Keggin Structures

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Structural Link between Giant Molybdenum Oxide Based Ions and Derived Keggin Structure: Modular Assemblies Based on the $[BW_{11}O_{39}]^{9-}$ Ion and Pentagonal $\{M'M_5\}$ Units ($M' = W$; $M = Mo,W$)**

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Polyoxometalate (POM) chemistry represents a large growing area in inorganic chemistry,[1] and the ongoing interest is driven mainly by their potential applications in (electro)-catalysis,[2] medicine, biology,[3] and nanochemistry.[4] The properties of this class of molecular materials are intimately related to their structural architecture and composition. Thus, the possibility to design new architectures and thereby to increase the library of available topological structures is an important goal in today's chemical research. Actually, until the beginning of the 1990s, this wide class of compounds was dominated by a few structural archetypes, namely, the Linqvist, Keggin, and Dawson anions.[5] From 1994,[6] Müller has advanced the knowledge of polyoxometalate chemistry with numerous reports on unprecedented nanosized arrangements based on molybdenum oxide clusters.[7] These topological structures are characterized by a striking pentagonal building unit $\{Mo(Mo_5)\}$, which condenses with metallic cations to form either spheroidal capsules (keplerate) or wheel-shaped clusters. Very recently, a mixed metal $\{W_{72}Mo_{60}\}$ keplerate anion was reported, made up of 12 tungsten pentagonal motifs $\{W(W_5)\}$ mutually connected by 30 $\{Mo_2O_4OOCCH_3\}^+$ linkers.[8] Until now, the pentagonal motifs were found only in such classes of nanosized molecular materials and never observed among the wide class of numerous heteropolyoxotungstates deriving from conventional Keggin or Dawson structural archetypes. Hence, the present work establishes the first link between both subclasses of POM compounds.

The peculiar reactivity of the monovacant ion $[HBW_{11}O_{39}]^{8-}$ was previously reported by Tézé et al., who demonstrated that addition of tungstate to $[HBW_{11}O_{39}]^{8-}$ under acidic conditions does not lead directly to the thermodynamically stable α-$[BW_{12}O_{40}]^{5-}$ saturated Keggin ion, but gives monomeric, dimeric, or trimeric species, all built up from the $\{BW_{13}O_{46}\}^{11-}$ unit (abbreviated hereafter as $\{BW_{13}\}$).[9,10] The $\{BW_{13}\}$ unit behaves as a lacunary polyoxotungstate and can be used to produce mixed-metal arrangements.[11] Afterwards, the phosphate analogue of this rare derivative, that is, the $\{BW_{13}O_{46}\}^{11-}$ unit, was reported as a building block in modular tungstophosphates.[12] The most important feature of this work shows that addition of molybdate on $[HBW_{11}O_{39}]^{8-}$ ion leads to the formation of mixed pentagonal units $\{W(Mo_5)\}$ and $\{W(WMo_4)\}$ trapped as linkers in the resulting modular assemblies. Condensation reactions appear to proceed through a complex pathway that involves the release of monomeric tungstate resulting from the partial degradation of the $\{HBW_{11}O_{39}\}^{8-}$ precursor. It is worth noting that $[HBW_{11}O_{39}]^{8-}$ deviates markedly from the other monovacant Keggin anions such as $[PW_{11}O_{39}]^{7-}$ and $[SiW_{11}O_{39}]^{8-}$, which react instantaneously with monomolybdate in aqueous acidic medium to afford the corresponding mixed saturated ions $[PW_{11}MoO_{40}]^{3-}$ and $[SiW_{11}MoO_{40}]^{4-}$, respectively.[13]

