498272	-1.1990708
O	2.7898311	-0.5875228	-2.0091574
O	2.7090901	-3.3797688	-1.5369432
O	1.8629588	-2.7860437	0.9612172
O	4.2738830	-1.6918562	-0.0393479
O	-0.6766683	0.1264055	-3.4189767
O	1.9506539	0.9808829	-4.0444616
O	1.2249341	-1.6669703	-4.1070067
O	-3.0389673	1.4114717	-3.1412691
O	-0.7877217	2.9562080	-3.4332906

$[SbW_6O_{24}]^{7-}$

W	-2.6603678	1.9295856	0.5997888
W	-1.2076726	0.2629022	3.1037244
W	1.4547019	-1.6644997	2.5041242
Sb	0.0000035	0.0000033	0.0000017
O	0.5129583	1.1869677	-1.5390145
O	-1.8384483	0.3308736	-0.7423150
O	-0.5865763	1.4260938	1.2899597
O	-2.8043977	0.6231736	2.0418735
O	-2.7632423	3.4343821	1.5158925
O	-1.9102053	2.7939711	-0.9797799
O	-4.3347058	1.7162932	0.0844686

O	0.6647736	-0.1563410	3.4571485
O	-2.0052820	-0.9582719	4.0973006
O	-1.2177835	1.6576219	4.1851224
O	3.0501178	-1.4296264	3.2207661
O	0.8350606	-3.0115776	3.4612700
W	2.6603705	-1.9295727	-0.5997801
W	1.2076768	-0.2628901	-3.1037234
W	-1.4547014	1.6645068	-2.5041299
O	-0.5129588	-1.1869705	1.5390157
O	1.8384451	-0.3308741	0.7423129
O	0.5865775	-1.4260973	-1.2899613
O	2.8043965	-0.6231765	-2.0418747
O	2.7632457	-3.4343905	-1.5158974
O	1.9102055	-2.7939706	0.9797795
O	4.3347034	-1.7162922	-0.0844697
O	-0.6647763	0.1563376	-3.4571491
O	2.0052799	0.9582651	-4.0972998
O	1.2177811	-1.6576285	-4.1851229
O	-3.0501182	1.4296289	-3.2207656
O	-0.8350613	3.0115731	-3.4612658

$[W_{12}O_{40}]^{8-}$

O	12.1265246	-0.3516175	10.4116112
W	12.2662838	1.4098398	10.3401221
O	12.5128166	1.9261788	12.0118213
O	13.7058062	1.8432677	9.3307641
O	10.7708477	2.1384711	9.6673147
W	9.1278942	3.0194176	8.6099511
O	8.7513919	3.9709815	10.0109019
O	8.1745098	1.5911181	8.9074635
O	8.0220473	3.8320920	7.3329958
W	14.8162275	3.0239115	7.9926917
O	15.5354086	1.5881206	7.2975151
O	15.9974691	3.4405439	9.2064569
O	15.2566800	4.2929169	6.6911189
O	13.3595189	4.3955197	8.5725299
O	10.1552336	2.0156435	6.9809919
W	11.4433332	2.2754569	5.7514632
O	11.5717734	0.7929265	4.8208609
O	12.9918809	2.5769052	6.5769842
W	12.1283418	5.5623354	7.8894707
O	10.6971270	4.4716057	8.0219960
W	14.8875554	5.6467887	5.3068240
O	15.5463565	4.6078192	4.0711863
O	16.1405662	6.7863072	5.7184602
O	12.1786585	6.7672091	9.1356311
O	10.8789552	6.8971386	6.7110601
W	10.4497283	8.2549919	5.6088011
O	10.3213594	9.7374967	6.5393263
O	8.9011904	7.9535496	4.7832208
O	11.7378382	8.5146876	4.3792106
O	11.0141271	3.6332689	4.6491400
W	9.7646636	4.9680674	3.4707959
O	11.1959792	6.0587816	3.3381853
O	8.5335524	6.1349013	2.7876935
W	7.0055260	4.8836330	6.0534155
O	6.3467336	5.9226356	7.2891423
O	5.7524234	3.7441641	5.6418268
O	9.7144011	3.7631864	2.2245743
O	6.6363600	6.2375478	4.6691628
W	7.0768531	7.5064900	3.3675413
O	6.3576635	8.9423634	4.0627574
O	5.8955789	7.0899268	2.1538214
O	8.1872604	8.6871706	2.0294759
W	9.6267653	9.1204964	1.0200642
O	9.3802033	8.6040639	-0.6515975
O	9.7665784	10.8819335	0.9484840
O	11.1222163	8.3918437	1.6928954
W	12.7651909	7.5109596	2.7502540
O	13.1416670	6.5593279	1.3493418
O	13.7185212	8.9391866	2.4527277
O	13.8709812	6.6982611	4.0272283
O	13.2582475	5.8565484	6.4056831
O	8.6348215	4.6738456	4.954551

