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Hexazirconium- and Hexahafnium-Containing Tungstoarsenates(III) and Their Oxidation Catalysis Properties

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Exploring the interaction of lacunary polyoxometalates (POMs) with Group 4 (Ti, Zr, and Hf) transition-metal ions has been mainly driven by the fact that potential products may serve as oxidation catalysts or even as soluble molecular analogues of known Ti- and Zr-containing heterogeneous catalysts.[1] Bearing in mind that zirconium(IV) and hafnium(IV) can have larger coordination numbers than titanium(IV), the chemistry of the former pair compared to the lighter congener is expected to be different, leading to different structural assemblies. There are significantly fewer reports on Zr/Hf-POMs than Ti-POMs in the literature, and the former can be classified according to the composing lacunary POM fragments as follows: Keggin type ($[PW_{11}O_{39}]^{7-}$, $[SiW_{11}O_{39}]^{8-}$, $[GeW_{11}O_{39}]^{8-}$, $[\beta\text{-}SiW_{10}O_{37}]^{10-}$, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$, $[PW_9O_{34}]^{9-}$, and $[SiW_9O_{34}]^{10-}$),[2] Wells–Dawson type ($[\alpha_2\text{-}P_2W_{17}O_{61}]^{10-}$, $[\alpha\text{-}P_2W_{16}O_{59}]^{12-}$, and $[\alpha\text{-}P_2W_{15}O_{56}]^{12-}$),[3] and Lindqvist type ($[W_5O_{18}]^{6-}$).[4] Our group has reported the first two examples of peroxo-Zr/Hf polyanions.[2h,k] In addition, the unique, asymmetric structure $[Zr_2(\mu\text{-}OH)(H_2O)_2(AsOH)_2(AsW_7O_{28})(AsW_{10}O_{36})]^{9-}$ has been obtained from the reaction of $[NaAs^{III}{}_4W_{40}O_{140}]^{27-}$ with Zr^{IV} ions, and does not belong to any of the above-mentioned classes.[5]

Whereas the reactivity of the 'classical' trilacunary Keggin ions $[PW_9O_{34}]^{9-}$ and $[SiW_9O_{34}]^{10-}$ with Ti^{IV}, Zr^{IV}, and Hf^{IV} ions is fairly well understood (vide supra), this is not the case for the lone pair containing Keggin family $[X^{III}W_9O_{33}]^{9-}$ (X = As, Sb, Bi), which displays different chemical reactivity and consequently results in structurally distinct products.[6] For all the above-mentioned reasons we decided to study in detail the reactivity of $[AsW_9O_{33}]^{9-}$ with zirconium(IV) and hafnium(IV).

Here we report on the two Zr_6- and Hf_6-containing tungstoarsenates(III) $[M_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]^{11-}$ (M = Zr, **1**; Hf, **2**, see Figure 1), which have been isolated as the hydrated mixed cesium–sodium salts $Cs_6Na_5[Zr_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]\cdot 80\,H_2O$ (**CsNa-1**)[7] and $Cs_6Na_5[Hf_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]\cdot 80\,H_2O$ (**CsNa-2**).[8] These compounds were characterized in the solid state by single-crystal X-ray dif-

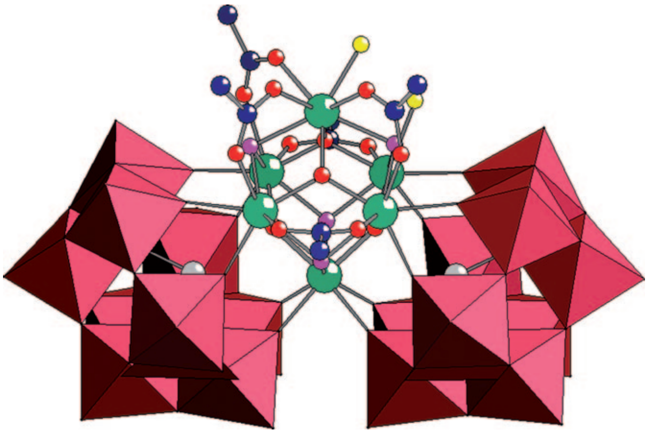

Figure 1. Combined polyhedral/ball-and-stick representation of $[M_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]^{11-}$ (M = Zr, **1**; Hf, **2**). Color code: WO_6 octahedra: dark red; Zr/Hf: green; As: gray; O: red; monoprotonated O: pink; diprotonated O: yellow; C: dark blue; H not shown.

