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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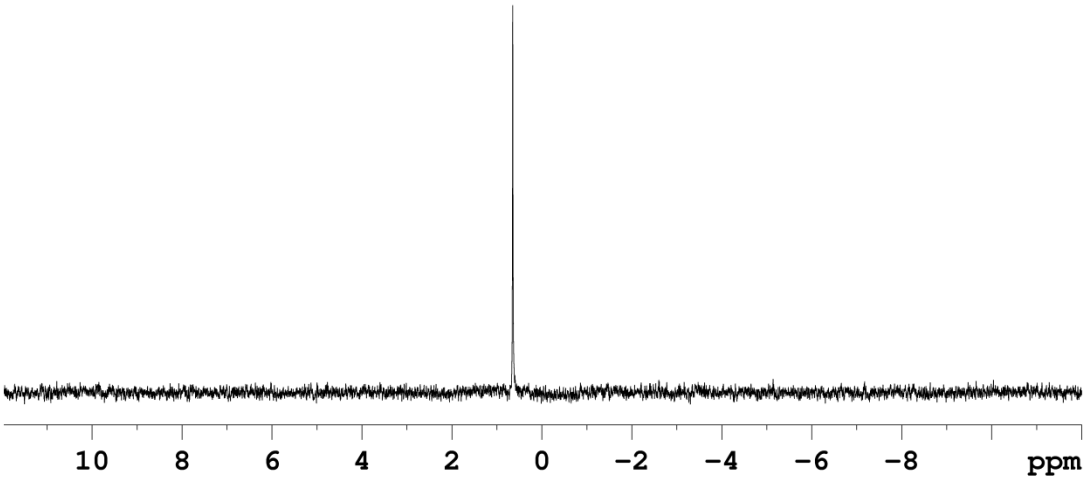

Figure 1S. ^{9}Be NMR spectra of **1a** (0.1 M) in CD_3CN at room temperature (26.5 ± 2° C), D1 = 30.0 sec, AQ = 11.65 sec, experiment total time = 11 min.

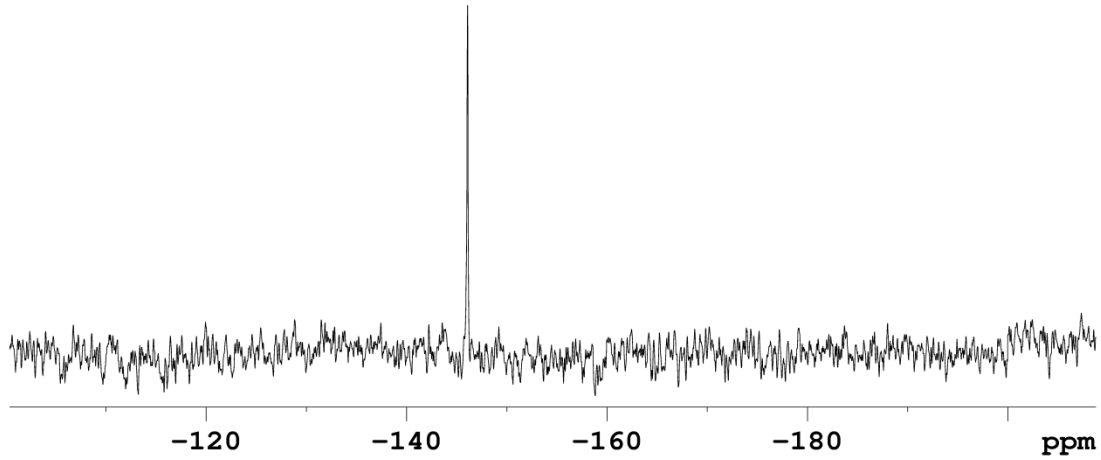

Figure 2S. ^{183}W NMR spectra of **1a** (0.1 M) in CD_3CN at room temperature (24.5 ± 2° C), D1 = 5.0 sec, AQ = 1.57 sec, experiment total time = 15 h.

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 Na_2SO_4 electrolyte was prepared using distilled water. Na_2CO_3 was used to increase pH of the investigated solution to 8.9.