Herein, we report the synthesis and the structural characterization of two compounds, structurally characterized by single-crystal X-ray analysis as a dimer (**1**) and a tetramer (**2**).[14]

$$K_{15}Na_2[K_2 \subset \{(BW_{11}O_{39})_2(H_5Mo_{13}W_2O_{48})\}] \cdot 42\,H_2O$$
$$\mathbf{1} \equiv (K_{15}Na_2\text{-}\mathbf{1a} \cdot 42\,H_2O)$$

$$Cs_{10.5}(NH_4)_{16.5}[Cs \subset \{(BW_{11}O_{39})_4(H_{16}Mo_8W_8O_{52})\}] \cdot 48\,H_2O$$
$$\mathbf{2} \equiv (Cs_{10.5}(NH_4)_{16.5}\text{-}\mathbf{2a} \cdot 48\,H_2O)$$

Under acidic conditions (pH 3), the reaction of $Na_2MoO_4{\cdot}2\,H_2O$ and $K_8[HBW_{11}O_{39}]{\cdot}13\,H_2O$ in 6:1 molar ratio, followed by addition of KCl leads to the formation of **1**, which was obtained as yellowish crystals in 39% yield. Structurally, the molecular arrangement of **1a** can be described as two equivalent $\{BW_{11}O_{39}\}^{9-}$ subunits that connect a central unprecedented mixed Mo/W cluster $\{Mo_{13}W_2O_{48}\}$ in overall C_s symmetry (Figure 1). The latter unit is built up from two equivalent mixed pentagonal clusters $\{WMo_5O_{27}\}$, which fuse through two edge-shared junctions. In contrast to all mixed W/Mo POMs reported until now, **1a** has a perfectly ordered Mo/W arrangement; in fact, the center of each pentagonal cluster $\{WMo_5O_{27}\}$ is 100% occupied by a sevenfold coordinated tungsten atom surrounded by five molybdenum atoms. The $\{Mo_{13}W_2O_{48}\}$ cluster is completed by a $\{Mo_2O_{10}\}$ dimolybdenum group, which bridges the two

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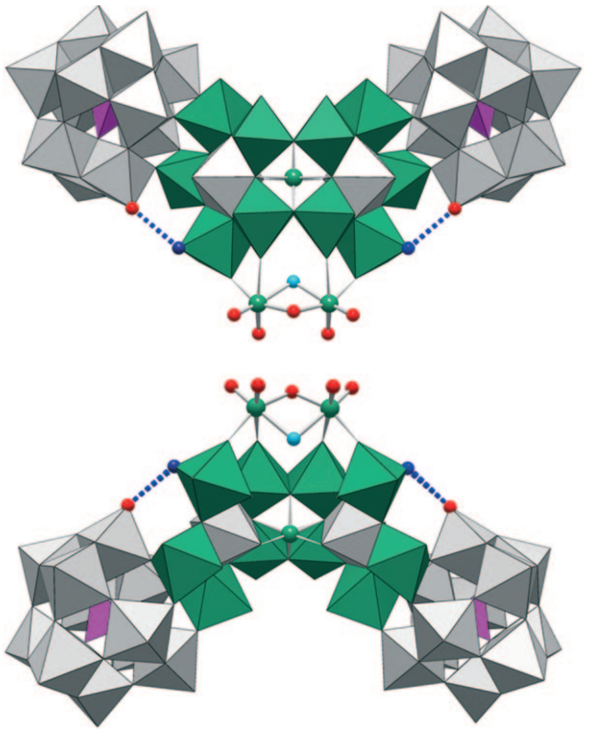

Figure 1. Two combined ball and stick/polyhedral representations of **1a**. Blue dotted lines: intramolecular hydrogen bonds; light gray octahedra: WO_6; green octahedra: MoO_6; pink tetrahedra: BO_4; green spheres: Mo; red spheres: oxo groups, light blue spheres: hydroxo group; deep blue spheres: aquo groups.

