Synthesis and characterization of new Keggin anion: [BeW_{12}O_{40}]^{6-}: the first example of s-element acting as central atom in POM

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Figure 1S. $^{9}$Be NMR spectra of $1a$ (0.1 M) in CD$_3$CN at room temperature ($26.5 \pm 2^\circ$ C), D1 = 30.0 sec, AQ = 11.65 sec, experiment total time = 11 min.

Figure 2S. $^{183}$W NMR spectra of $1a$ (0.1 M) in CD$_3$CN at room temperature ($24.5 \pm 2^\circ$ C), D1 = 5.0 sec, AQ = 1.57 sec, experiment total time = 15 h.
Electrochemistry

The cyclic voltammetry measurements were carried out using an electrochemical analyzer 797 VA Computrace (Metrohm, Switzerland). A conventional three electrode glass cell of 10 ml capacity was used. A 2 mm diameter glassy carbon disk electrode was used as working electrode (GCE). A platinum wire served as the counter electrode. An Ag/AgCl reference electrode, filled with 3 M KCl, was used. All solutions were deoxygenated using argon gas for 10-15 min prior to electrochemical experiments. Measurements were carried out at ambient temperature (20 ± 2°C). All reagents were of analytical grade or higher and purchased from Sigma-Aldrich. 1 M Na₂SO₄ electrolyte was prepared using distilled water. Na₂CO₃ was used to increase pH of the investigated solution to 8.9.

Cyclic voltammogram of a 2 mM solution of (Me₂NH₂)₆[BeW₁₂O₄₀] in 0.1 M Na₂SO₄ shows two irreversible reduction processes at E_p = -0.69 V and E_p = -0.93 V (vs. Ag/AgCl). Going to 1M Na₂SO₄ and increasing pH of the solution to 8.9 causes an appearance of two quasi-reversible reduction processes (Fig. 4S). E_{1/2} values for both couples were determined to be ½(-0.515 + (-0.605)) = -0.560 (V, vs. Ag/AgCl) and ½(-0.735 + (-0.849)) = -0.792 (V, vs. Ag/AgCl) at 0.01 V·s⁻¹. ΔE_p values calculated as -0.515 V – (-0.605 V) = 0.090 V and -0.735 V – (-0.849 V) = 0.114 are bigger than 0.059 which is characteristic for fully reversible one-electron process. The reversibility of the electrochemical processes decreases with an increase in the scan rate from 0.01 to 0.1 V·s⁻¹ (Fig. 5S).

Cyclic voltammogram of (Me₂NH₂)₆[BeW₁₂O₄₀] was also recorded in 1M sodium acetate buffer (pH = 5.5) (Fig. 6S). Similarly two consecutive quasi-reversible reduction processes were detected in the range 0 to -1 V. E_{1/2} values were determined to be -0.587 (V, vs. Ag/AgCl) and -0.774 (V, vs. Ag/AgCl) at 0.01 V·s⁻¹. ΔE_p values are equal to 0.060 V and 0.070 V at 0.01 V·s⁻¹, respectively, and increase with an increase in the scan rate from 0.01 to 0.1 V·s⁻¹. Lowering the pH of the acetate buffer to 3.5 leads to the almost complete disappearance of the redox processes.
**ESI mass spectrometry**

Electrospray Ionization (ESI) mass spectra were obtained on c.a. $1 \times 10^{-5}$ M sample solutions in water or acetonitrile; solutions were introduced at a flow rate of 10 $\mu$L min$^{-1}$ in a Waters QTOF Premier instrument with orthogonal Z-spray electrospray interface operating with capillary voltage of 3.3 kV in the negative scan mode (V-mode at a resolution of *ca.* 10000 FWHM). The cone voltage ($U_c$) was set to low value $U_c = 10$V to control the extent of fragmentation of the gas-phase detected species. The desolvation and source block temperature was typically set at 200 °C and 120 °C, respectively. The desolvation and cone gas was nitrogen at 300 L h$^{-1}$ and 30 L h$^{-1}$, respectively.
Figure 3S. Comparison of the simulated and experimental isotopic pattern for a) 4- charged species of general formula [BeW_{12}O_{40} + 2cat]^4+; b) 3- charged species of general formula [BeW_{12}O_{40} + 3cat]^3- in each display and c) doubly- charged species of general formula [BeW_{12}O_{40} + 4cat]^2- where cat denotes H+ or tetrabutylammonium (TBA+) cations.