Cyclic voltammogram of a 2 mM solution of $(Me_2NH_2)_6[BeW_{12}O_{40}]$ in 0.1 M Na_2SO_4 shows two irreversible reduction processes at E_p^c = -0.69 V and E_p^c = -0.93 V (vs. Ag/AgCl). Going to 1M Na_2SO_4 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 $V \cdot s^{-1}$. 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 $V \cdot s^{-1}$ (Fig. 5S).

Cyclic voltammogram of $(Me_2NH_2)_6[BeW_{12}O_{40}]$ 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 $V \cdot s^{-1}$. ΔE_p values are equal to 0.060 V and 0.070 V at 0.01 $V \cdot s^{-1}$, respectively, and increase with an increase in the scan rate from 0.01 to 0.1 $V \cdot s^{-1}$. 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. 1×10^{-5} M sample solutions in water or acetonitrile; solutions were introduced at a flow rate of 10 μL 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 (Uc) was set to low value Uc = 10V to control the extent of fragmentation of the gas-phase detected species. The desolvation and source block temperature was typically set at 200 ºC and 120 ºC, respectively. The desolvation and cone gas was nitrogen at 300 L h^{-1} and 30 L h^{-1}, respectively.

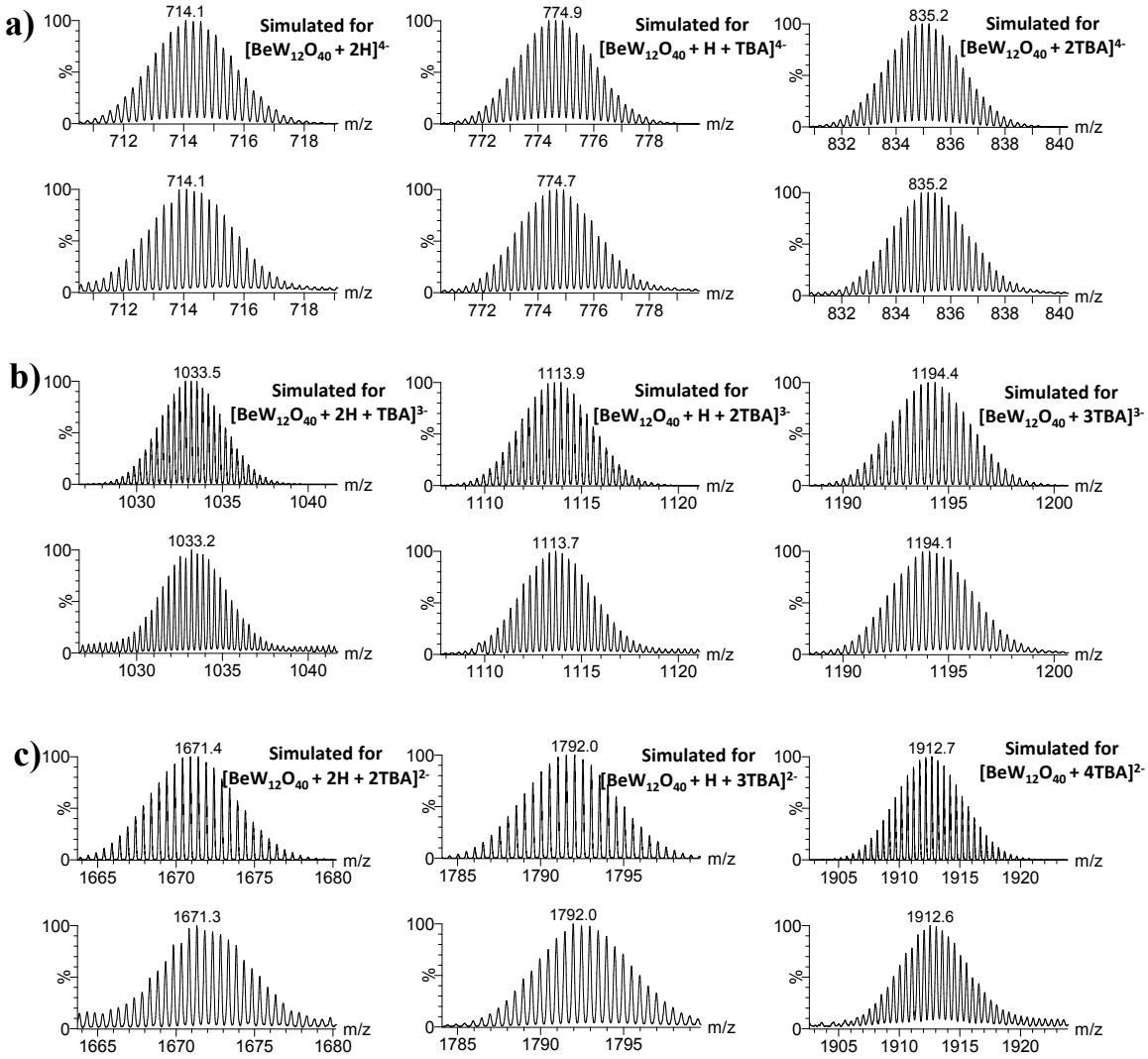

Figure 3S. Comparison of the simulated and experimental isotopic pattern for a) 4- charged species of general formula $[BeW_{12}O_{40} + 2cat]^{4-}$; b) 3- charged species of general formula $[BeW_{12}O_{40} + 3cat]^{3-}$ in each display and c) doubly- charged species of general formula $[BeW_{12}O_{40} + 4cat]^{2-}$ where cat denotes H^+ or tetrabutylammonium (TBA^+) cations.

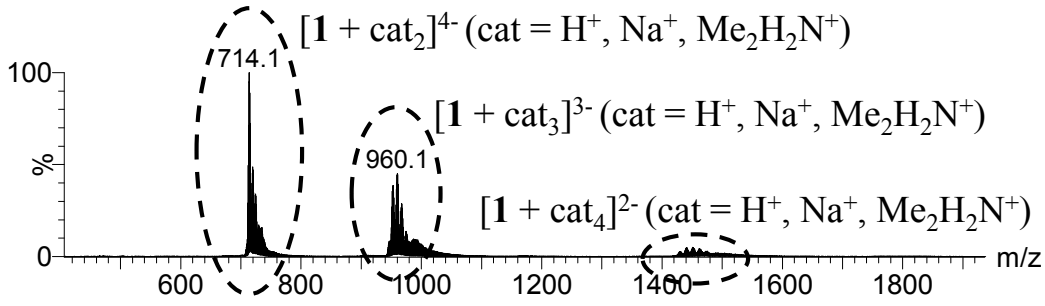

Figure 4S. Negative ESI mass spectrum of compound **1b** in H_2O recorded at Uc = 5 V. Circled regions include the species featuring the 4-, 3- and 2- charge states derive from the $[BeW_{12}O_{40}]^{6-}$ ($\mathbf{1}^{6-}$) polyanion.