pentagonal units through four corner-shared junctions and one single Mo atom located in a central octahedral site defined by six oxygen atoms of both $\{W(Mo_5)\}$ units. Elemental analysis reveals unambiguously that **1a** contains five protons. According to bond length analysis, they are distributed among a hydroxo bridge inside the dimolybdenum group (Mo–OH 2.215(8) Å) and two equivalent terminal aquo ligands ($Mo{-}OH_2$ 2.38(1) Å). Each aquo ligand interacts with one terminal oxygen atom belonging to the $\{BW_{11}O_{39}\}^{9-}$ subunits through a hydrogen bond (O···O ≈2.79(1) Å; see Figure 1). The central Mo atom does not possess any terminal oxygen atom. It is located at the center of a distorted octahedron, which displays two short (1.745(7) Å), two medium (1.83(1)–1.84(1) Å), and two long (2.317(7) Å) Mo–O bonds. Furthermore, two potassium ions interact with the central cluster and fit closely inside anionic pockets lined by peripheral terminal or bridging oxygen atoms of the cluster (see Figure SI1 in the Supporting Information); this arrangement suggests that potassium ions could be involved in the stability of **1a** by decreasing the negative charge of the central core.[15] Strikingly, the central $\{H_5Mo_{13}W_2O_{48}\}$ core contains all the constitutive building blocks that are part of the giant ring-shaped molybdenum oxide based ions, that is, pentagonal $\{M(M_5)\}$, dinuclear $\{M_2\}$, and mononuclear $\{M_1\}$ units, but herein they are mutually assembled through a distinct mode of connection.

Compound **2** was obtained by treating $K_8[HBW_{11}O_{39}]\cdot 13H_2O$ with two equivalents of sodium molybdate at pH 1. Subsequent precipitation by cesium chloride and crystallization from aqueous ammonium chloride gave **2** in a low yield (7.6%) as a mixed cesium/ammonium salt. Single-crystal analysis of **2** reveals a large nanosized tetrameric anion **2a** (3.3×2.2 nm^2), made up of four $\{BW_{11}O_{39}\}$ subunits connected through a striking planar mixed Mo/W cluster of overall C_{2v} idealized symmetry (Figures 2 and 3). The cluster contains two mixed pentagonal units $\{W(WMo_4)\}$, linked through two corner-connected $\{W_2\}$ dimers (Figure 3). As observed for **1a**, the Mo and W atoms are not disordered: the center of the pentagonal unit is occupied by a W atom and the remaining W atoms of the cluster are involved in a six-membered W central ring. These structural results for **1a** and **2a** show the higher trend of W versus Mo to adopt the sevenfold coordination in the pentagonal motif. Also, the bond lengths and angles within the mixed $\{MM_5\}$ motifs are comparable to those observed for the Mo- or W-containing

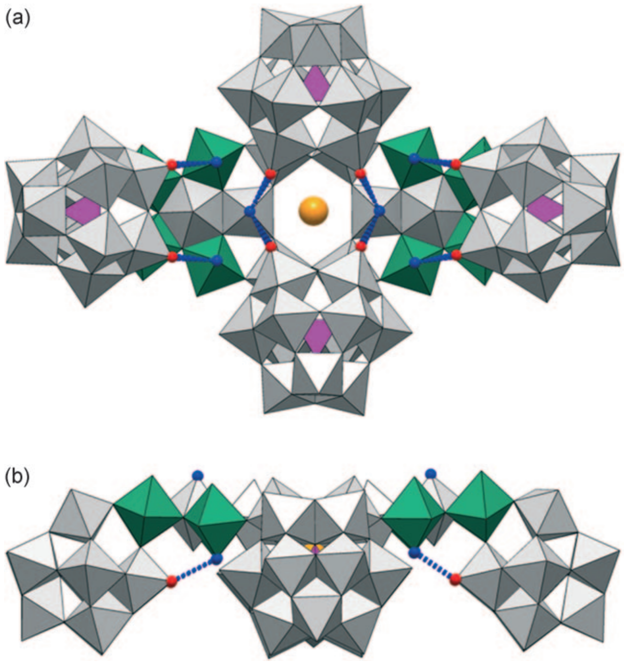

Figure 2. Tetrameric assembly **2a**. a) Top view showing the four $\{BW_{11}\}$ units connected to the large central planar arrangement and the intramolecular hydrogen-bond network. b) Side view highlighting the four $\{BW_{11}\}$ units hinged on the same side of the cluster (same color code as used in Figure 1).

