Polyoxometalates

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A Mixed-Valence Manganese Cubane Trapped by Inequivalent Trilacunary Polyoxometalate Ligands**

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Paramagnetic cage complexes of d- or f-block transition metals with bridging and/or chelating organic ligands have been widely studied.[1,2] For instance, many manganese-based clusters have been targeted, as many exhibit large spin ground states,[3,4] but also because of their relevance in biological systems; for example, in the oxygen-evolving complex (OEC) of photosystem II (PSII),[5] where the photosynthetic oxidation of water to dioxygen occurs. Although the precise details of the OEC structure are still debated, it is now widely accepted that manganese ions assembled in a $\{Mn_3CaO_4\}$ cubane form the heart of the water-oxidation machinery in this enzyme.[6]

An alternative approach for the synthesis of the active cubane core in PSII and magnetically interesting species is to utilize polyoxometalates[7] (POMs) as inorganic supporting ligands. POMs themselves represent a vast class of anionic molecular metal oxide clusters based on principally tungsten, molybdenum, vanadium, and niobium in their highest oxidation states and have many applications,[8,9] including activity in catalytic water oxidation.[10,11] We recently reported a mixed-valence manganese double-cubane cluster core $[Mn^{III}_4Mn^{II}_2O_4(H_2O)_4]^{8+}$ anchored between two rigid lacunary Keggin $[XW_9O_{34}]^{10-}$ polyoxometalate clusters that exhibits single-molecule magnet (SMM) behavior.[4]

Herein we report the complex $K_{18}[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]\cdot 40\,H_2O$ (**1**), which is composed of three distinct and inequivalent lacunary silicotungstate Keggin fragments. The trimeric asymmetric (C_1) sandwich complex **1** (Figure 1) crystallizes in triclinic space group $P\bar{1}$ as well-formed radiant orange-brown plates. The compound has been fully characterized by single-crystal X-ray diffraction, flame atomic absorption spectroscopy, flame photometry, IR and UV spectroscopy, thermogravimetric analysis, electrochemistry, and magnetic measurements. The asymmetric unit contains one molecule, which displays two pertinent features: the presence of three inequivalent lacunary Keggin fragments; and the presence of an appended $\{Mn_5\}$ cubane core, which is ligated by all three Keggin fragments. To our knowledge this is the first cubane motif of this kind encapsulated by POM ligands, and it is also

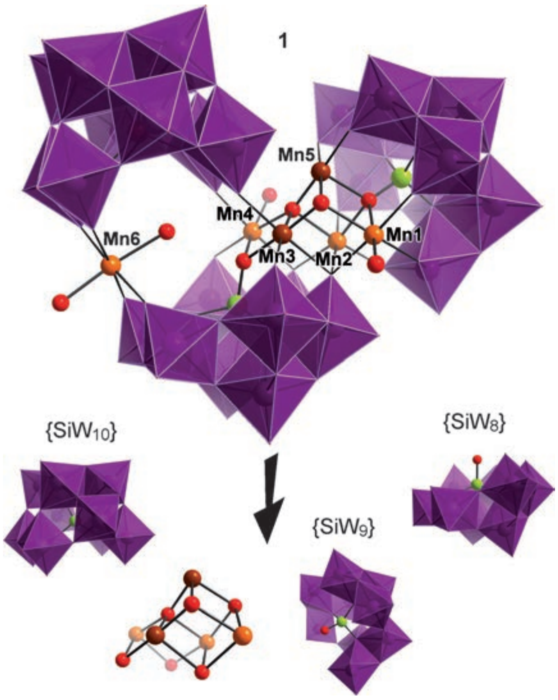

Figure 1. $[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]^{18-}$ (**1a**) showing the three inequivalent silicotungstate Keggin fragments $\{SiW_8\}$, $\{SiW_9\}$, and $\{SiW_{10}\}$ and the appended $\{Mn_4O_4\}$ cubane core with an appended "pendant" Mn ion very similar to that found in the structure of photosystem II. WO_6 purple polyhedra, Mn orange and brown, Si green, O red. Potassium and solvent water molecules have been omitted.

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the first time that all three {B-β-SiW_8O_{31}}, {B-β-SiW_9O_{34}}, and {γ-$SiW_{10}O_{36}$} (hereafter {SiW_8}, {SiW_9} and {SiW_{10}}) lacunary silicotungstates have been observed together, coordinated within one discrete molecule.