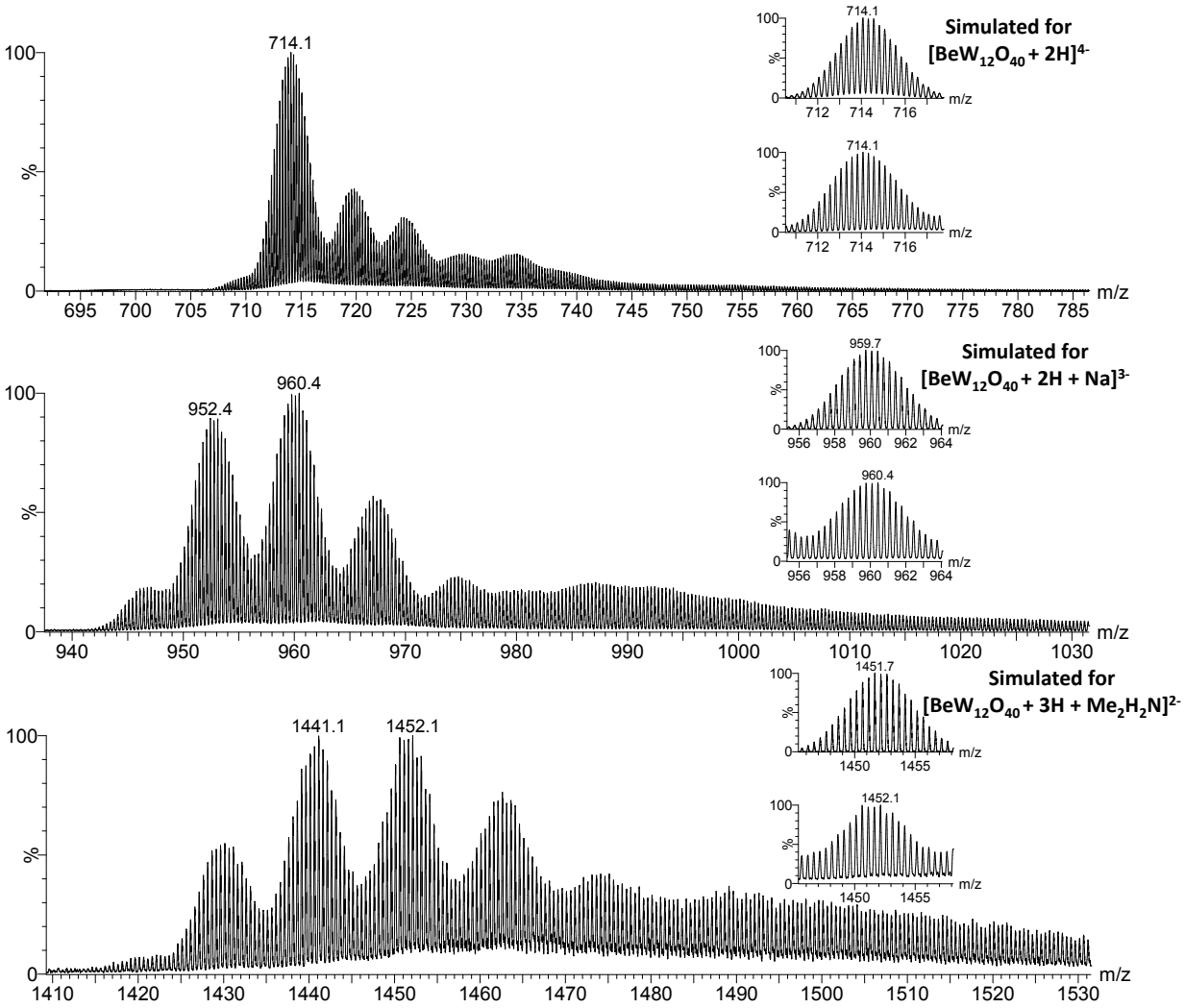

Figure 5S. Expanded regions of the negative ESI mass spectrum of compound **1b** in H_2O recorded at Uc = 5 V that include 4- charged species (top), 3- charged species (middle) and doubly-charged anions (bottom). Insets show a comparison of the simulated and experimental isotopic pattern for the largest peak in each display.

Table 1S. Peak assignments for samples **1a** recorded in CH_3CN and **1b** recorded in H_2O. Note that for sample **1b** overlapping of peaks due to $Me_2H_2N^+$ and $2Na^+$ adducts is observed.

Charge state	**Sample $(Bu_4N)_{4.8}Na_{1.2}[BeW_{12}O_{40}]$ 1a m/z value; adduct composition**	**Sample $(Me_2NH_2)_6[BeW_{12}O_{40}]$ 1b m/z value; adduct composition**
4- charged peaks	835.2; $[BeW_{12}O_{40} + 2TBA]^{4-}$ 774.9; $[BeW_{12}O_{40} + H + TBA]^{4-}$ 714.1; $[BeW_{12}O_{40} + 2H]^{4-}$	730.8; $[BeW_{12}O_{40} + Na + Me_2H_2N]^{4-}$ 725.3[a]; $[BeW_{12}O_{40} + H + Me_2H_2N]^{4-}$ 719.6; $[BeW_{12}O_{40} + H + Na]^{4-}$ 714.1; $[BeW_{12}O_{40} + 2H]^{4-}$
Triply-charged peaks	1194.1; $[BeW_{12}O_{40} + 3TBA]^{3-}$ 1113.7; $[BeW_{12}O_{40} + H + 2TBA]^{3-}$ 1033.2; $[BeW_{12}O_{40} + 2H + TBA]^{3-}$	982.4; $[BeW_{12}O_{40} + H + 2Me_2H_2N]^{3-}$ 974.8[b]; $[BeW_{12}O_{40} + H + Na + Me_2H_2N]^{3-}$ 967.1[c]; $[BeW_{12}O_{40} + 2H + Me_2H_2N]^{3-}$ 960.1; $[BeW_{12}O_{40} + 2H + Na]^{3-}$ 952.8; $[BeW_{12}O_{40} + 3H]^{3-}$
Doubly-charged peaks	1912.3; $[BeW_{12}O_{40} + 4TBA]^{2-}$ 1792.0; $[BeW_{12}O_{40} + H + 3TBA]^{2-}$ 1671.3; $[BeW_{12}O_{40} + 2H + 2TBA]^{2-}$	1474.6[d]; $[BeW_{12}O_{40} + 2H + 2Me_2H_2N]^{2-}$ 1462.6[e]; $[BeW_{12}O_{40} + 2H + Na + Me_2H_2N]^{2-}$ 1451.6[f]; $[BeW_{12}O_{40} + 3H + Me_2H_2N]^{2-}$ 1440.1; $[BeW_{12}O_{40} + 3H + Na]^{2-}$ 1429.1; $[BeW_{12}O_{40} + 4H]^{2-}$