$[P_4W_{14}O_{58}]^{12-}$

W	0.3091449	11.3546128	11.0651599
W	-1.7772762	8.5723107	9.4859791
W	-2.6172761	5.9395698	11.5782687
W	-1.3326914	6.1828201	15.1663936
W	2.1877367	6.1994594	13.8404375
W	1.0177845	6.2346844	10.5369641
W	3.0249205	8.8420708	11.7434657
P	-0.4965097	8.4848994	12.7638126
P	2.5557275	11.6291350	13.6548606
O	-0.2892002	9.9885931	12.6280276
O	-1.6093626	8.0320309	11.7465102
O	-0.9050447	8.0487755	14.1658865
O	0.8360420	7.7527575	12.3739535
O	-0.7277795	10.0887881	9.9878907
O	-2.4706649	6.7738246	9.8153794
O	-2.1000002	5.7749050	13.4105484
O	0.5302940	5.6829378	14.3598205
O	3.3499972	7.5601683	13.1392228
O	2.0371044	5.4614120	12.1296308
O	2.6658370	7.4435419	10.5569781
O	1.9029264	10.0090897	10.9293268
O	0.1298822	7.4891189	9.5839875
O	-0.5057033	5.4932684	11.1684572
O	2.9103566	10.1610327	13.3423313

O	1.6543677	12.1389223	12.4817900
O	3.8819536	12.4508993	13.7727393
O	1.7925110	11.8164563	14.9820487
O	0.9485955	12.2518157	9.6932003
O	-0.9694022	12.4496064	11.5300881
O	-1.6533979	8.5394226	7.7175228
O	-3.3436086	9.3611547	9.6249091
O	-3.0172653	4.2787073	11.1031072
O	-4.2473490	6.5259774	11.8833135
O	-1.4958372	4.5489223	15.7982119
O	-2.7289503	6.9061989	15.9257729
O	3.2623182	5.0118456	14.5134167
O	1.5786849	5.0824831	9.3103117
O	4.6060354	9.2515613	11.1511071
W	3.5523095	7.9597260	19.3729461
W	5.6387252	10.7420301	20.9521262
W	6.4787250	13.3747695	18.8598364
W	5.1941462	13.1315166	15.2717109
W	1.6737191	13.1148770	16.5976673
W	2.8436761	13.0796456	19.9011410
W	0.8365306	10.4722607	18.6946473
P	4.3579636	10.8294340	17.6742913
P	1.3057301	7.6852023	16.7832457
O	4.1506504	9.3257362	17.8100750
O	5.4708185	11.2823026	18.6915951
O	4.7664994	11.2655600	16.2722251
O	3.0254165	11.5615818	18.0641511
O	4.5892350	9.2255485	20.4502116
O	6.3321243	12.5405134	20.6227265
O	5.9614582	13.5394340	17.0275568
O	3.3311586	13.6313982	16.0782810
O	0.5114568	11.7541665	17.2988827
O	1.8243481	13.8529267	18.3084760
O	1.1956207	11.8707930	19.8811260
O	1.9585279	9.3052464	19.5087812
O	3.7315713	11.8252160	20.8541162
O	4.3671580	13.8210704	19.2696524
O	0.9510992	9.1533017	17.0957732
O	2.2070851	7.1754091	17.9563138
O	-0.0205006	6.8634366	16.6653658
O	2.0689472	7.4978765	15.4560561
O	2.9128623	7.0625166	20.7449118
O	4.8308628	6.8647265	18.9080176
O	5.5148556	10.7749077	22.7205786
O	7.2050712	9.9531716	20.8131890
O	6.8787262	15.0356252	19.3349999
O	8.1088075	12.7883535	18.5547925
O	5.3572922	14.7654064	14.6398903
O	6.5904014	12.4081316	14.5123296
O	0.5991366	14.3024814	15.9246931
O	2.2827664	14.2318503	21.1277988
O	-0.7445745	10.0627724	19.2869992