The divacant silicodecatungstate [γ-$SiW_{10}O_{36}$]$^{8-}$ starting material has variable stability in aqueous media and undergoes structural transformations at both low and high pH values.[12] This complex thus serves as useful verification of postulated isomerization mechanisms of {SiW_{10}} in aqueous solution.[13] The rearrangement of lacunary Keggin {SiW_{10}} in aqueous solution yields both {SiW_8} and {SiW_9}, effectively giving access to a dynamic library of three cluster anions. In recent years, one to three of such species have been linked together with transition metals to give sandwich- and trimeric-type species,[13,14] but these three anionic lacunary Keggin species have not yet been observed together in union. Since the starting polyanion for the reaction is the divacant lacunary Keggin species {γ-SiW_{10}}, it appears that the formation of **1** may involve an initial loss of two tungsten oxo units (converting {γ-SiW_{10}} into {β-SiW_8}) and subsequent gain of one tungsten oxo unit ({β-SiW_8} to {β-SiW_9}) to generate all three Keggin fragments in solution.[13] From a synthetic point of view this certainly seems to be the case, since using alternative anions such as [α-SiW_9O_{34}]$^{10-}$ or [β$_2$-$SiW_{11}O_{39}$]$^{8-}$, including mixtures thereof, failed to produce **1** and resulted only in common POM sandwich motifs or Mn-substituted Keggin clusters. Finally, Mn inserts into the vacancies of the lacunary polyanions, thereby stabilizing these highly charged species in solution. The presence of Mn^{III} centers in **1** results from air oxidation of Mn^{II} to Mn^{III} by vigorous stirring of the alkaline Mn^{II} POM solution. In this way it can be postulated that various transition-metal-substituted lacunary species occur in solution, but specific synthetic conditions trap all three such transition-metal-substituted POM motifs in one compound.

Structurally, the {SiW_{10}}–{SiW_8} linking in **1** is highly reminiscent of the [M(H_2O)$^{2-}$(γ-$SiW_{10}O_{35}$)$_2$]$^{10-}$ dimer,[14a] while the {SiW_9} fragment can be considered a β-Keggin isomer substituted by three manganese ions. The {B-β-SiW_9O_{34}} fragment has been well described in the recent literature, particularly in relation to sandwich-type polyanions.[15] The {Mn_5} fragment can be regarded as a {Mn_4O_4} cubane core attached to a Mn^{II} atom through one of the oxygen atoms of the cube. The entire {Mn_5} unit consists of three Mn^{II} and two Mn^{III} centers, where three μ$_3$-O^{2-} ions, two μ$_2$-O^{2-} ions, and one μ$_4$-O^{2-} ion act as ligands. In its simplest form, the extended cubane unit can therefore be regarded as a {Mn_5O_6} core. On the basis of bond valence sum (BVS)[16] and elemental analysis, the five manganese centers have been assigned to three Mn^{II} and two Mn^{III} (Tables S1–S5 in the Supporting Information), and these details have been confirmed by redox titrations and electrochemical studies (see the Supporting Information). Also, the {Mn_5O_6} cluster can be more accurately described as a [Mn$^{III}_2$Mn$^{II}_2$O$_4$]$^{2+}$ cubane, whereby the Mn1, Mn2, Mn3, and Mn5 are connected to the fifth manganese(II) atom (Mn4) through oxygen atom O107 from the cubane and oxygen atoms O2 and O15 of the {SiW_9} cluster. A representation of the fully coordinated Mn centers of the {Mn_5O_6} core is shown in Figure 2. Intriguingly, this {Mn_4O_4} cuboidal moiety formed by Mn1, Mn2, Mn3, and Mn5, is reminiscent of the proposed structures for active site of PSII[6] (see Figures S3 and S4 in the Supporting Information). In fact, the calcium(II) center in the {Mn_3O_4Ca} cubane present in PSII imposes a more significant distortion of the cubane owing to the longer Ca–O bond length of approximately 2.55 Å.

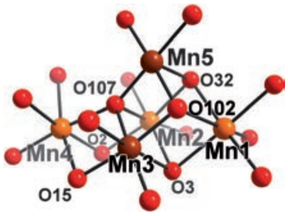

Figure 2. The {Mn_5O_6} cubane core of **1**, described as an appended [Mn$^{III}_2$Mn$^{II}_2$O$_4$]$^{2+}$ cubane where Mn1, Mn2, Mn3, Mn5 are connected to manganese atom Mn4 through oxygen atom O107 from the cube and oxygen atoms O2 and O15 of the {SiW_9} cluster. Mn^{II} orange, Mn^{III} brown, O red.