[a] this peak is overlapped with $[BeW_{12}O_{40} + 2Na]^{4-}$; [b] this peak is overlapped with $[BeW_{12}O_{40} + 3Na]^{3-}$; [c] this peak is overlapped with $[BeW_{12}O_{40} + H + 2Na]^{3-}$; [d] this peak is overlapped with $[BeW_{12}O_{40} + H + 2Na + Me_2H_2N]^{2-}$; [e] this peak is overlapped with $[BeW_{12}O_{40} + H + 3Na]^{2-}$; [f] this peak is overlapped with $[BeW_{12}O_{40} + 2H + 2Na]^{2-}$

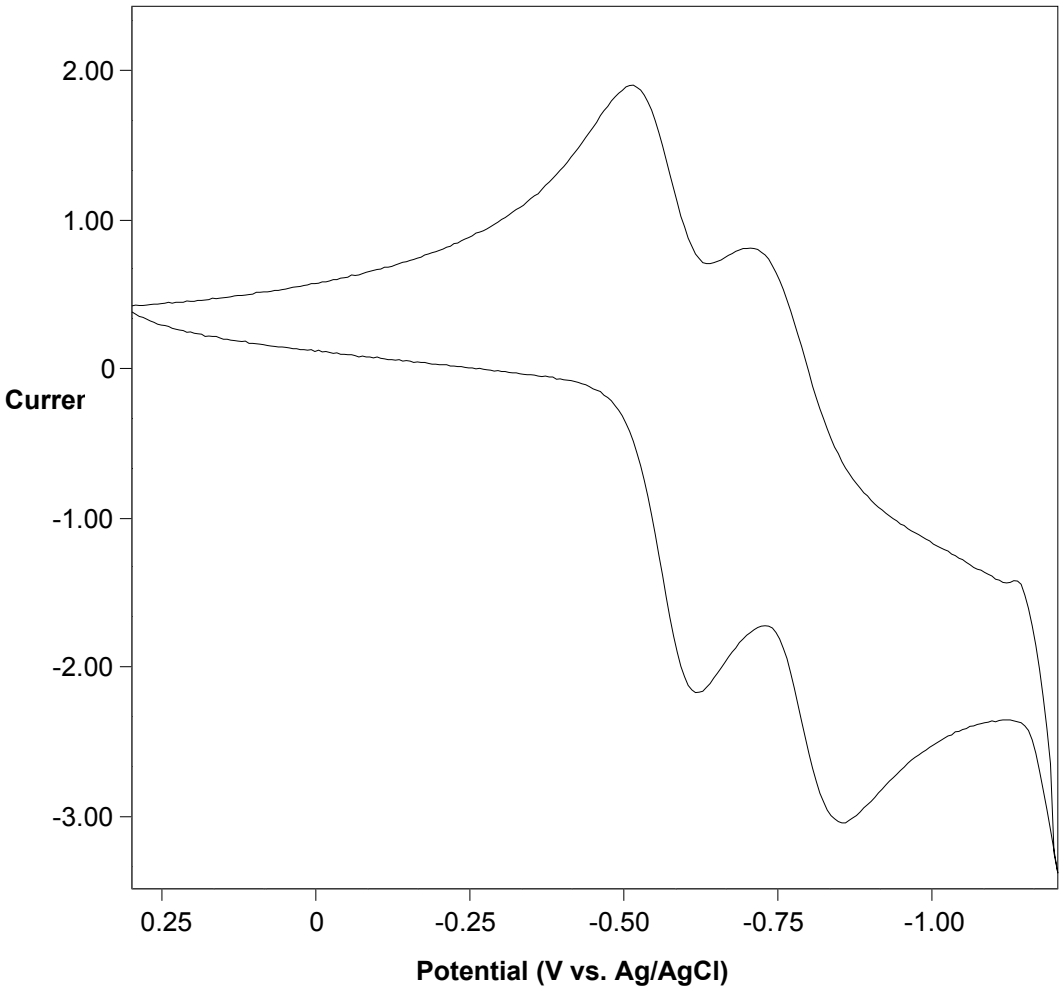