$Na_6[As_2W_{18}O_{68}]^{12-}$

W	5.3694087	2.8978017	27.1859223
W	8.1362933	3.0249838	24.6299776
As	5.4585870	5.4584433	24.6267997
Na	10.1872027	6.2101165	23.8767409
O	4.4783565	4.4774969	25.6068975
O	5.1155477	5.1156660	23.0202568
O	6.5806015	2.4365313	25.8449911
O	3.9359408	2.0572912	26.1491479
O	9.1791569	4.0274575	23.5762072
O	8.8023667	3.8146744	26.2705352
O	6.8486249	2.7543774	23.2367061
O	5.6104386	1.6625829	28.4204770
O	8.9958939	1.4965592	24.6564109
O	5.1150025	7.0646870	24.9704644
O	7.0650903	5.1155400	24.9699508
W	2.8993212	2.8979548	24.7156534
W	3.0245628	5.4548755	21.9495837
Na	6.2090002	6.2104021	19.8983023
O	2.4370808	4.2390387	23.5049965
O	2.0585379	3.9338060	26.1496316
O	4.0262764	6.5095098	20.9068665
O	3.8149973	3.8149632	21.2828172
O	2.7534637	6.8475636	23.2377683
O	1.6647124	1.6628175	24.4744591
O	1.4959754	5.4279279	21.0902688
Na	6.2080016	10.1874280	23.8778016
O	3.9354343	3.9336967	28.0266542
O	6.5079901	9.1784153	26.0601024
O	3.8136647	8.8010316	26.2718121
O	6.8475148	6.8473222	27.3321198
W	3.0238564	8.1350075	24.6312923
O	2.4364462	6.5787251	25.8460703
O	4.0255924	9.1785668	23.5775263
O	1.4950531	8.9939126	24.6583238
W	5.4554614	3.0251422	21.9489571
O	4.2403107	2.4366720	23.5045287
O	6.5093598	4.0276097	20.9062167
O	5.4290007	1.4967577	21.0892656
W	8.1356397	5.4545777	27.0610220
Na	8.8332169	4.8562685	21.2523143
Na	8.8322110	8.8332686	25.2318414
Na	4.8540064	8.8335715	21.2534104
O	6.5801138	4.2387923	27.6483240
O	11.0156080	5.8650932	21.5525062
O	8.5319095	11.0160220	24.2239820
O	5.8627065	8.5345489	19.0707459
O	9.1784750	6.5092070	26.0594301

O	5.8620746	11.0162479	21.5540254
O	11.0149592	8.5340836	24.2232310
O	8.5331739	5.8653251	19.0699763
O	8.9948507	5.4274987	28.5896566
W	2.8986397	5.3673955	27.1865633
W	5.4540863	8.1348664	27.0616992
O	4.2391765	6.5786188	27.6489271
O	1.6636224	5.6074999	28.4215097
O	5.4269947	8.9936869	28.5905486
W	12.1425253	9.6763674	17.9435510
W	12.0173298	6.9086961	20.4987498
As	9.5826150	9.5852619	20.5033484
O	10.5628398	10.5662328	19.5232656
O	9.9256795	9.9279975	22.1099004
O	12.6047361	8.4650041	19.2840033
O	12.9826511	11.1099332	18.9805150
O	11.2275001	6.2427151	18.8582221
O	12.2877455	8.1960925	21.8923030
O	13.3775214	9.4363052	16.7085802
O	13.5461382	6.0497777	20.4716705
O	7.9761127	9.9281858	20.1602337
O	9.9261903	7.9790277	20.1596369
W	12.1419010	12.1457389	20.4145330
W	9.5857953	12.0185115	23.1812610
O	10.8009234	12.6069969	21.6256904
O	11.2262611	11.2286436	23.8473565
O	8.1926080	12.2893158	21.8935424
O	13.3765148	13.3808645	20.6557505
O	9.6122869	13.5468641	24.0409921
O	11.1057262	11.1101082	17.1035192
O	6.2388216	11.2290963	18.8597090
O	8.1936486	8.1964674	17.7980215
W	6.9049231	12.0187452	20.5002776
O	8.4605976	12.6072189	19.2852651
O	6.0453241	13.5471764	20.4738941
W	12.0166719	9.5887488	23.1805336
O	12.6041434	10.8046224	21.6251463
O	13.5452681	9.6156517	24.0398294
W	9.5870681	6.9089149	18.0683913
O	10.8019786	8.4651678	17.4811708
O	9.6141287	6.0501265	16.5395065
W	9.6717719	12.1459779	17.9443004
W	6.9055339	9.5892124	18.0691792
O	8.4610550	10.8050099	17.4818819
O	9.4307259	13.3812397	16.7097900
O	6.0462991	9.6163334	16.5405459
O	11.1052549	12.9864555	18.9810842

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