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Temperature-Resolved Assembly of a Series of the Largest Scandium-Containing Polyoxotungstates

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We report the temperature-resolved assembly of a sereis of novel nanoscale hexmeric Sc-containing polyoxometalates of $\{Sb_6Sc_{11}W_{60}\}$, $\{Sb_8Sc_7W_{60}\}$, and $\{Sb_8Sc_6W_{60}\}$. These compounds exhibit the largest Sc-containing polyoxotungstates and contain the largest number of Sc^{3+} ions of any polyoxotungstates reported to date.

Due to diverse structures, compositions, and properties, there has long been an interest in introducing transition metals (TMs) into polyoxometalates (POMs) to construct TM-containing POM materials,¹⁻⁶ especially for the multi-TM-containing POMs. Up to now, most 3d TMs including Ti⁴⁺, Mn^{2+/3+}, Fe^{2+/3+}, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺ have been successfully incorporated into POMs to form a vast library of TM-containing POMs with remarkable structural diversity (e.g., from monomeric, dimeric to multimeric structures).² What's more, a diversity of intriguing multi-TM-containing POMs with dozens of 3d TM centers have been obtained. Some typical examples include multimeric ${Mn_{40}P_{32}W_{224}O_{888}},^{3a}$ cage-lile {Mo₇₂Fe₃₀},^{3b} tetrameric {[Co4(OH)3PO4]4(PW9O34)4]},3c octameric {[Ni6(Tris)- $(en)_{3}(BTC)_{1.5}(PW_{9}O_{34})]_{8}$ and $\{Cu_{25.5}O_{8}(Nb_{7}O_{22})_{8}\},^{3d,e}$ which contain the largest number of Mn, Fe, Co, Ni and Cu centers in molecular POMs, respectively.

In comparison, the introduction of 3d Sc³⁺ into POMs remains largely unexplored probably owing to the relative difficulty in crystallization of Sc-based complexes. To date, the known Sccontaining POMs are very rare. In polyoxotungstate (POT) chemistry, only a dimeric Sc-containing POT constructed from two mono-metal-containing {Sc(H₂O)(α -SiW₁₁O₃₉)} clusters has been reported to our knowledge.⁷ It has been shown that Scbased composite materials, such as Sc-organic frameworks and Sc-containing alloys, have attractive potential applications in the areas of heterogeneous catalysis, gas adsorption, separation, ferroelectric relaxors, and ceramics.⁸ The integration of Sc³⁺ ions with POMs could afford new types of Sc-based materials with novel structures and interesting properties. There is thus a strong impetus for us to explore the Sc-containing POM chemistry.

Herein, we report the first series of hexameric Sc-containing POTs, namely 11-Sc-containing Na₄K₅H₁₈[Sc₁₁W₆O₂₀(OH)₂(-H₂O)₁₆(SbW₉O₃₃)₆]·18H₂O (Na₄K₅H₁₈[1]), 7-Sc-containing Na₆K₂-H₂₃[Sc₇Sb₂W₆O₂₀(H₂O)₈(SbW₉O₃₃)₆]·16H₂O (Na₆K₂H₂₃[2]), and 6-Sc-containing Na₅K₁₀H₁₇[Sc₆Sb₂W₆O₁₉(H₂O)₆(SbW₉O₃₃)₆]·48H₂O (Na₅K₁₀H₁₇[3]). These novel POTs not only are the largest Sc-containing POTs, but also contain the largest number of Sc centers of any POTs to date. Interestingly, the giant polyanions 1, 2, and 3 were obtained from the same reaction at different temperatures of 100°C, room temperature (RT, about 30 °C), and 180 °C, respectively. Moreover, a rare structural transformation from chair-like configuration to boat-like configuration between nanosized POM hexamers can be found.



Figure 1. a)-c) Structures of $\{Sc_5(SbW_9)_3\}$, $\{ScW_6\}$, and polyanion 1, respectively. Tungstate octahedra: red/yellow.

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Figure 2. a)-c) Structures of $\{Sc_{11}W_6(OH)_2O_{20}\}$, $\{Sc_7Sb_2W_6O_{16}\}$, and $\{Sc_6Sb_2W_6O_{15}\}$, respectively.

All polyoxoanions **1-3** crystallized in the triclinic space group *P*-1 and as mixed sodium-potassium salts, whose phase purities have been confirmed by PXRD measurements except that **1** is some impure (Figures S1-3).

