Polyoxometalates

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A Planar $\{Mn_{19}(OH)_{12}\}^{26+}$ Unit Incorporated in a 60-Tungsto-6-Silicate Polyanion**

Bassem S. Bassil, Masooma Ibrahim, Rami Al-Oweini, Marie Asano, Zhenxing Wang, Johan van Tol, Naresh S. Dalal, Kwang-Yong Choi, Rosa Ngo Biboum, Bineta Keita, Louis Nadjo, and Ulrich Kortz**

Polyoxometalates (POMs) are discrete metal–oxo anions of early transition-metals in high oxidation states (e.g. W^{VI}, Mo^{VI}, V^{V}) and they are usually synthesized in aqueous, acidic medium.[1] Most classical POMs are based on edge- and corner-shared MO_6 octahedra. However, the recently discovered POM subclass of noble metalates comprises linked square-planar MO_4 units ($M = Pd^{II}$, Au^{III}).[2] Lacunary (vacant) POMs can be considered as inorganic, multidentate ligands, and hence they are good candidates for the encapsulation of large, multinuclear d- and f-block metal–oxo fragments, sometimes resulting in compounds with interesting magnetic properties.[3]

A pioneering result in this area was the synthesis of $[Mn_{12}(CH_3COO)_{16}(H_2O)_4O_{12}]$ (**Mn_{12}**) by Lis in 1980, which was shown to exhibit single-molecule magnet (SMM) behavior by Gatteschi's group 13 years later.[4] During the past two decades many high-nuclearity, transition-metal based, coordination complexes with interesting electronic and magnetic properties have been prepared.[5] High-nuclearity manganese complexes have been amongst the most studied in this class, and there are examples containing up to 84 manganese ions.[4,6]

To date there are only a few high-nuclearity manganese–oxo-containing POMs, such as $\{[XW_9O_{34}]_2[Mn^{III}_4Mn^{II}_2O_4(H_2O)_4]\}^{12-}$ ($X = Si$, Ge)[7a] and $[Mn^{III}_{13}Mn^{II}O_{12}(PO_4)_4(PW_9O_{34})_4]^{31-}$.[7b]

Herein we report the synthesis and structure as well as the magnetic and electrochemical properties of a 19 manganese(II) center containing 60-tungsto-6-silicate, $[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-}$ (**1**), which was isolated as a hydrated sodium salt, $Na_{34}[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]\cdot 115\,H_2O$ (Na-**1**).

Single-crystal X-ray diffraction[8] revealed that polyanion **1** consists of a cationic $\{Mn_{19}(OH)_{12}\}^{26+}$ (Mn_{19}) assembly stabilized by six dilacunary $[\alpha\text{-}SiW_{10}O_{37}]^{10-}$ units resulting in a structure with S_6 point-group symmetry (Figure 1, top). To the best of our knowledge, **1** is the highest nuclearity manganese-containing POM known to date. All 19 Mn^{II} ions lie in the same plane forming a hexagonal structure based on edge-shared MnO_6 octahedra. The Mn^{II} ions in Mn_{19} are connected by a total of twelve μ_3-hydroxo bridges, as determined by bond valence sum (BVS) calculations (Supporting Information, Table S1).[9] The discrete Mn_{19} nanosheet (Figure 1, bottom) is held in place by six dilacunary $[\alpha\text{-}SiW_{10}O_{37}]^{10-}$ units through μ_4-, μ_3-, and μ_2-oxo bridges. The central Mn^{II} ion in Mn_{19} is hexacoordinated in a regular octahedral fashion with average Mn–O bond lengths of 2.21(4) Å. This unique Mn^{II} ion is bridged to the six surrounding Mn^{II} ions by six hydroxo bridges, resulting in a compact Mn_7 core-fragment resembling the Anderson–Evans structure type.[10] This fragment has a hexagonally closest-packed brucite structure, in which the Mn^{II} ions are located in the octahedral holes. This type of Mn_7 core aggregate has been observed in several coordination complexes.[5,6a,11]

