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Cryst. Growth Des., Just Accepted Manuscript • DOI: 10.1021/acs.cgd.8b01474 • Publication Date (Web): 30 Nov 2018

Downloaded from http://pubs.acs.org on December 1, 2018

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A New Hepta-Nuclear Ti-Oxo-Cluster-Substituted Tungstoantimonate and Its Catalytic Oxidation of Thioethers

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Dedicated to Professor Xintao Wu on the occasion of his 80th birthday

ABSTRACT: A neoteric hepta-nuclear Ti-oxo-cluster substituted tetrameric tungstoantimonate $[H_2N(CH_3)_2]_{22}Na_{18}{Ti_7O_6(SbW_9O_{33})_4}_2\cdot124H_2O$ (1) has hydrothermally been synthesized and tested by single-cryatal/powder X-ray diffraction, IR spectrum, and thermal analysis. The glamorous feature of this tetrameric polyoxoanion is an uncommon hepta-nuclear Ti-oxo-cluster octahedron $[Ti_7O_6]^{16+}$ enclosed in four $[B-\alpha-SbW_9O_{33}]^{9-}$ building units. As a heterogeneous catalyst, the investigation on catalytic oxidation with



 H_2O_2 for multiple thioethers indicated that 1 possesses high conversion and remarkable selectivity. Additionally, 1 exhibits good stability and excellent recyclability.

As extremely interesting nanoscale polynuclear metal-oxygen Clusters polyoxometalates (POMs) have attracted great attention mainly due to two aspects: 1) architectural aesthetic appreciation (metalcentered polyhedral connections by sharing angles, edges or faces can polymerize into a variety of configurations); 2) potential application performance (in catalysis, electrochemistry, magnetism and material science etc).¹⁻⁴ In the huge family of POMs, tungstoantimonates (TAs), an significant subfamily, has tremendous variety of constructions and properties. In addition, vacant TAs can serve as multidentate inorganic ligands to combine interesting organic moieties, functional metallic centers or metal-oxygen clusters (such as p, d, and f blocks).²⁻⁸

Ti-oxo-clusters (TOCs) as one of the most important types of cluster materials have a surge in recent reports on chemical, energy and environmental sciences.9 Nevertheless, the majority of relevant reports are mainly concentrated on organic TOCs, in which the N, O atoms of the organic ligands are beneficial to structural stability and construction. Since Ti⁴⁺ ion is susceptible to hydrolyze, inorganic aqueous TOCs are difficult to obtain. Using vacant POMs as multidentate inorganic ligands to stabilize TOCs and further make TOCs-substituted POMs are full of meaning and challenge,¹⁰ which is due to the terminal hydroxyl oxygens of the Ti atoms easily form Ti-O-Ti bonds by intermolecular dehydration, therefore, Ti-substituted POMs are prone to generate oligomeric constructions.¹¹ Ti-containing POMs as an important area have drawn immense attention in the past few decades.¹² Some examples of Ti-containing polyoxotungstates (POTs) have been unremittingly discovered. The first Ti-containing POT [CITiW₁₁PO₃₉]⁴⁻ corresponding to a mono-Ti substituted tungstophosphate, was reported in 1983 by Knoth et al.¹³ In 1993, Finke and co-workers reported a hexa-nuclear TOC-sandwiched silicotungstate [Si₂W₁₈Ti₆O₇₇]¹⁴⁻¹⁴ Kortz and co-workers made some great achievements of Ti-substituted