Fig. 6S. Cyclic voltammogram of 2 mM solution of $(Me_2NH_2)_6[BeW_{12}O_{40}]$ in 1 M Na_2SO_4 at pH = 8.9 between 0.3 ↔ -1.2 V at 0.01 $V \cdot s^{-1}$ scan rate.

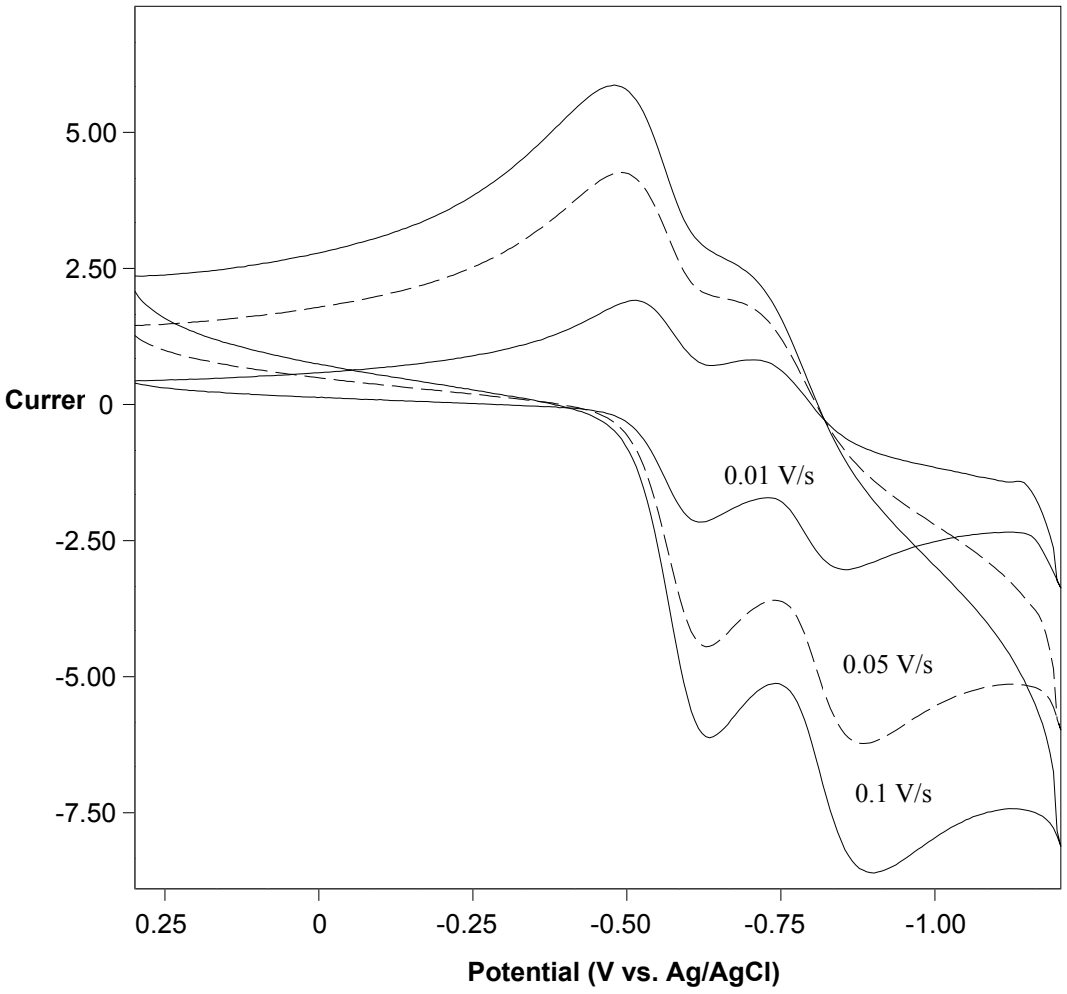

Fig. 7S. The cyclic voltammetry responses for 2 mM solution of $(Me_2NH_2)_6[BeW_{12}O_{40}]$ in 1 M Na_2SO_4 at pH = 8.9 with a scan rate of 0.01, 0.05 and 0.1 $V \cdot s^{-1}$. Scan route: 0.3 ↔ -1.2 V.