The redox behavior of **1** was studied in aqueous solution. Figure 3 shows the main characteristic peaks associated with W and Mn redox couples of **1** between +1.500 and −1.000 V versus Ag/AgCl at a scan rate of 20 mV s^{-1}. At this scan rate and scanning towards the negative region of potential values, the reduction of W centers occurred in three separated steps, with the corresponding $E_{1/2}$ peak potentials located at −0.514, −0.629, and −0.785 V (vs. Ag/AgCl).[17] At the positive region of potential values, two quasi-reversible oxidation peaks were observed, with the $E_{1/2}$ peak potentials located at +0.575 and +0.986 V.

The simultaneous oxidation of all four Mn^{II} centers can be observed first, with subsequent oxidation of Mn^{III} to Mn^{IV}. The characteristic sharpness of the oxidation wave is indicative of the presence of a surface-active species.[18] At different scan rates we found that the W-centered and the first Mn-centered peak currents were proportional to the square root

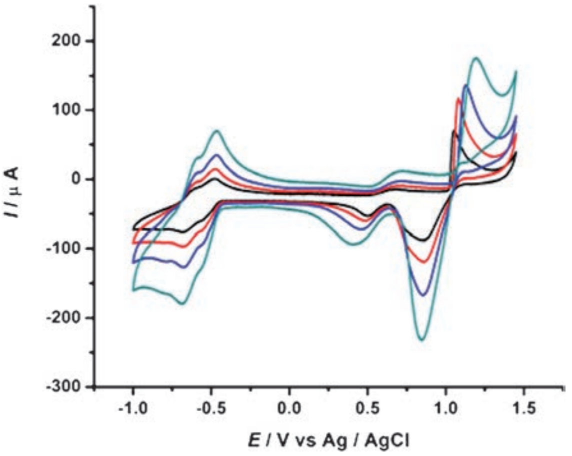

Figure 3. Cyclic voltammograms of **1** (2×10^{-3} M) in a pH 3.2 solution (1 M Na_2SO_4/H_2SO_4) at scan rates (from inner to outer) of 5, 10, 20, and 50 mV s^{-1}. The working electrode was glassy carbon (1.5 mm) and the reference electrode was Ag/AgCl.

of the scan rate, thus indicating a diffusion-controlled process, while the second Mn-centered peak currents were found to be proportional to the scan rate, thus indicating a surface-controlled process specifically at low values of scan rate (5–20 $mV\,s^{-1}$). Furthermore, the electrochemical behavior of **1** was studied by solid-state electrochemistry measurements (see the Supporting Information). In these investigations, we observed a slight shift towards negative potential values; however, the form of the W waves remained the same and is commensurate with the solution-state studies, thus indicating the stability of the material in solution.

This unexpected yet apparent stability of **1** in solution required further verification. We conducted ESI-MS experiments, which revealed that the complex is indeed exceptionally stable in solution. Single crystals of **1** were dissolved in a minimum amount of water, and a few drops of this aqueous solution were mixed with approximately 5 mL acetonitrile. This solvent mixture enabled us to transfer the water-soluble species into the mass spectrometer by electrospray ionization. Consequently, gas-phase studies confirmed that **1** retained its integrity in solution (see Figure 4), and the observed envelopes can be assigned to $\{Mn_6O_2(H_2O)_4(SiW_8O_{31})(SiW_9O_{34})(SiW_{10}O_{36})\}^{x-}$ (**1a**). Critical analysis of the spectra allowed us to accurately assign three envelopes of differently charged species of **1**, namely −4, −5, and −6. These envelopes were assigned to $\{Mn_2^{III}Mn_4^{II}O_2(H_2O)_4(SiW_8O_{31})(SiW_9O_{34})(SiW_{10}O_{36})K_5H_9(H_2O)_{12}\}^{4-}$ (*m/z* 1879.44), $\{Mn_2^{III}Mn_4^{II}O_2(H_2O)_4(SiW_8O_{31})(SiW_9O_{34})(SiW_{10}O_{36})K_5H_8(H_2O)_5\}^{5-}$ (*m/z* 1478.13), and $\{Mn_2^{III}Mn_4^{II}O_2(H_2O)_4(SiW_8O_{31})(SiW_9O_{34})(SiW_{10}O_{36})K_4H_8(H_2O)_4\}^{6-}$ (*m/z* 1222.28), respectively. In addition, the fully reduced Mn^{II} version of **1**, $\{Mn_6^{II}O_2(H_2O)_4(SiW_8O_{31})(SiW_9O_{34})(SiW_{10}O_{36})K_5H_{10}(H_2O)_5\}^{5-}$, gave an envelope centered at *m/z* 1478.54. Examples of reductions and/or oxidations of transition metals in the gas phase have been reported by our group and others.[19]