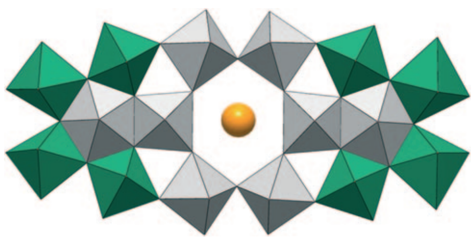

Figure 3. Central core of **2a** resulting from the planar connection of two mixed pentagonal units $\{W_2Mo_4\}$ through two corner-shared ditungsten groups. The center of the six-membered ring is occupied by a Cs^+ cation (yellow sphere).

pentagonal motifs in keplerates.[16] Furthermore, the four hanging $\{BW_{11}O_{39}\}$ moieties lie on the same side of the central planar cluster (Figure 2 b). The W and Mo atoms not attached to the $\{BW_{11}\}$ subunits are bound to one water molecule (M–OH_2 2.327(8)–2.396(5) Å) in the position *trans* to the terminal M=O bond (1.698(5)–1.751(7) Å). Unlike numerous examples in POM chemistry,[10,17] these oxo and aquo ligands are not statistically disordered. Both are involved in an intramolecular hydrogen-bond network, which should contribute to the ordering and the cohesion of the molecular framework. The water molecule attached to the heptacoordinated W center is directed toward the opposite side of the hanging $\{BW_{11}O_{39}\}$ moieties, whereas the three remaining aquo ligands interact through hydrogen bonds with terminal oxygen atoms of the $\{BW_{11}O_{39}\}$ units (O···O 2.725(8)–2.770(5) Å; Figure 2). In addition, the six-membered W ring line a central pocket filled by a cesium cation with 10 ionic contacts (Cs–O 3.264(4)–3.452(5) Å; Figure 3 and Figure SI2 in the Supporting Information).

In summary, this work demonstrates that the $[HBW_{11}O_{39}]^{8-}$ ion displays unique abilities to generate and trap mixed pentagonal units, thus establishing the link between the Keggin ions derivatives and the giant molybdenum oxide and keplerate ions. In further work, we will attempt to incorporate stereoselectively other metal components with the aim to exploit these new cluster topologies for the formation of large interconnected pentagonal motifs, such as those observed within some mixed Mo-based oxides.[18,19]

Experimental Section

1: $K_8\{\alpha\text{-}HBW_{11}O_{39}\}\cdot 13\,H_2O$ (16 g, 5 mmol) and $Na_2MoO_4\cdot 2\,H_2O$ (7.3 g; 30 mmol) were suspended in water (160 mL). The solution was then acidified to pH 3 by a 6 mol L^{-1} hydrochloric acid solution (ca. 10 mL), which instantaneously clarified the cloudy starting solution. Potassium chloride (12.5 g, 168 mmol) was added. After 1 h, the solution was filtered and left to stand in an open vessel for crystallization. After 5 days, well-shaped yellowish parallelepipedic crystals, suitable for X-ray diffraction analysis, were collected. Yield: 9 g (39 % based on $\{BW_{11}\}$). IR (KBr): $\tilde{\nu} = 1005$(sh), 981(sh), 958(s), 905(s), 885(sh), 838(s), 784(s), 678(m), 621(m), 574(w), 532(m), 490(w), 376(m), 328 cm^{-1} (m); elemental analysis (%) calcd for $H_{89}Na_2K_{17}B_2W_{24}Mo_{13}O_{168}$: Na 0.50, K 7.25, B 0.23, W 48.12, Mo 13.61; found: Na 0.46, K 7.31, B 0.34, W 47.58, Mo 13.62.