vacant Keggin by aqueous solution method, for example, a cyclic tetrameric silicotungstate $[(Ti_2SiW_{10}O_{39})_4]^{24}$ built by four $[\beta$ -Ti₂SiW₁₀O₃₉]⁶⁻ fragments via Ti-O-Ti linkages,15 two cyclic Ti₉-/T₁₀-based trimers of $[Ti_{9}(PO_{4})(PW_{9}O_{38})_{3}]^{18-/}[Ti_{10}(H_{2}O)_{3}(SiW_{9}O_{37}OH)_{3}]^{17-}$ with three Ti₃oxo-cluster substituted Keggin units linked by three Ti-O-Ti bonds and a capping group,¹⁶ a Ti₂-containing sandwiched arsenotungstate¹⁷ as well as Ti₇-oxo-cluster-centred arsenotungstate а [Ti₆(TiO₆)(AsW₉O₃₃)₄]^{20-.18} Nomiya et al. reported some Ti-substituted architectures, such as two oxalic acid modification tungstophosphates $[Ti_{2}(OH)_{2}(ox)_{2}OPW_{11}O_{39}]^{7-}$ and $[Ti_{4}(ox)_{4}(H_{2}O)_{4}O_{3}PW_{10}O_{37}]^{7-}, 19-20$ and several multi-core Ti-oxo- cluster-substituted Dawson tetrameric/trimeric POTs { $[Ti(OH)_3]_4Cl-(P_2W_{15}Ti_3O_{62})_4$ }⁴⁵⁻, $[(NH_4)(P_2W_{15}Ti_3O_{60})_4]^{35-}$, $[Ca_7(CO_3)(OH)(H_2O)_{18}\text{-} Ca(H_2O)_3(P_2W_{15}Ti_3\ O_{61})_3]^{19-\underbrace{21-23}}\ Cronin\ et\ al.$ reported two Ti-embedded sandwiched POTs [TiO(SbW9O33)2]16- and [Ti₄(H₂O)₁₀(AsTiW₈O₃₃)₂]⁶⁻ in 2010.²⁴ Li and co-workers made two Ti-substituted organic-inorganic hybrid POTs in 2015.25

It is quite clear that most of the previous literature about Ti-containing POMs were synthesized by conventional aqueous solution at ambient temperature. Furthermore, the configurations of TOC-containing TAs have been reported rarely. Herein, a novel hepta-nuclear-TOC-substituted POT, $[H_2N(CH_3)_2]_{22}Na_{18}{Ti_7O_6(SbW_9O_{33})_4}_2\cdot124H_2O$ (1) has been made, which is first Ti₇-oxo-cluster-substituted TA tetramer built by four trivacant Keggin $[B-\alpha$ -SbW₉O₃₃]⁹⁻ fragments and an octahedronal [Ti₇O₆]¹⁶⁺ cluster.

Compound 1 was hydrothermally made in the molar ratio of $Na_9[B-\alpha-SbW_9O_{33}]$ ·19.5H₂O, Na_2WO_4 ·2H₂O, $[H_2N(CH_3)_2]$ ·Cl, Li₂CO₃ and TiOSO₄ is 1.1:1.0:8.1:5.6:2.0. It should be particularly pointed out that the WO₄^{2–} plays a subtle role in the experiment, although it does not appear in the final product, the yield of 1 is very low in the absence of WO₄^{2–} anion. Additionally, when the usage amount of WO₄^{2–} anions is higher than 0.500 g, it is liable to gain the isopolytungstate. Furthermore, the amount of precursor is a vital factor: the usage amount in the range

of 1.700–2.300 g is favor to the formation of **1**. Finally, the usage amount of $TiOSO_4$ also has a great influence on the experiment, which is beneficial to form **1** in the range of 0.180–0.240 g, and the optimal dosage is 0.198 g. Apart from aforementioned usage amount aspects, the pH is also an important factor that must be taken into consideration in the reaction system for the formation of product. It is difficult to get **1** when the pH is higher than 4.5 or lower than 3.6, and the optimum acidity is 4.0. Here, we control the pH of the reaction system by introducing Li_2CO_3 and adding diluted HCl. The pH of after reaction is 4.4.



Figure 1. (a) The TA polyoxoanion of **1a**. (b) The simplified architecture of **1a**. (c) The hepta-nuclear-TOC $[Ti_7O_6]^{16+}$ fragment. (d) The simplified architecture $[Ti_7O_6]^{16+}$. Color codes: WO₆: red; TiO₅/TiO₆/Ti⁴⁺: bright yellow; antimony: bright green. A: -1-*x*+*y*, -2-*x*, *z*. B:-2-*y*, -1+*x*-*y*, *z*.

