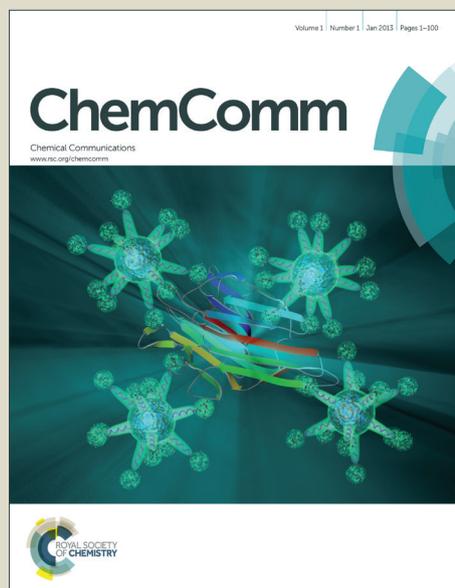This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

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Synthesis and characterization of new Keggin anion: $[BeW_{12}O_{40}]^{6-}$

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The first Keggin-type Be-containing heteropolyanion $[BeW_{12}O_{40}]^{6-}$ (1^{6-}) has been obtained by hydrothermal synthesis from sodium tungstate and $Be(NO_3)_2$. It was crystallized as
10 **$(Bu_4N)_{4.8}Na_{1.2}[BeW_{12}O_{40}]$ (1a) and $(Me_2NH_2)_6[BeW_{12}O_{40}]\cdot 4H_2O$ (1b) salts, which were characterized by ^9Be and ^{183}W NMR, ESI-MS, CV, and single crystal X-ray diffraction analysis.**

The Keggin-type ("1:12") heteropolyoxometalates $[XW_{12}O_{40}]^{n-}$ constitute, both from historical and practical
15 point of view, the most familiar and at the same time most important single class of polyoxometalates (POM). The Keggin structure involves both edge and corner-sharing of 12 MO_6 (typically, WO_6) octahedra assembled around a central tetrahedral XO_4 unit.[1] The heteroatoms in tetrahedral
20 coordination include various elements: P^2, Ge^3, Si^3, Fe^4, Co^5, Cu^6, B^7, V^8, Al^9, Zn^{10}, Ga^{11}, $(H_2)^{12}$, As^{13}. It should be stressed that almost all heteroatoms in this list are p- or d-elements, except H. In this paper we report preparation and characterization of $[BeW_{12}O_{40}]^{6-}$ (**1**) as the first example of an
25 alkaline earth metal incorporated in a heteropolyoxotungstate anion as a part of the tetrahedral building block.

Non-lacunary Keggin anions such as $[PW_{12}O_{40}]^{3-}$ or $[SiW_{12}O_{40}]^{4-}$ are poor ligands (though can participate in the formation of coordination polymers). Enhancing the negative
30 charge (e.g. by reduction of $[PMo_{12}O_{40}]^{3-}$ with Na/Hg) gives strongly basic highly negatively charged species $[PMo_{12}O_{40}]^{n-}$ which can act as tetradentate ligand towards various metal ions[14]. Reducing positive charge of X (e.g. by going from P to Be) will lead to higher negative charge of
35 heteropolyoxotungstate and higher Lewis basicity, which should enable coordination of transition metal ions. POMs with Keggin structure are efficient catalysts and photocatalysts: for example, they catalyse photooxidation of various organic subtsrates, including degradation of polluting
40 waste[15-18]. Near-spherical Keggin anions can be used as anionic part in hybrid materials with useful solid state properties[19].