2: $K_8\{\alpha\text{-}HBW_{11}O_{39}\}\cdot 13\,H_2O$ (16 g, 5 mmol) was suspended in water (125 mL). Then, 1 mol L^{-1} Na_2MoO_4 solution (10 mL) and 6 mol L^{-1} hydrochloric acid solution (ca. 6 mL) were added until a pH of 1 was reached, which instantaneously clarified the cloudy starting solution. After 10 min, cesium chloride (9.3 g, 55 mmol) was added, which led to the precipitation of a white solid. The crude product was collected by filtration, washed with ethanol, and dried by rinsing with diethyl ether. The solid (5.0 g) was dissolved in 0.5 mol L^{-1} ammonium chloride solution (175 mL) under moderate heating (40 °C). The cloudy solution was filtered off and allowed to stand for crystallization. After 13 days, diamond-shaped colorless crystals, suitable for X-ray diffraction analysis, were collected. Yield: 0.49 g (7.6 %). IR (KBr): $\tilde{\nu} = 1000$(sh), 981(w), 955(m), 900(s), 879(s), 838(s), 785(s), 676(m), 626(m), 579(w), 546(m), 490(w), 381(m), 334 cm^{-1} (m); elemental analysis (%) calcd for $H_{176}Cs_{12}N_{16}B_4W_{52}Mo_8O_{256}$: Cs 9.69, N 1.36, B 0.26, W 58.0, Mo 4.66; found: Cs 9.25, N 1.20, B 0.27, W 59,1 Mo 4.10.

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[1] D.-L. Long, E. Burkholder, L. Cronin, *Chem. Soc. Rev.* **2007**, *36*, 105.

[2] a) C. L. Hill, *J. Mol. Catal. A* **2007**, *262*, 1; b) M. E. Davis, C. J. Dillon, J. H. Holles, J. Labinger, *Angew. Chem.* **2002**, *114*, 886; *Angew. Chem. Int. Ed.* **2002**, *41*, 858; c) B. Keita, L. Nadjo, *J. Mol. Catal. A* **2007**, *262*, 190.

[3] a) J. T. Rhule, C. L. Hill, D. A. Judd, R. F. Shinazi, *Chem. Rev.* **1998**, *98*, 327; b) Y. Tajima, *Trends Inorg. Chem.* **2004**, *8*, 107; c) B. Hasenknopf, *Front. Biosci.* **2005**, *10*, 275; d) T. Yamase, *J. Mater. Chem.* **2005**, *15*, 4773.

[4] D.-L. Long, L. Cronin, *Chem. Eur. J.* **2006**, *12*, 3698.

[5] a) M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer, Berlin, **1983**; b) M. T. Pope, A. Müller, *Angew. Chem.* **1991**, *103*, 56; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 34.

[6] a) A. Müller, W. Plass, E. Krickemeyer, S. Dillinger, H. Bögge, A. Armatage, A. Proust, C. Beugholt, U. Bergmann, *Angew. Chem.* **1994**, *106*, 897; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 849.

[7] a) A. Müller, E. Krickemeyer, J. Meyer, H. Bögge, F. Perters, W. Plass, E. Diemann, S. Dillinger, F. Nonnenbruch, M. Randerath, C. Menke, *Angew. Chem.* **1995**, *107*, 2293; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122; b) A. Müller, J. Meyer, E. Krickemeyer, E. Diemann, *Angew. Chem.* **1996**, *108*, 1296; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1206; c) A. Müller, E. Krickemeyer, H. Bögge, M. Schmidtmann, F. Peters, *Angew. Chem.* **1998**, *110*, 3567; *Angew. Chem. Int. Ed.* **1998**, *37*, 3359; d) L. Cronin, C. Beugholt, E. Krickemeyer, M. Schmidtmann, H. Bögge, P. Kögerler, T. K. K. Luong, A. Müller, *Angew. Chem.* **2002**, *114*, 2929; *Angew. Chem. Int. Ed.* **2002**, *41*, 2805; e) A. Müller, E. Beckmann, H. Bögge, M. Schmidtmann, A. Dress, *Angew. Chem.* **2002**, *114*, 1210; *Angew. Chem. Int. Ed.* **2002**, *41*, 1162; f) A. Merca, H. Bögge, M. Schmidtmann, Y. Zhou, E. T. K. Haupt, M. K. Sarker, C. L. Hill, A. Müller, *Chem. Commun.* **2008**, 948.