Interestingly, a triplet of envelopes centered at *m/z* 1715.50, 1725.00, and 1734.48 can be assigned to the fully oxidized version of isostructural species, $\{Mn_6^{III}O_2(H_2O)_4(SiW_8O_{31})_2(SiW_9O_{34})KH_{11}(H_2O)_9\}^{4-}$, $\{Mn_6^{III}O_2(H_2O)_4(SiW_8O_{31})_2(SiW_9O_{34})K_2H_{10}(H_2O)_9\}^{4-}$, and $\{Mn_6^{III}O_2(H_2O)_4(SiW_8O_{31})_2(SiW_9O_{34})K_3H_9(H_2O)_9\}^{4-}$, where the $\{W_{10}\}$ lobe has reorganized, losing two W centers, to give the $\{W_8\}$ lacunary Keggin unit. In a similar manner, the envelope centered at *m/z* 1659.51 can be assigned to $\{Mn_6^{II}O_2(H_2O)_4(SiW_8O_{31})_3K_2H_{16}(H_2O)_7\}^{4-}$, where all the W lobes have been reorganized to the $\{SiW_8\}$ anion. This observation hints at the possibility of gaining important information regarding the speciation mechanism and the relative stabilities of the system under investigation using ESI-MS. It is unclear whether this isomerization occurs solely under the conditions employed for these experiments or whether the cluster in fact rearranges readily in solution. Such observations also indicate that the thermodynamic and kinetic stabilities of all the possible isostructural species constructed from any of the $\{SiW_8\}$, $\{SiW_9\}$, and $\{SiW_{10}\}$ fragments have very similar ground-state energies. This highly complex speciation in the gas phase appears to substantiate our initial experimental difficulties in consistently isolating compound **1**. Theoretical calculations which could potentially provide additional confirmation of the aforementioned suggestion are currently underway.

Not only is this compound solution-stable, crystals of **1** are also suitable to form emergent POM-based microtubular structures, which can be observed using optical microscopy, when the compound is immersed in a solution of cations as described previously.[20] Immersion of a single crystal of **1** in a droplet of dilute 6 mmol dihydroimidazophenanthridinium (DIP)[21] in water results in the formation of microtubes after approximately 30 seconds. Tubes grew rapidly with little directional stability and had overall diameters of 1–2 μm (see Figure 5). Given the relatively high water solubility of the crystal, this type of rapid growth is expected. Since the tube growth direction can be controlled, these tubular systems could be used to form complex patterns for catalytic device manufacture, especially if photoactive cations are employed.[22]

To conclude, we have synthesized an unprecedented trimeric POM cluster $K_{18}[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]\cdot 40\,H_2O$ (**1**). The presence of an embedded mixed-valence $\{Mn_4O_4\}$ cubane core with an appended Mn ion and the lacunary Keggin fragments $\{SiW_8\}$, $\{SiW_9\}$, and $\{SiW_{10}\}$ in one discrete molecule are unique observations. Contrary to the parent polyanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, **1a** retains its structural integrity in solution

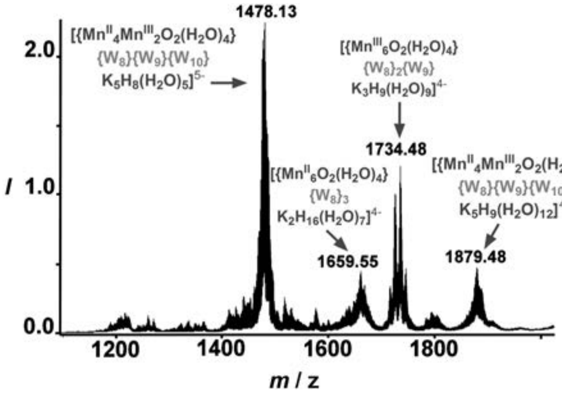

Figure 4. ESI mass spectra of the H_2O/CH_3CN solution of **1**. The envelopes of compound **1** and re-organized isostructural species were observed. $\{W_8\} = \{SiW_8O_{31}\}$, $\{W_9\} = \{SiW_9O_{34}\}$, and $\{W_{10}\} = \{SiW_{10}O_{36}\}$.