The structural analysis demonstrates that 1 crystallizes in the trigonal space group R-3m and the molecular structure has two extraordinary tetrameric polyoxoanions { $Ti_7O_6(B-\alpha-SbW_9O_{33})_4$ } (1a, Figure 1a), 22 [H₂N(CH₃)₂]⁺, 18 Na⁺ and 124 H₂O. BVS calculation²⁶ reveals that the W, Sb and Ti atoms are in the +6, +3 and +4 oxidation states, respectively (Table S2). The tetrameric 1a consists of an uncommon Ti7-oxo-cluster and four [B-a-SbW9O33]9- fragments and this heptanuclear TOC [Ti₇O₆]¹⁶⁺ is packed into four trivacant fragments, in which four $[B-\alpha-SbW_9O_{33}]^{9-}$ fragments are evenly distributed around the octahedronal [Ti₇O₆]¹⁶⁺ (Figure 1b) and each [B-α-SbW₉O₃₃]⁹⁻ fragment is linked to three pent-coordinate TiO₅ groups of $[Ti_7O_6]^{16+}$ via six μ -O atoms. In addition, in [B-α-SbW9O33]9- fragment the W-O distances are in the range of 1.699(17)-2.38(2) Å, and the Sb-O bond lengths vary from 1.974(18) to 1.999(17) Å. In $[Ti_7O_6]^{16+}$, although three Ti⁴⁺ cations are unique, only show two coordination modes, a hexa-coordinate octahedron and a pent-coordinate tetragonal pyramid (Figure 1c). The central Ti3 atom shows hexa-coordinate octahedron, which is linked to six Ti atoms (3 Ti1 and 3 Ti2) situated in the apex of the octahedron via six μ -O atoms (Ti-O: 1.948(17)-1.966(19) Å). The coordination environments of other six pent-coordinate tetragonal pyramid Ti atoms are similar and the apex oxygen atoms of each tetragonal pyramid are both from the center Ti3O₆ [Ti-O: 1.728(19)-1.741(17) Å], and the bottom four μ -O atoms come from two $[B-\alpha$ -SbW₉O₃₃]⁹⁻ fragments [Ti-O: 1.933(14)-1.954(14) Å]. In addition, the length of each side of the octahedronal [Ti₇O₆]¹⁶⁺ cluster is about 5.2 Å, and the distance between the Ti atoms of the six vertices of the octahedron and the central Ti atom is close to 3.7 Å (Figure 1d).



Figure 2. (a), (b) The 2-D network packing and the simplified packing of 1.

Additionally, an interesting feature is that each **1a** anion (simplified as tetrahedron (red color) shown in Figure 2) is linked to surrounding three same ones via three hexa-coordinate Na1⁺ cations, each Na1O₆ octahe- dron connects two **1a** polyanions with apical opposite direction (Figure 2). In the Na1O₆ group, four O atoms are derived from two **1a** clusters and the other two O atoms are from coordination water molecules. Specifically, six Na1⁺ ions and three pairs of **1a** with opposite direction give birth to a ring, and the outer ring diameter is about 47.37 Å, and the inner ring diameter is approximately 14.40 Å (Figure S2).

Selective oxidation of organic thioethers has attracted a topical interest due to the sulfones and sulfoxides owning versatile utilities (biochemistry, chemical industry and medicinal chemistry).²⁷ H₂O₂ is generally considered to be a "green" oxygen donor and is therefore a preferred oxidant in organic oxidation reactions.²⁸ The most fascinating application value of POMs is to act as a catalyst because POMs possess redox properties, flexible acidity and high stability etc.²⁹ Recalling previous reports, in the presence of Ti-containing POMs as a catalyst, organic thioethers can be efficiently oxidized by H₂O₂ to obtain sulfones and sulfoxides.³⁰ In this catalytic experiment, **1** was investigated as a heterogeneous catalyst in the oxidation of various aromatic thioethers by H₂O₂ oxidant under 3 mL acetonitrile solvent (Scheme S1). The products of thioethers oxidation were recognized by GC-MS spectra and the selectivity of sulfoxide and sulfone as well as the conversion of

thioethers was identified by GC spectra (Figure S6,7).