[8] C. Schäffer, A. Merca, H. Bögge, A. M. Todea, M. L. Kistler, T. Liu, R. Thouvenot, P. Gouzerh, A. Müller, *Angew. Chem.* **2009**, *121*, 155; *Angew. Chem. Int. Ed.* **2009**, *48*, 149.

[9] A. Tézé, M. Michelon, G. Hervé, *Inorg. Chem.* **1997**, *36*, 505.

[10] N. Leclerc-Laronze, J. Marrot, G. Hervé, R. Thouvenot, E. Cadot, *Chem. Eur. J.* **2007**, *13*, 7234.

[11] S. Reinoso, M. H. Dickman, M. F. Matei, U. Kortz, *Inorg. Chem.* **2007**, *46*, 4383.

[12] C. P. Pradeep, D.-L. Long, C. Streb, L. Cronin, *J. Am. Chem. Soc.* **2008**, *130*, 14946.

[13] a) R. Contant, J.-M. Fruchart, G. Hervé, A. Tézé, *C. R. Hebd. Seances Acad. Sci. Ser. C* **1974**, *278*, 199; b) R. Massart, R. Contant, J.-M. Fruchart, J.-P. Ciabrini, M. Fournier, *Inorg. Chem.* **1977**, *16*, 2916; c) J.-M. Fruchart, G. Hervé, J.-P. Launay, R. Massart, *Inorg. Nucl. Chem.* **1976**, *38*, 1627.

[14] Crystal data for **1**: $W_{24}Mo_{13}K_{17}Na_2O_{168}B_2H_{89}$, $M = 9169.79$ g mol^{-1}, orthorhombic space group, $a = 29.665(1)$ Å, $b = 39.688(1)$ Å, $c = 13.9573(4)$ Å, $V = 16433(1)$ Å^3, $Z = 4$, $\rho = 3.449$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 18.095$ cm^{-1}, $F(000) = 15004$, crystal size $= 0.15 \times 0.10 \times 0.06$ mm^3. A total of 203031 reflections ($0.86 < \theta < 30.08°$) were collected of which 23050 were unique ($R_{int} = 0.0422$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXTL-97 to $R = 0.0447$ for 20 470

reflections with $I > 2\sigma(I)$, $R = 0.1232$ for all reflections; max/min residual electron density 4.492/−6.988 e Å^{-3}. Crystal data for **2**: $W_{52}Mo_8Cs_{12}N_{17}O_{256}B_4H_{176}$, $M = 16463.44$ g mol^{-1}, monoclinic space group, $a = 44.833(1)$ Å, $b = 25.3156(6)$ Å, $c = 26.0622(6)$ Å, $V = 26942(1)$ Å^3, $Z = 4$, $\rho = 3.857$ g cm^{-3}, μ-($Mo_{K\alpha}$) = 24.081 cm^{-1}, $F(000) = 26786$, crystal size = 0.15 × 0.10 × 0.08 mm^3. A total of 231065 reflections ($0.86 < \theta < 30.09°$) were collected of which 40374 were unique ($R_{int} = 0.0727$). An empirical absorption correction using equivalent reflections was performed with the program SADABS 2.03. The structure was solved with the program SHELXS-97 and refined using SHELXTL-97 to $R = 0.0719$ for 20890 reflections with $I > 2\sigma(I)$, $R = 0.1194$ for all reflections; max/min residual electron density 5.370/−5.129 e Å^{-3}. Crystals of **1** and **2** were mounted in a capillary tube and intensity data collections were carried out at room temperature with a Bruker X8 APEX2 CCD using the $Mo_{K\alpha}$ wavelength ($\lambda = 0.71073$ Å). Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-420255 and -420256 for **1** and **2**, respectively.