Be^{2+} with its tetrahedral stereochemistry[20,21] is expected to behave similarly to B^{III}, P^V, Si^{IV}, by promoting condenstion of
45 tungstate with the formation of beryllotungstates; chemistry of silicotungstates and borotungstates is also well known[22-24]. For example, more than 20 phosphotungstates have been described[25]. In the literature we could find only an old publication about $\{BeW_9\}$, characterized only by elemental
50 analysis[26]. We have not been able to confirm this result. In 1982 Weakley reported a series of $\{BeW_{11}M\}$ complexes with various M^{2+} and M^{3+} which were prepared directly from Be^{2+},

WO_4^{2-} and appropriate transition metal salt, without isolation of putative parent lacunary $\{BeW_{11}\}$ species. Though the
55 presence of Be was confirmed by elemental analysis, it could not be localized from X-ray data.[27] To the best of our knowledge, $[BeW_{12}O_{40}]^{6-}$ was not reported. In this work synthesis of $[BeW_{12}O_{40}]^{6-}$ was achieved only under hydrothermal conditions. Typically, a solution of
60 $Na_2WO_4\cdot 2H_2O$ (7.730 g, 23.40 mmol) and 0.400 mg (1.95 mmol) of $Be(NO_3)_2\cdot 4H_2O$ (pH was adjusted to 3.5 by HNO_3) was placed into a Teflon-lined Parr digestion bomb. The bomb was kept at 160°C for 7 days. After cooling down and opening the bomb, the solution was filtered. Addition of TBA nitrate
65 excess to the filtrate gave a white precipitate. After 1 hour the precipitate was collected by filtration, washed with cold water (4 x 20 ml), and dried over P_2O_5 *in vacuo*. Yield of **1a** 27 %.[x] Addition of excess of $(Me_2NH_2)NO_3$ solution to the filtrate and slow evaporation in air within a week gave colorless
70 crystals of **1b**. Crystals were filtred off and washed with ice cold water (4x10 ml). Yield 32 %.[xx] This reaction is Ph-sensitive: at pH ≤ 3.0 the main product was WO_3 (identified by powder XRD).

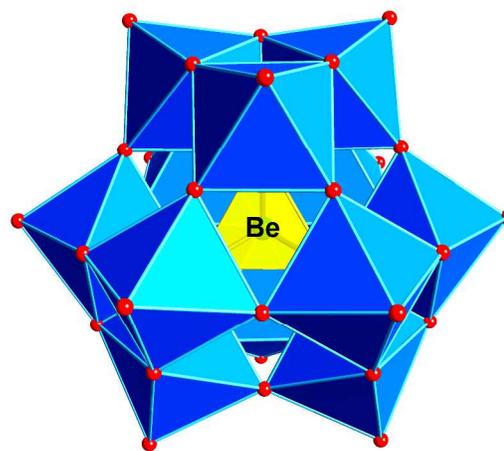75 Figure 1. Polyhedral representation of the $[BeW_{12}O_{40}]^{6-}$ anion in **1b**. WO_6 and BeO_4 polyhedra are depicted as blue octahedra and yellow tetrahedron, respectively.

According to X-ray diffraction analysis, the heteropolyanion
80 $[BeW_{12}O_{40}]^{6-}$ in **1b** possesses classical Keggin structure (Fig. 1).[xxx] It is built up of four W_3O_{13} groups, which result from the association of three edge-sharing WO_6 octahedra. The

tetrahedral arrangement of the W_3O_{13} groups around the central Be heteroatom makes it possible to consider the whole unit as the α-Keggin isomer (idealized T_d symmetry). The only atom of the anion located in a special position (on a 2-fold axis) is the Be atom. Therefore, the anion in **1b** has crystallographically imposed symmetry C_2, leading to six crystallographically independent W atoms. The main bond lengths and angles are consistent with those reported for other $[XW_{12}O_{40}]^{n-}$ anions. The W···W separations range from 3.2537(5) to 3.2659(5) Å, while the W–O_{term}, W–O and W–O_{tet} (O_{term} – terminal O atoms, O_{tet} – O atoms belonging to the BeO_4 tetrahedron) bond lengths fall in the intervals of 1.705(6)–1.734(6), 1.878(6)–1.953(6), and 2.224(5)–2.273(5) Å, respectively. The Be–O_{tet} bond distances are 1.689(10) and 1.701(10) Å, and the O_{tet}–Be–O_{tet} angles are in the range 108.1(8)–109.9(3)°, which indicate a small distortion of the BeO_4 tetrahedron. It is worth to note that the observed Be–O values are somewhat larger than typical bond distances (1.64 Å) within BeO_4 tetrahedra. This may indicate a diffculty in adapting small Be^{2+} inside a rigid $\{W_{12}O_{40}\}$ cage, as well as a high degree of ionicity of the Be-O bonds.