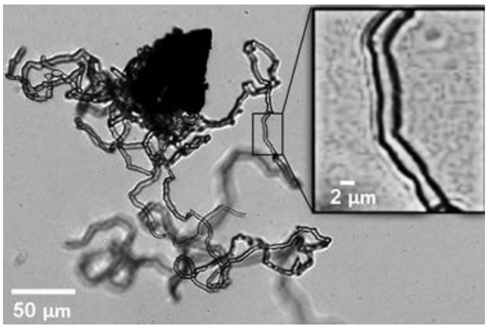

Figure 5. Image of microtubule growth (ca. 2 μm in diameter) from a single crystal of **1** after addition of a 6 mM aqueous solution of DIP.[21] The wandering pattern of growth arises from the relatively high solubility of **1** in the DIP solution.

as observed by ESI-MS and electrochemistry, and crystals of the cluster compound are robust enough to be refabricated from crystalline form into tubular architectures. The ability to fabricate tubes from **1** opens the way for the development of device architectures based upon electronically interesting POMs.

Experimental Section

Full experimental, crystallographic, electrochemistry, magnetism, and structural details are described in the Supporting Information.

Synthesis of **1**: $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12\,H_2O$ (1.45 g, 0.5 mmol) was added to H_2O (25 mL) in a 100 mL beaker and warmed to 40 °C while the mixture was stirred. To monitor the temperature, a temperature probe was placed through the lid of a 14 mL vial filled with 10 mL water (also stirred magnetically). When the temperature reached approximately 38 °C, $MnCl_2$ (anhydrous, 98% beads, 0.13 g, 1.0 mmol) was added. The solution turned yellow and the pH value dropped slightly below pH 7.0. 2 M K_2CO_3 (aq) was used to raise the pH value to just below 8.40 (the solution became noticeably darker with each addition, turning from yellow to orange/brown). Importantly, the 2 M K_2CO_3 must be added dropwise with the next addition only when the pH value starts to fall. It typically takes less than 1 mL to reach pH 8.40. At pH 8.40, 0.2 M K_2CO_3 (aq) was used to give more accurate control of the pH value. The pH value was kept between 8.40 and 8.50 for 40 min—this required adding a drop of 0.2 M K_2CO_3 (aq) approximately every 30 seconds. Over the 40 min period the solution turned dark brown. After 40 min, the pH meter was removed and the solution was stirred at 40 °C for four hours. After this period, the beaker was removed from the hot plate and left to cool to room temperature. A brown precipitate formed upon cooling, which was removed by centrifugation (5 min at 4400 rpm). The resulting dark brown/orange solution was decanted into a 50 mL wide-neck conical flask and left overnight in a temperature-controlled crystallization room (18 °C). The next day the flask contained “islands” of very dark single crystals. Yield = 0.40 g, 0.047 mmol (34.8% based on W). Characteristic IR spectroscopy bands (cm^{-1}): 3528(b), 1620(s), 947(s), 852(s), 785(s), 673(s), 457(w), 430(w). UV band: $\lambda = 253$ nm, $\varepsilon = 7.14 \times 10^{-4}\,\text{M}^{-1}\,cm^{-1}$. Elemental analysis for the partially dehydrated material $H_8K_{18}Mn_6O_{107}Si_3W_{27}$, MW = 7801.33 $g\,mol^{-1}$ (crystallized solvent water molecules lost; %) calculated: Mn 4.23, W 63.67, K 8.99; found Mn 4.08, W 63.28, K 9.12. TGA water loss from 25 to 300 °C (%) calculated: 8.72, found 8.70.

Crystallographic data and structure refinement for **1**: $H_{82}K_{18}Mn_6O_{147}Si_3W_{27}$, MW = 8467.49 $g\,mol^{-1}$, orange block crystal, 0.2 × 0.1 × 0.04 mm3. Triclinic, space group $P\bar{1}$, $a = 17.0465(6)$, $b = 17.1916(4)$, $c = 24.3736(7)$ Å, $\alpha = 95.627(2)$, $\beta = 102.071(3)$, $\gamma = 93.364(2)°$, $V = 6928.2(4)$ Å^3, $Z = 2$, $\rho = 4.085\,g\,cm^{-3}$, λ (MoK_α) = 0.71073 Å, 66283 reflections measured, 22260 unique ($R_{int} = 0.0418$), which were used in all calculations. Final $R1 = 0.0443$ and $wR2 = 0.1248$ (all data). CDS-422945 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from FIZ Karlsruhe via http://www.fiz-karlsruhe.de/icsd.html.

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