[15] Attempts to characterize **1a** in solution by ^{183}W NMR spectroscopy indicated that **1a** is unstable under cation-exchange conditions, either as sodium salt in aqueous solution or as tetrabutylammonium salt in aprotic solvent (acetonitrile or DMSO). In DMSO, the ^{183}W NMR spectrum of **1a** as tetrabutylammonium salt reveals two distinct sets of resonances ranging between $\delta = -110$ and -130 ppm and 50 and 80 ppm, respectively (see Figure SI3 in the Supporting Information). The low-frequency signals correspond to mixed Mo/W saturated Keggin ions, whereas the high-frequency resonances are attributed to the presence of mixed $[W_{6-x}Mo_xO_{19}]^{2-}$ Linqvist anions. These assignments were further supported by ^{11}B NMR spectroscopy, which gives six sets of narrow resonances observed between $\delta = 3.9$ and 1.9 ppm (see Figure SI3 in the Supporting Information). These signals are characteristic of $\{BO_4\}$ groups in a quite symmetrical environment (T_d or close to T_d) and correspond to a distribution of $[BW_{11-x}Mo_xO_{40}]^{5-}$ Keggin anions with x varying from 0 to 5. From the solution used for ^{183}W NMR spectroscopy in DMSO, crystalline materials deposited as colorless and yellow crystals, identified as β-$[Mo_8O_{26}]^{4-}$ and $[Mo_6O_{19}]^{2-}$, respectively, by single-crystal X-ray structural analysis. Aqueous solutions of **1a** as sodium salt behave similarly.

[16] Analysis of the W−O bond lengths of the heptacoordinated W atom of the mixed $\{WMo_5\}$ and $\{W(WMo_4)\}$ motifs in **1a** and **2a** reveals short (1.701(7)–1.722(8) Å) and long (2.297(7)–2.328(9) Å) axial W−O bonds, and five equatorial W−O bonds in the range 1.911(9)–2.053(7) Å. Such a coordination pattern appears to be close to that observed in the $\{W_{72}Mo_{60}\}$ keplerate, which exhibits similar bond lengths (see ref. [8]). The bond lengths of the five peripheral atoms of the pentagonal units (i.e. Mo in **1a**; Mo and W in **2a**) are in the usual range for octahedral coordination in POMs: short (1.653(6)–1.751(6) Å) and long (2.261(6)–2.397(7) Å) for terminal oxo and aquo ligands, respectively, and medium (1.852(7)–1.943(7) Å and 1.910(7)–2.160(7) Å) for singly bonded μ_2- and μ_3-oxido atoms, respectively.

[17] V. Béreau, E. Cadot, H. Bögge, A. Müller, F. Sécheresse, *Inorg. Chem.* **1999**, *38*, 5803.

[18] a) L. Kihlborg, *Acta Chem. Scand.* **1969**, *23*, 1834; b) P. DeSantos, Jr., D. J. Buttrey, R. K. Grasselli, C. G. Lugmair, A. F. Volpe, B. H. Toby, T. Vogt, *Top. Catal.* **2003**, *23*, 23.

[19] M. Sadakane, K. Yamagata, K. Kodato, K. Endo, K. Toriumi, Y. Ozawa, T. Ozeki, T. Nagai, Y. Matsui, N. Sakaguchi, W. D. Pyrz, D. J. Buttrey, D. A. Blom, T. Vogt, W. Ueda, *Angew. Chem.* **2009**, *121*, 3840; *Angew. Chem.* **2009**, *48*, 3782.