The electronic absorption spectrum of **1a** and **1b** is dominated by a single intense band with λ_{max} = 252 nm, ε = 55000 $M^{-1} \cdot cm^{-1}$, which corresponds to the characteristic (O→W) LMCT band in all POM with Keggin structure. Room temperature ^9Be NMR spectrum of **1a** in CD_3CN exhibits one signal at 0.65 ppm (taking $[Be(H_2O)_4]^{2+}$ as 0.00 pm) (Fig. 1S), and ^{183}W NMR spectrum – one signal at -146.1 ppm (Fig. 2S), in agreement with the retention of the α-Keggin-type structure in solution. Further evidence for the integrity of **1** in solution is provided by ESI-MS of **1a** and **1b**. This technique proved to be very useful for characterization of POMs.[28-30] ESI(-)-MS of **1a** in CH_3CN is shown in fig. 2 and displayed a series of signals corresponding to $[BeW_{12}O_{40}]^{6-}$ (**1**$^{6-}$) adducts with H^+ and Bu_4N^+ (simulation and peak assignments are shown in fig. 3S and table 1S), displaying 4-, 3- and 2- charge states. ESI(-)-MS of **1b** in H_2O is shown in Fig. 2S, and also displays the signals of 4-, 3- and 2- charged species from $[BeW_{12}O_{40}]^{6-}$ adducts with H^+, Na^+, and $Me_2NH_2^+$.
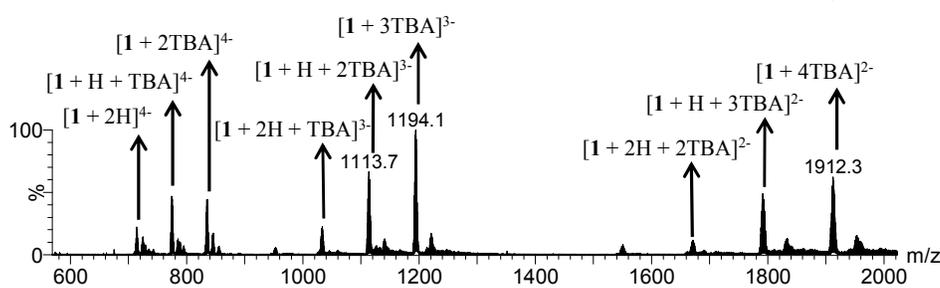

Figure 2. Negative ESI mass spectrum of compound **1a** in CH_3CN recorded at Uc = 5 V. Peak assignments include species featuring the 4-, 3- and 2- charge states derive from the $[BeW_{12}O_{40}]^{6-}$ (**1**$^{6-}$) polyanion and protons and tetrabutylammonium (TBA) cations.

Cyclic voltammetry of **1b**, dissolved in 1 M Na_2SO_4 at pH = 8.9 shows two successive quasi-reversible reduction waves with $E_{1/2}$ = -0.560 V and -0.792 V (vs. Ag/AgCl), which were assigned to W(V)/W(VI) couples (Fig. 6S). These potentials are in agreement with those displayed by other hexanegatively charged POMs, namely $[H_2W_{12}O_{40}]^{6-}$ and $[CoW_{12}O_{40}]^{6-}$, thus obeying the linear decrease of the reduction potentials of the Keggin tungstates with the increase of the negative anion charge[31]. The reductions are most likely correspond to two consequtively 1e reductions. Cyclic voltammogram 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 in this case were -0.587 (V, vs. Ag/AgCl) and -0.774 (V, vs. Ag/AgCl). Thus, **1** is stable up to pH = 9, but at high pH the solutions become cloudy, indicating decomposition. We suppose that increased negative charge of **1** makes it less susceptible to the attack by OH^-, than $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$, or $[BW_{12}O_{40}]^{5-}$ species, which are only stable in acidic solutions ($\{PW_{12}\}$ at pH ≤ 1.5, $\{SiW_{12}\}$ at pH ≤ 4.5, $\{BW_{12}\}$ at pH ≤ 6.5).[25] It appears that in the $[EW_{12}O_{40}]^{n-}$ series increase of n by one unit pushes the upper stability limit by 2-3 pH units towards more basic solutions. The IR spectra of **1a** and **1b** show all bands expected from a non-lacunary POM with the Keggin structure: the W=O_t bands appear as strong bands at 949 (Bu_4N^+) and 939 ($Me_2NH_2^+$) cm^{-1}, the bands associated with asymmetric W-O-W vibrations within the $\{W_3O_{13}\}$ triplets – at 781 (791) cm^{-1}, and those from W-O-W vibrations involving oxygen bridges between adjacent $\{W_3O_{13}\}$ triplets – at 897 (893) cm^{-1}. The characteristic vas (BeO_4) vibration is expected below 900-800 cm^{-1} and is obscured by much stronger W-O-W bands.