Firstly, methyl phenyl sulfide (MPS) was employed as a substrate to oxidize to acquire methyl phenyl sulfoxide (MPSO) and methyl phenyl sulfone (MPSO₂) in the case of **1** as a catalyst in 3 mL acetonitrile solution. The results exhibited that the substrate was completely disappeared (the conversion was 100 %) and the selectivity of MPSO₂ was 32% at 35°C (Table S3). Under the same conditions, the parallel tests were conducted, exhibiting that the conversion of MPS in the introduction of {SbW₉}, TiOSO₄ and in the absence of catalyst was 97%, 12% and 10% respectively, and the selectivity of MPSO₂ was 20%, 0 and 0 respectively. Hence, parallel test results indicate that compound **1** is an excellent catalyst.

However, under above experimental conditions, the selectivity of MPSO₂ is still relatively low in the presence of compound 1. Therefore, we further optimized the experimental condition by adjusting the reaction temperature. When the reaction temperature up to 50°C, other conditions remained unchanged (2.8 molar ratio for O/S, 1 h reaction time, 1000 molar ratio for S/C and 3mL MeCN), the conversion of MPS and the selectivity of MPSO₂ were both 100% (Table 1, entry 1). In addition, under the same experimental conditions, we also investigated the oxidation catalysis of different aromatic thioethers. We examined the steric hindrance effect, as shown in Table 1 (entries 2-4), when the steric hindrance increased, although the conversions of substrates were still 100%, the selectivity of sulfone was low, 59% (entry 2), 79% (entry 3) and 98% (entry 4). The effect of different substituents on the sulfone product was also taken into account. As shown in Table 1 (entries 5-7), the stronger the electron-withdrawing group, the lower the selectivity. Comparing entry 7 and 8 in Table 1

Table 1. Selective oxidation of various aromatic thioethers to sulfones using catalyst 1 $^{\left[a\right] }$

Entry	Substrate	Time.	Temp.	Cov. ^[b]	Selectivity (%) ^[c]	
		(h)	(°C)	(%)	RR'SO/R'RSO ₂	
1	C s	1	50	100	0	100
2	∩ ^s ⊖	1	50	100	41	59
3	SОН	1	50	100	21	79
4	Const	1	50	100	2	98
5	os	1	50	98	12	88
6	O2N-S	1	50	98	48	52
7	Br — S	1	50	100	21	79
8	Br	1	50	100	92	8
9		1	50	11	55	45

[a] Catalytic conditions: substrate (0.5×10⁻³ mol), the molar ratio of oxidizer and substrate is 2.8, the molar ratio of substrate and catalyst is 1000, MeCN (3 mL), 50°C. [b] Conversion based on substrate consumption and determined by GC-FID using an internal standard technique. [c] The selectivity of sulfones was authenticated by GC-MS. found that the substituent on the aromatic ring occupying the orthoposition resulted in a low selectivity of sulfone. This phenomenon is consistent with the literature.⁶ Finally, under the same reaction conditions, we also studied the catalytic oxidation of benzothiophene. It is clear that the conversion and selectivity of benzothiophene was lower than that of other aromatic thioethers.