Interestingly, all of these six outer Mn^{II} ions are heptacoordinated, each with four "normal" Mn–O bonds (ca. 2.1–2.2 Å) and three long Mn–O bonds (ca. 2.4–2.6 Å). BVS calculations reveal a combined contribution of approximately 1.5 bond valences from the four shorter bonds and 0.5 from the three longer ones, resulting in the expected total bond valence of 2.0 for each of the six Mn^{II} ions (Supporting Information, Table S1). Heptacoordination for Mn^{II} is not unusual in coordination chemistry.[12] The Mn_7 core is surrounded by a ring of 12 Mn^{II} ions, which are all hexacoordinated in a distorted octahedral fashion with Mn–O bond lengths ranging from 2.02(3) to 2.37(2) Å. These 12 outer Mn^{II}

[*] Dr. B. S. Bassil,[+] M. Ibrahim,[+] R. Al-Oweini, M. Asano, Prof. U. Kortz
Jacobs University, School of Engineering and Science
P.O. Box 750561, 28725 Bremen (Germany)
Fax: (+49) 421-200-3229
E-mail: u.kortz@jacobs-university.de
Homepage: http://www.jacobs-university.de/ses/ukortz

Z. Wang, Dr. J. van Tol, Prof. N. S. Dalal
Department of Chemistry and Biochemistry
National High Magnetic Field Laboratory
Florida State University, Tallahassee, FL 32306 (USA)
E-mail: dalal@chem.fsu.edu

Prof. K.-Y. Choi
Department of Physics, Chung-Ang University
Seoul 156-756 (Republic of Korea)

R. Ngo Biboum, Dr. B. Keita, Prof. L. Nadjo
Laboratoire de Chimie Physique
Université Paris-Sud 11, 91405 Orsay Cedex (France)

[+] These authors contributed equally to this work.

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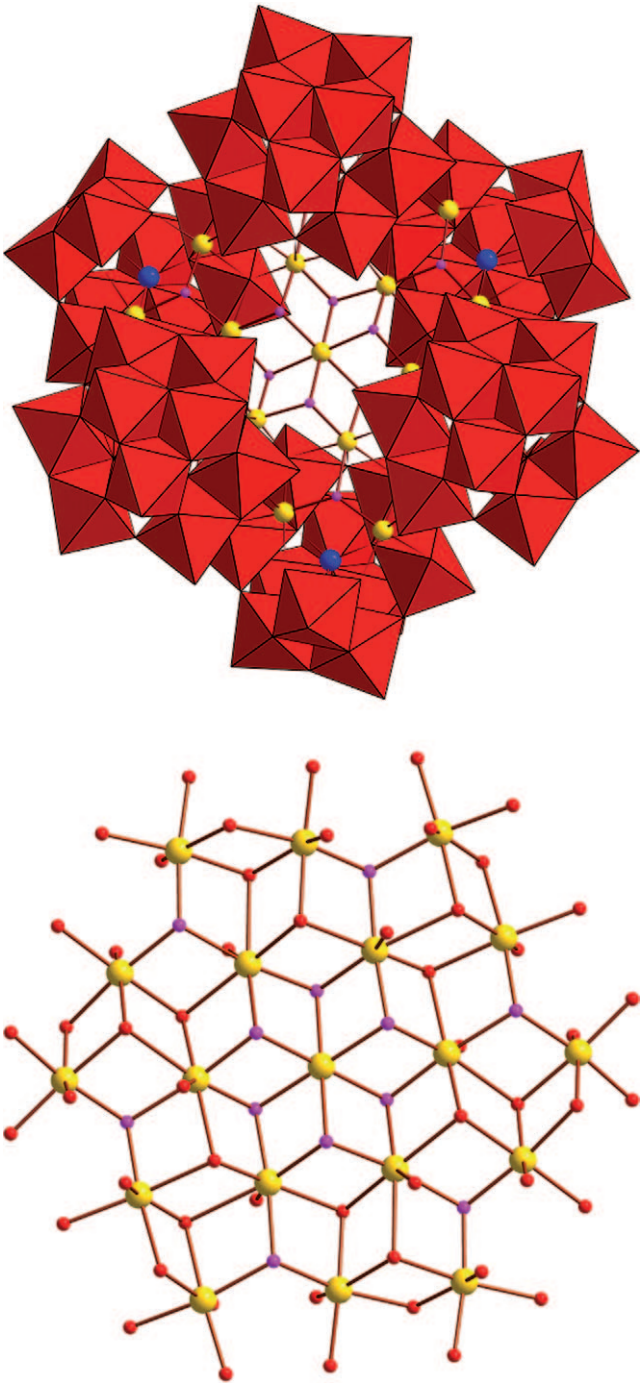