To conclude, a new Keggin-type polyoxometalate with Be has been prepared. Its preparation demonstrates the possibility of an alkaly earth element incorporation inside a polytungstate framework. Related experiments are underway.

Notes and references

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† Electronic Supplementary Information (ESI) available: CV data See DOI: 10.1039/b000000x/

^{X} Elemental analysis (%) calc. for $C_{12}H_{48}N_6BeW_{12}O_{40}$ C, 4.60; H, 1.54; N, 2.68; Found: C, 4.58; H, 1.50; N, 2.61. IR, cm^{-1}: 3415 br, 2962 m, 2948 m, 2875 m, 1639 w, 1483 m, 1383 w, 1157 w, 1076 w, 939 s, 893 s, 793 s, 588 m, 419 m.

^{XX} Elemental analysis (%) calc. for $C_{76,8}H_{172,8}N_{4,8}Na_{1,2}BeW_{12}O_{40}$ C, 22.80; H, 4.30; N, 1.66; Be 0.22; W 54.22. Found: C, 22.80; H, 4.50; N, 1.60; Be 0.25; W 54.60. IR, cm^{-1}: 3464 br, 3195 m, 2792 m, 2455 w, 1626 w, 1574 w, 1462 m, 1417 w, 1385 w, 1020 w, 949 s, 897 s, 781 s, 584 m, 553 m, 492 w, 419 m.

^{XXX}. Crystal data for $C_{12}H_{56}BeN_6O_{44}W_{12}$ (**1b**): M = 3203.84, monoclinic, $C2/c$, a = 13.1943(3) Å, b = 19.4817(5) Å, c = 21.0895(5) Å, β = 105.2180(10)°, V = 5230.9(2) Å^3, Z = 4, T = 296(2) K, D_{calcd} = 4.068 g

cm^{-3}. Crystal color and size: colorless, $0.10 \times 0.07 \times 0.05$ mm^3. 33930 reflections were measured on a Bruker-Nonius X8 Apex diffractometer (4K CCD area detector, MoKα radiation, graphite monochromator, combined φ- and ω-scans of narrow frames, $2\theta_{max} = 71.38°$), of which 11991 were unique ($R_{int} = 0.0327$) and 10035 were observed with $I > 2\sigma(I)$. Semi-empirical absorption corrections were applied using the SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL software package (Bruker AXS Inc. (2004). APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11) and SHELXTL (Version 6.12). Bruker Advanced X-ray Solutions, Madison, WI, USA). All non-H atoms were refined anisotropically. Hydrogen atoms of Me$_2$H$_2$N$^+$ cations were located geometrically and refined as riding with $U_{iso}(H) = 1.2U_{eq}(N)$ and $U_{iso}(H) = 1.5U_{eq}(C)$. Hydrogen atoms of lattice water molecules were not located. Final R-factors were: $R_1 = 0.0405$ for 10035 observed reflections, $wR_2 = 0.0923$ and GooF = 1.131 for all reflections with 356 refined parameters. Min. and max. residual electron densities were −2.603 and 3.038 e Å^{-3}. Crystallographic data have been deposited at the Cambridge Crystallogrphic Data Centre under the number CCDC 993391 and may be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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