Under the above conditions, although the conversion of most aromatic thioethers was higher than 98%, the selectivity was relatively low. We slightly augmented the O/S molar ratio and increased the reaction temperature aiming at optimizing selectivity (Table 2). Here, under the optimal conditions of 60°C, 3 O/S molar ratio, 1 h reaction time, 3 mL acetonitrile and 1000 S/C molar ratio, the conversion of most aromatic thioethers was greater than 99%, and the selectivity of almost all sulfones were 100% (Table 2, entries 1-6). The selectivity of 2-bromothioanisole was still relatively low under above optimal conditions although which was improved. We extended the reaction time for the purpose of increasing the selectivity of 2-bromophenyl methyl sulfone, when which was extended from 1 h to 3 h, the selectivity increased from 41% to 71% (Table 2, entry 7). Similar to the conditions of 2-bromothioanisole, when the reaction time was up to 3 h, the conversion of benzothiophene and the selectivity of sulfone were both above 90% (Table 2, entry 7).

Furthermore, the cyclic test was conducted to evaluate the stability of catalytic performance of **1** during catalytic oxidation of MPS under the same conditions. In this heterogeneous catalytic system, the catalyst was

Table 2. Selective oxidation of various aromatic thioethers to sulfones using catalyst $1\,^{\rm [a]}$

Entry	Substrate	an:	Tarra Cau b Salastinity (9/)(6			
		Time.	Temp.	Cov. ^[0]	Selectivity (%) ^[c]	
		(h)	(°C)	(%)	RR'SO/R'RSO ₂	
1	() ^s ()	1	60	100	0	100
2	S_OH	1	60	100	0	100
3		1	60	100	0	100
4	os	1	60	99	0	100
5	0 ₂ N-S	1	60	100	0	100
6	BrS	1	60	100	0	100
7	Br	1	60	100	59	41
		2		100	45	55
		3		100	29	71
8	$\langle \rangle$	1	60	51	6	94
	× ·	3		92	1	99

[a] Catalytic conditions: substrate $(0.5 \times 10^{-3} \text{ mol})$, the molar ratio of oxidizer and substrate is 3, the molar ratio of substrate and catalyst is 1000, MeCN (3 mL), 60°C. [b] Conversion based on substrate consumption and determined by GC-FID using an internal standard technique. [c] The selectivity of sulfones was authenticated by GC-MS.

collected by filtration at the end of each experiment, and then reused for

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Figure 3. Recycling of the catalytic system for the oxidation of MPS at 50°C, 2.8 O/S molar ratio.

the next catalytic oxidation of MPS. In these five cycles of experiments, the substrates were completely disappeared (100% conversion) and the selectivity of MPSO₂ was slightly reduced for the fifth time (Figure 3). IR spectrum after the cycle test was well consistent with that of **1** (Figure S8), demonstrating that **1** does not change after the catalytic reaction and has a good stability.

CONCLUSIONS

In summary, a novel Ti₇-oxo-cluster-substituted TA has been prepared, in which the hepta-nuclear TOC, $[Ti_7O_6]^{16+}$, connects four $[B-\alpha$ - SbW₉O₃₃]⁹⁻ fragments via 24 μ -O atoms. Interestingly, 6 Na⁺ cations and 6 polyanions join each other to give birth to a ring. To acquire further insight into the thermal stability of **1**, IR spectra at different temperatures were recorded, indicating that **1** is stable below 400°C. Additionally, we used **1** as a catalyst to carry out oxidation catalysis tests on different aromatic thioethers, showing the most aromatic thioethers' conversions and sulfone selectivities are 100% under the conditions of 3 O/S molar ratio, 1000 S/C molar ratio, 1 h reaction time, 60°C reaction temperature and 3 mL acetonitrile solvent. With regard to the more difficult oxidation catalysis of benzothiophene and 2-bromothioanisole, we have also obtained satisfactory catalytic efficiency and conversion by lengthening the reaction time.

ASSOCIATED CONTENT

Supporting Information

PXRD patterns, IR spectra, the related structure figures, TG curve, crystallographic data and structure refinements for 1 and the related catalytic experiments of 1.

Accession Codes

1869713 for 1 contains the supplementary crystallographic data for this article.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by the NSFC (no. 21571016, 21831001 and 91122028) and the NSFC for Distinguished Young scholars (no. 20725101).

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