Figure 1. Top: Combined polyhedral/ball-and-stick representation of **1**. Bottom: Ball-and-stick representation of the Mn_{19}-oxo-hydroxo core in **1**. Protonated oxygen atoms are shown in pink. WO_6 red octahedra, Si blue balls, Mn yellow balls, O red balls.

ions are arranged in six edge-shared pairs, each filling the lacunary sites of the six $[\alpha\text{-}SiW_{10}O_{37}]^{10-}$ units. Thermogravimetric analysis (TGA) of Na-**1** gave 115 waters of crystallization (Supporting Information, Figure S1), which is consistent with elemental analysis (see below).

Notably, in 2001 Westin's group also reported a planar Mn_{19} magnetic core in an oxo–alkoxide complex, $[Mn_{19}O_{12}(moe)_{14}(moeH)_{10}]$ ({Mn_{19}org}, see Supporting Information, Figure S2), which was synthesized in an inert atmosphere by reaction of $MnCl_2$ with potassium methoxyethoxide in toluene/$HOC_2H_4OCH_3$.[13] This Mn_{19} assembly is in fact very similar, but not identical, to that of **1**. The magnetic properties of {Mn_{19}org} were investigated by Gatteschi's group and modeled using the Monte Carlo method.[14] Moreover, Powell's group synthesized an Fe_{19}-containing coordination complex stabilized by chelating NOOO ligands.[5b]

A number of synthetic factors play a significant role in the formation of polyanion **1**, such as the type of reactant salt, ratio of reactants, pH value, temperature, and solvent. The synthesis of polyanion **1** is only successful when starting with the sodium salt of the trilacunary precursor $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ and if no other countercations are present in solution during the reaction. An extra tungsten center is inserted into $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ in situ, as a result of partial decomposition of some of the lacunary POM precursor in solution. Interestingly, addition of one equivalent of sodium tungstate at any point during the reaction did not result in **1**.

The synthesis of **1** consists of two steps. The first step involves reaction of Mn^{II} ions with the trilacunary precursor $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ at room temperature and pH 8 for about 30 min, and the second step involves addition of sodium phosphate while keeping the pH at 8, followed by moderate heating of the solution for around 1 h. These two steps appear to be crucial for the successful synthesis of polyanion **1**. If the reaction is performed directly in phosphate buffer, **1** is not formed. The pH value is also critical, as pH < 7 or pH > 9 does not lead to the formation of **1**. The temperature of step 2 is also crucial, as the yield improves with increasing temperature, but above 70 °C an unidentified, black-brown side-product is formed. Also, step 2 seems to work only in sodium phosphate buffer. Efforts to reproduce polyanion **1** by addition of CH_3COONa, Na_2CO_3, or NaCl instead of Na_3PO_4 to the reaction mixture, while keeping the pH value at 8, were all unsuccessful. All this reflects the difficulty of rationalizing the mechanistic pathways of POM formation.

We have also investigated the electrochemistry of **1** in aqueous solution (see Supporting Information for details). In short, the reduction of **1** in pH 5 medium gives two well-defined waves assigned to tungsten located at −0.850 V and −0.960 V versus the saturated calomel electrode (SCE; Supporting Information, Figure S3). Controlled potential coulometry indicates that the reduced form associated with the first tungsten redox couple is already active for the hydrogen evolution reaction. The first step of Mn^{II} oxidation proceeds to the Mn^{IV} state via the Mn^{III} state, in agreement with previous results.[15a] Controlled potential coulometry indicates that all the manganese centers are electroactive and have a +2 oxidation state.