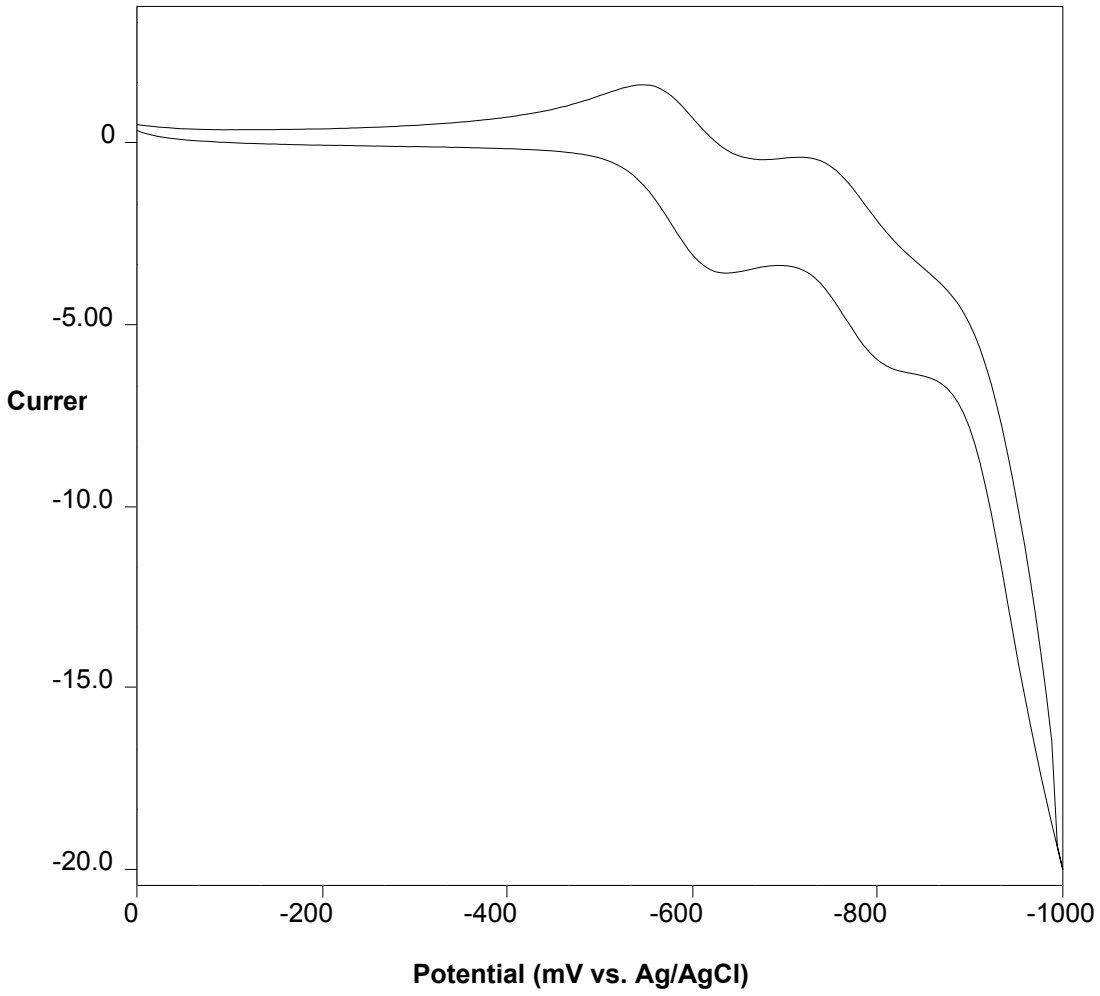

Fig. 8S. Cyclic voltammogram of 3 mM solution of $(Me_2NH_2)_6[BeW_{12}O_{40}]$ in 1 M sodium acetate buffer (pH = 5.5) between 0 ↔ -1 V at 0.01 $V \cdot s^{-1}$ scan rate.