To begin with, polyoxoanion 1 is the largest Sc-containing POT with 60 W, 11 Sc, and 6 Sb centers, which was obtained from the hydrothermal reaction of $Na_9[B-\alpha-Sb^{III}W_9O_{33}]$,⁸ ScCl₃·6H₂O, and KCl in NaAc/HAc buffer solution (pH=4.8) at 100 °C. Polyanion 1 has a centrosymmetric structure built from two identical ${Sc_5(Sb^{III}W_9)_3}$ trimers joined by a ${ScW_6}$ fragment (Figure 1). The $\{Sc_5(SbW_9)_3\}$ trimer is composed of three trilacunary {SbW₉O₃₃} clusters interlinked by three Sc³⁺ cations into a triangular ring (Figure 1a), which encapsulates an additional binuclear {Sc₂(OH)} unit onto the vacancies of one of its three $\{SbW_9O_{33}\}$ clusters. Additionally, as shown in Figure 1b, the {ScW₆} linker consists of two V-shaped trinuclear W₃O₁₀ units with three corner-sharing WO₆ octahedra, which are C_i -symmetry-related by a central $[Sc(H_2O)_2]^{3+}$ cation. The 11 Sc³⁺ cations in polyanion **1** are all 6-coordinate octahedral configurations but can be divided into three groups in accord with their positions in 1. The first group includes the 6 Sc³⁺ linkers between adjacent {SbW9O33} clusters within the two ${Sc_5(SbW_9)_3}$ trimers, each of which coordinates with four μ -O atoms from two {SbW $_9O_{33}$ } clusters, one μ -O atom from the central {ScW₆} unit, and one terminal water ligand. The two {Sc₂(OH)} dimers occupying at the vacant sites of two {SbW₉O₃₃} clusters form the second group, in which each Sc³⁺ cation bonds to one μ -OH group, one μ -O atom from a {SbW₉O₃₃} cluster, two μ -O atoms from the central {ScW₆} unit, and two terminal water ligands. The third group is the Sc3+ cation located at the inversion center of 1, whose octahedral configuration is completed by four μ -O atoms from four WO₆ octahedra and two terminal water ligands. All the Sc-O and Sc- H_2O bond lengths are in the ranges of 1.904(1)-2.259(1) Å and 2.011(1)-2.403(1) Å, respectively.

Notably, without regard to the {SbW₉O₃₃} clusters in **1**, the remainder 17 metals including 11 Sc³⁺ and six W⁶⁺ cations can be interconnected by 22 μ -O bridges to give rise to a unique 17-nuclearity bimetal-oxide core {Sc₁₁W₆(OH)₂O₂₀} instead of spatially separated or isolated each other (Figure 2a). And thus, the nanosized polyanion **1** with dimensions of 3.0 × 1.9 × 1.4 nm³ (atom-to-atom distance) also can be described as a hexamer with chair-like conformation constructed from six trilacunary {SbW₉O₃₃} clusters hold together by a heterometal core {Sc₁₁W₆(OH)₂O₂₀}.



Figure 3. a)-d) Structures of 1, 2, 3, $\{Sc_3Sb_2(SbW_9)_3\}$, and $\{W_6O_7\}$ core, respectively. Tungstate octahedra: red/yellow.

Fascinatingly, the reaction of 1 can yield different hexameric Sc-containing POTs at different reaction temperatures. If reaction temperature is decreased to 30 °C, a new hexameric polyanion 2 can be isolated. While if reaction temperature is increased to 180 °C, the third kind of hexameric polyanion 3 can be obtained. Crystallographic analyses reveal polyanions 2 and **3** represent the first 7-Sc-containing POT and the first 6-Sccontaining POT, respectively. As shown in Figure 3, structure 2 can be derived from 1 by replacing the two binuclear {Sc₂(OH)} units with two Sb atoms. And thus, similar to 1, compound 2 can be described as a centrosymmetric structure built from two identical trimers of {Sc₃Sb₂(SbW₉)₃} (Figure 3d) joined by a {ScW₆} fragment. Alternatively, structure **2** can also be viewed as a chair-like hexamer formed by six trilacunary {SbW₉O₃₃} clusters joined by a 15-nuclearity trimetal-oxide core $\{Sc_7Sb_2W_6O_{16}\}$ (Figure 2b).