Finally, a new, very intense oxidation wave is observed at more positive potential values (Supporting information, Figure S4). This wave is mainly attributed to the oxygen evolution reaction (OER) from water.[15a] Taking into account the diversity of reported experimental conditions, **1** displays very competitive kinetic parameters for the OER: 1) a good linearity was observed between an overpotential of 330 mV to 600 mV (Supporting Information, Figure S4), this observation coincides roughly with two remarkable results obtained

recently for nanotubes decorated with a ruthenium-containing POM[15b] and for a catalyst containing phosphate and Co^{II}.[15c] 2) in contrast, the slope of the Tafel line ((135 ± 10) mV) lies in-between those which could be estimated from these reports (310 mV [15b] and 83 mV [15c]). Thus, **1** shows better OER kinetics than the ruthenium-containing POM. 3) The exchange current density, i_0, expressed in $A\,cm^{-2}$ ($\log i_0 = -6.8 \pm 0.2$) compares favorably with analogous reported values.[15c] The efficiency of **1** might be attributed to its multiple μ-hydroxo/oxo bridging units connecting adjacent metal centers, a situation analogous to that in the $CaMn_4O_4$ cluster used by nature to oxidize water at low overpotential.

The Mn_{19} core in polyanion **1** is of interest for its magnetic properties, as this structure presents an intermediate between an infinite, two-dimensional, spin-frustrated, triangular lattice and a small molecular complex with a well-defined spin ground state. Spin-frustrated triangular lattices show a variety of phase transitions and magnetic structures.[16,17] As mentioned above, the magnetic properties of Westin's organic-capped coordination complex {Mn_{19}org} have been investigated, but the EPR measurements were reported to be somewhat problematic because of saturation effects.[14] Extensive Monte Carlo simulations of the magnetic susceptibility showed that the magnetic properties of {Mn_{19}org} are dominated by strong antiferromagnetic interactions ($J = -24$ K) between the seven central Mn^{II} ions, with a ground state of $S = 5/2$. The role of the other, peripheral 12 Mn^{II} ions was minor.

Our motivation was to study the magnetic and EPR properties of the Mn_{19} assembly in polyanion **1**, comparing them with those of {Mn_{19}org} and examining if the inorganic ligands in **1** modify the magnetic properties of the Mn_{19} core. We carried out detailed EPR measurements over the frequency range 54–432 GHz and the temperature range 3–285 K, magnetic susceptibility over 1.8–300 K and magnetization measurements in an applied field of 0–7 T. The SQUID data yielded a $\chi_m T$ value of 85.04 emu K mol^{-1} at room temperature, close to the expected value (83.125 emu K mol^{-1} taking $g_{av} = 2$) for 19 uncoupled Mn^{II} ions ($S = 5/2$). Upon lowering the temperature, the value of $\chi_m T$ decreased gradually owing to the development of antiferromagnetic correlations. At the lowest temperatures, the spin state corresponds approximately to a total spin of $S = 5/2$ for the Mn_{19} unit (Supporting Information, Figure S5). However, the finer details of the magnetization and susceptibility curves could not be fully simulated, because of the complexity of this large complex with its competing exchange interactions.

Figure S6 in the Supporting Information shows the spin topology of the Mn_{19} core in **1**. The 19 exchange-coupled Mn^{II} ions ($S = 5/2$) form a distorted, finite, two-dimensional triangular spin lattice with 21 slightly different exchange interactions. Since a Hilbert space of $6^{19} = 6.09 \times 10^{14}$ is huge, the magnetic behavior of the Mn_{19} core would be described by a classical Heisenberg model in a continuum limit $\hat{H} = J_{ij} S_i S$. This conjecture was fully supported by our EPR measurements over a broad temperature and microwave-frequency range as stated above. Under all conditions, only a single, inhomogeneously broadened peak was observed, without any sign of fine structure or hyperfine splitting (Supporting information, Figure S7).