Figure 4S. Negative ESI mass spectrum of compound 1b in H2O recorded at Uc = 5 V. Circled regions include the species featuring the 4-, 3- and 2- charge states derive from the [BeW_{12}O_{40}]^{6-} (1^{6-}) polyanion.
Figure 5S. Expanded regions of the negative ESI mass spectrum of compound 1b in H₂O recorded at Uc = 5 V that include 4- charged species (top), 3- charged species (middle) and doubly-charged anions (bottom). Insets show a comparison of the simulated and experimental isotopic pattern for the largest peak in each display.
Table 1S. Peak assignments for samples 1a recorded in CH$_3$CN and 1b recorded in H$_2$O. Note that for sample 1b overlapping of peaks due to Me$_2$H$_2$N$^+$ and 2Na$^+$ adducts is observed.

<table>
<thead>
<tr>
<th>Charge state</th>
<th>Sample (Bu$<em>4$N)$<em>4$Na$</em>{1.2}$[BeW$</em>{12}$O$_{40}$] 1a m/z value; adduct composition</th>
<th>Sample (Me$<em>2$NH)$<em>6$[BeW$</em>{12}$O$</em>{40}$] 1b m/z value; adduct composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>4- charged peaks</td>
<td>835.2; [BeW$<em>{12}$O$</em>{40}$ + 2TBA]$^4^+$ 774.9; [BeW$<em>{12}$O$</em>{40}$ + H + TBA]$^4^+$ 714.1; [BeW$<em>{12}$O$</em>{40}$ + 2H]$^4^+$</td>
<td>730.8; [BeW$<em>{12}$O$</em>{40}$ + Na + Me$<em>2$H$<em>2$N]$^4^+$ 725.3; [BeW$</em>{12}$O$</em>{40}$ + H + Me$<em>2$H$<em>2$N]$^4^+$ 719.6; [BeW$</em>{12}$O$</em>{40}$ + H + Na]$^4^+$ 714.1; [BeW$<em>{12}$O$</em>{40}$ + 2H]$^4^+$</td>
</tr>
<tr>
<td>Triply-charged peaks</td>
<td>1194.1; [BeW$<em>{12}$O$</em>{40}$ + 3TBA]$^3^-$ 1113.7; [BeW$<em>{12}$O$</em>{40}$ + H + 2TBA]$^3^-$ 1033.2; [BeW$<em>{12}$O$</em>{40}$ + 2H + TBA]$^3^-$</td>
<td>982.4; [BeW$<em>{12}$O$</em>{40}$ + H + 2Me$<em>2$H$<em>2$N]$^3^-$ 974.8; [BeW$</em>{12}$O$</em>{40}$ + H + Na + Me$<em>2$H$<em>2$N]$^3^-$ 967.1; [BeW$</em>{12}$O$</em>{40}$ + 2H + Me$<em>2$H$<em>2$N]$^3^-$ 960.1; [BeW$</em>{12}$O$</em>{40}$ + 2H + Na]$^3^-$ 952.8; [BeW$<em>{12}$O$</em>{40}$ + 3H]$^3^-$</td>
</tr>
<tr>
<td>Doubly-charged peaks</td>
<td>1912.3; [BeW$<em>{12}$O$</em>{40}$ + 4TBA]$^2^-$ 1792.0; [BeW$<em>{12}$O$</em>{40}$ + H + 3TBA]$^2^-$ 1671.3; [BeW$<em>{12}$O$</em>{40}$ + 2H + 2TBA]$^2^-$</td>
<td>1474.6; [BeW$<em>{12}$O$</em>{40}$ + 2H + 2Me$<em>2$H$<em>2$N]$^2^-$ 1462.6; [BeW$</em>{12}$O$</em>{40}$ + 2H + Na + Me$<em>2$H$<em>2$N]$^2^-$ 1451.6; [BeW$</em>{12}$O$</em>{40}$ + 3H + Me$<em>2$H$<em>2$N]$^2^-$ 1440.1; [BeW$</em>{12}$O$</em>{40}$ + 3H + Na]$^2^-$ 1429.1; [BeW$<em>{12}$O$</em>{40}$ + 4H]$^2^-$</td>
</tr>
</tbody>
</table>

* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 2Na]$^4^+$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 3Na]$^3^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + H + 2Na]$^3^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + H + 3Na]$^3^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + H + 2Na + Me$_2$H$_2$N]$^3^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + H + 3Na]$^3^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 2H + 2Na]$^2^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 3H + Me$_2$H$_2$N]$^2^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 3H + Na]$^2^-$;  
* this peak is overlapped with [BeW$_{12}$O$_{40}$ + 4H]$^2^-$.
Fig. 6S. Cyclic voltammogram of 2 mM solution of (Me₂NH₂)₆[BeW₁₂O₄₀] in 1 M Na₂SO₄ at pH = 8.9 between 0.3 ↔ -1.2 V at 0.01 V·s⁻¹ scan rate.
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