Similar to **2**, polyanion **3** consists of two $\{Sc_3Sb_2(SbW_9)_3\}$ trimers, however, their structures are remarkably different. As shown in Figure 3c, the two trimeric $\{Sc_3Sb_2(SbW_9)_3\}$ subunits in **3** are fused together in a face-to-face manner via a unique belt-like hexanuclear W-O core $\{W_6O_7\}$ to form the hexameric polyanion **3** with a boat-like conformation, which is different from polyanions **1** and **2** with a chair-lie conformation. Further, the belt-like hexanuclear $\{W_6O_7\}$ core is formed by six cornersharing WO₆ octahedra (Figure 3e), differing from the figure-8shaped heptanuclear heterometal-oxide core $\{ScW_6O_8\}$ found in **1** and **2** (Figure 1b). Additionally, the 6-Sc-containing polyanion **3** also can be viewed as a hexameric POM formed by six trilacunary $\{SbW_9O_{33}\}$ clusters linked together by a 14Published on 26 April 2017. Downloaded by Freie Universitaet Berlin on 26/04/2017 13:52:16.

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nuclearity trimetal-oxide core ${Sc_6Sb_2W_6O_{15}}$ instead of ${Sc_{11}W_6(OH)_2O_{20}}$ in 1 and ${Sc_7Sb_2W_6O_{16}}$ in 2 (Figure 2c).

It is worth mentioning that a common feature of polyanions 1-3 is that all of them contain two trimeric fragments of ${Sc_3(SbW_9)_3}$ made up of three ${SbW_9O_{33}}$ clusters bridged by three Sc^{3+} cations (Figure S4), indicating the $\{Sc_3(SbW_9)_3\}$ fragment should be an essential building unit and exist in the reaction solution over the whole reaction temperature range from RT to 180 °C. Fascinatingly, the ${Sc_3(SbW_9)_3}$ fragments can sanwich various multi-nuclearity Sc/W-O cores (such as $\{Sc_5W_6\}$ in 1, $\{ScSb_2W_6\}$ in 2, and $\{W_6\}$ in 3) at different temperatures. Additionally, another common feature in 1-3 is that part of {SbW₉O₃₃} clusters within the {Sc₃(SbW₉)₃} trimer has disordered W₃O₁₃ groups (Figure S5). It has been known that the starting ordered $\{B-\alpha-SbW_9O_{33}\}$ cluster is composed of three corner-sharing W₃O₁₃ groups. While, some W₃O₁₃ groups within 1-3 are found to be disordered, each of which is disordered into two groups (Figure S6).

Temperature-resolved assembly of more than two kinds of crystalline POMs in the temperature range from RT to 200 °C is not common. The syntheses of **1-3** represent a rare temperature-resolved assembly of three types of nanosized POMs in the temperature range of RT to 180 °C. Bond-valence sum calculations show the oxidation states of all the W, Sc, and Sb atoms in **1-3** are +6, +3, and +3,⁹ respectively. To balance the charges, eighteen, twenty-three, and seventeen protons should be added into **1**, **2**, and **3**, respectively. These protons can not be located and are assumed to be delocalized on the overall structures, which are common in POMs.¹⁰

$$R-S-R'+H_2O_2 \xrightarrow{MeCN} R-S-R'+R-S-R'+H_2O_0$$

Scheme 1. Catalytic Oxidation of Thioethers.

Organosulfur compounds such as sulfoxides and sulfones remain a topical interest owing to its widely potential utilities.¹¹ The reported literatures show thioethers can be oxidized by H_2O_2 to produce sulfoxides RR'SO and sulfones RR'SO₂ (Scheme 1),¹² however, the conversion of substrates and selectivity of products RR'SO₂ and RR'SO are low. The conversion and selectivity of the above reactions can be increased by using some metals or metal complexes such as Sc, Ti, and POMs as catalysts,¹³ which triggers us to check if Sc-containing POMs can display excellent catalytic performances in the oxidation reactions of thioethers.

Compound **3** was taken as a representative example for the investigation of the catalytic oxidation of thioethers. Firstly, an initial oxidation reaction of 0.5 mmol methylsulfanyl-benzene (MSB) and 0.5 mmol 30% H_2O_2 in 10 ml MeCN was run to confirm that **3** is an effective catalyst for oxygenation of thioethers by H_2O_2 . And then, a series of experiments were conducted to obtain the optimum reaction conditions. The results showed that 0.5 mmol MSB could be completely converted into sulfone (RR'SO₂) in a 99% yield by refluxing the substrate in 10 ml MeCN with 1.1 mmol 30% H_2O_2 and 2.5 μ mol **3** at 80 °C for 3 h (Tables S1-4).