As the magnetic field increases, a gradual increase of the ground spin state and $\langle S_z \rangle$ is observed well below 7 T. Even at 1.8 K, no steps are observed in the magnetization. It is therefore an open question whether this system can be described by a series of discrete spin states, or if a description in terms of a continuum is more appropriate, somewhat reminiscent of short-range order in an infinite two-dimensional lattice. We note that our magnetic susceptibility data do not exhibit a round maximum, in contrast to {Mn_{19}org}, where a maximum was found at 12 K. The absence of a round maximum for **1** shows that its 21 antiferromagnetic J values are more or less continuously spread, leaving just one free Mn^{II} ($S = 5/2$) ion to control the magnetism of the ground state. This is the reason for the nonlinearity of the magnetization curve in Figure S8B (Supporting Information) for **1**, while no such nonlinearity was reported for {Mn_{19}org}. Regarding a magnetic comparison of **1** with {Mn_{21}},[6a] {Mn_{21}} consists of a {$Mn^{IV}{}_9O_{20}$} sheet held within a nonplanar {$Mn^{III}{}_{12}O_{12}$} ring, whereas the {$Mn_{19}(OH)_{12}$} core of **1** consists exclusively of Mn^{II} ions, and is essentially planar. Thus, it is very difficult to compare these two compounds.

In summary, we have prepared the novel, discrete polyanion **1**, comprising a cationic, planar $\{Mn_{19}(OH)_{12}\}^{26+}$ assembly incorporated in a 60-tungsto-6-silicate, by reaction of Mn^{II} ions with $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ in aqueous solution at room temperature. This approach is made possible by performing the reaction at pH 8, which is unusual in polyanion synthesis. The planar Mn_{19} magnetic cluster in **1** is unprecedented in POM chemistry, and in fact **1** contains more manganese ions than any other polyanion reported to date. A comparison of the structural and magnetic aspects of the inorganic capped Mn_{19} assembly in **1** with the organic capped {Mn_{19}org} exhibited significant differences. This result indicates a large potential for the preparation of polyanion capped analogues of the many known multinuclear, magnetic coordination complexes.[4,6] Here we have demonstrated that it is also possible to prepare unexpectedly large, magnetic metal–oxo assemblies using simple metal salts, without the need for multinuclear coordination complex precursors or cyclic, robust polyanion templates, such as $\{P_8W_{48}\}$.[18] Using the synthetic methodology described herein we have already prepared $\{Mn_8\}$, $\{Ni_{14}\}$, $\{Cu_{15}\}$, and $\{Co_{16}\}$[19] polyanions, which will be reported elsewhere.

Experimental Section

$Na_{34}[Mn_{19}(OH)_{12}(SiW_{10}O_{37})_6]\cdot 115\,H_2O$ (Na-**1**): $MnCl_2\cdot 4\,H_2O$ (0.13 g, 0.63 mmol) was dissolved in H_2O (20 mL). Then solid $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$[20] (0.50 g, 0.20 mmol) was added and stirred until a clear yellow solution was obtained. The pH value of the resulting mixture was adjusted to 8 with 4 M NaOH. The turbid solution was stirred for 30 min at room temperature. Then solid Na_3PO_4 (0.50 g, 3.0 mmol) was added to this solution in small portions, while maintaining the pH at 8 with HCl_{aq}. The mixture was heated to 70 °C for 1 h, allowed to cool to room temperature, and then filtered. The filtrate was allowed to evaporate in an open vial at room temperature. After two weeks a brown crystalline product started to appear. Evaporation was allowed to continue until the solution level had approached the solid product,

which was then collected by filtration and air dried. Yield 0.040 g (6.5%).

IR (2% KBr pellet): $\tilde{\nu}$ = 988 (w), 945 (m), 890 (s), 790 (s), 707 (m), 650 (m), 535 cm^{-1} (m), see Figure S9. Elemental analysis for Na-**1**, calcd: Na 4.1, Si 0.89, Mn 5.54, W 58.5; found: Na 4.2, Si 0.86, Mn 5.61, W 59.1.

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