Entry Substrate Time	Temp Conv	Selectivity
H_2O_2 catalyzed by 3 in MeCN.	DOI: 10.1039/	C7DT00892A
Table 1. Results for oxygenation of	various thioether	s with 30%

Co2 catalyzed by 5 III Mech.					
Entry	Substrate	Time (h)	Temp (°C)	Conv (%) ^a	Selectivity (%) ^b
1°	SCH3	3	80	100	99
2	Voltor S	3	80	100	99
3	SCH3	3	80	100	100
4	O ₂ N-SCH ₃	3	80	99	92
5	Br SCH3	3	80	99	95
6	H ₃ CO SCH ₃	3	80	99	97
7		3	80	97	77
8	\bigcirc	3	80	93	58
9	C s	3	80	Trace	
10	$\$	3	80	100	100

^aThe conversion is based on substrate consumed. ^b Selectivity (%) = sulfone (mol)/(sulfoxide (mol) +sulfone (mol)). ^cReaction conditions: substrate, 0.5 mmol; H₂O₂, 1.1 mmol; solid **3**, 0.25×10⁻² mmol; MeCN, 10 ml.

Further, the catalytic activity of compound 3 was evaluated by a series of H₂O₂-based catalytic oxidation reactions of MSB derivatives under the optimum reaction conditions. In the absence of 3, both conversion of substrates and selectivity of products RR'SO₂/RR'SO of all reactions are low (Table S5). When catalyst 3 was added into the reactions, conversion and selectivity of all reactions were greatly improved. Nevertheless, compound 3 exhibited different catalytic activity for different MSB derivatives. As shown in Table 1, compared with MSB, the introduction of electron-donating groups (e.g., CH₃ and CH₃O in entries 2 and 3) on the aromatic ring of MSB has no effect on the conversion of substrates and the selectivity of products. While, the introduction of electron-withdrawing groups (entries 4-6) leads to a slightly decrease of the conversion and selectivity. Additionally, through the reactions of entries 7-9, it can be found that steric hindrance has a significant effect on the catalytic oxidations of sulfides. With the increase of steric hindrance from entries 7 to 9, the conversion and selectivity decreased rapidly. Except for aryl sulfides, sample 3 also exhibits excellent catalytic activity for the oxidation of alkyl sulfides in high conversion and selectivity (such as the case of entry 10). Compound 3, as a kind of POM, has a strong redox nature, which is responsible for the catalytic activity of the thioether-POM system. A possible mechanism involves the peroxo functions of POM $\mathbf{3}$ by H_2O_2 , followed by an oxygen transfer to thioethers to yield the sulfoxide (SO) and sulfone (SO₂) products.¹⁵

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To confirm the recyclability of the catalyst **3**, the entry 6 worked as an example. Additional substrate and H_2O_2 were added into the reaction mixture when the previous run was completed. The results showed **3** has very good recyclability without an obvious loss of catalytic activity for at least five-run duplicate operations (Table S6), indicating **3** is a potential heterogeneous catalyst for the oxidation of thioethers. Moreover, both PXRD patterns and IR spectra confirmed that **3** could maintain its structural integrity after catalytic reaction (Figure S6,7). Finally, reactions of entries **1** and **6** based on using **1** and **2** as catalysts were performed as examples to show they also have good catalytic performance for catalytic oxidation of thioethers (Table S7,8).

In summary, it is rare to obtain a series of Sc-containing POM hexamers that can be synthesized sequentially as a function of temperature by using the same reaction. These compounds are by far the largest Sc-containing POTs. Interestingly, a structure transformation between nanoclusters from chair-like conformation to boat-like conformation can be observed, which is reminiscent of the chair/boat-isomerization of cyclohexane. The successful syntheses of **1-3** demonstrate the posibility of the inroduction of multi-Sc cations (\geq 3) into polyoxotungstates, which unveils the potential for further development of Sc-containing POM chmeistry.

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Graphical contents

Temperature-Resolved Assembly of a Series of the Largest

Scandium-Substituted Polyoxometalates

Zhen-Wen Cai, Tao Yang, Yan-Jie Qi, Xin-Xiong Li, and Shou-Tian Zheng*



The first series of hexameric scandium-substituted polyoxometalates have been isolated from the same reaction by a temperature-resolved crystallization process, which represent the largest scandium-containing polyoxometalates with the largest number of scandium cations.