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fraction, infrared spectroscopy, and thermogravimetric analysis.

Polyanions **1** and **2** consist of an unprecedented hexazirconium and hexahafnium core, respectively, with the metal ions occupying the vertices of an octahedron that is accommodated by two (B-α-AsW_9O_{33}) fragments (see Figure S2 in the Supporting Information). The Zr/Hf ions are octacoordinated with a square-anti-prismatic geometry. The eight faces of the Zr_6/Hf_6 octahedron are capped by four μ_3-O and four μ_3-OH bridges, each linking three zirconium/hafnium atoms (see Figure 1). The two {AsW_9} units in **1** and **2** are not eclipsed, but rather lie at an angle of about 74° with respect to each other, leaving a cavity perfectly suitable to host the M_6 unit. One of the vertices of the M_6 octahedron is pointing exactly inside this cavity, while the opposite one is pointing away from the polyanion. The 'equatorial plane' formed by the remaining four vertices serves as a kind of 'ceiling' for the cavity. The five 'inner' Zr/Hf atoms are directly bound to the lacunary site of the {AsW_9} fragments in the expected fashion through two Zr/Hf−O−W bonds involving corner-shared WO_6 octahedra of the {AsW_9} fragments. The outer, unique Zr/Hf atom is bridged by three acetate groups to three of the four Zr/Hf atoms in the equatorial plane of the M_6 octahedron. The unexpected absence of the fourth, symmetry-related acetate group is due to a slight distortion in the M_6 assembly introduced by bonding to the first three acetates. The outer, unique Zr/Hf is 3.56/3.54 Å from its non-acetate-bridged Zr/Hf neighbor, compared to a distance of 3.48/3.46 Å to the three equatorial, acetate-bridged Zr/Hf neighbors. This feature is perfectly reproducible for both polyanions **1** and **2**, as seen by single-crystal X-ray diffraction. The absence of this fourth acetate lowers the point group symmetry of the title polyanions from C_{2v} to C_1. The coordination sphere of the four equatorial Zr/Hf atoms is completed by two additional acetate groups (see Figure 1).

Polyanions **1** and **2** are isostructural and the respective salts **CsNa-1** and **CsNa-2** are in fact isomorphous. Notably, polyanion **1** exhibits a very minor (ca. 3%) crystallographic α-β-disorder. This means that in one of the two (AsW_9O_{33}) fragments one of the 'lower' (see Figure 1) edge-shared W_3O_{13} triads is rotated by 60° for 3% of the polyanions present in the single crystal measured. On the other hand, polyanion **2** is isomerically clean in the solid state.

We were also able to isolate polyanions **1** and **2** as tetra-*n*-butyl ammonium salts $[(n\text{-}C_4H_9)_4N]_7H_4[Zr_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]$ (**TBA-1**) and $[(n\text{-}C_4H_9)_4N)]_6H_5[Hf_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]$ (**TBA-2**) by addition of solid TBABr instead of the CsCl solution mentioned in the above-described procedures followed by filtration, washing with plenty of water, and drying in an oven at 50 °C overnight.

Solution NMR spectra that can be correlated with the polyanion structure in the solid state are considered compelling evidence that the molecule is stable after redissolution. Hence, the mixed cesium–sodium salt of **1** as well as the tetra-*n*-butyl ammonium salt of **2** were dissolved in H_2O/D_2O and MeCN, respectively, for multinuclear (^{183}W, ^{13}C, ^{1}H) NMR studies at room temperature. For **CsNa-1** we observed five signals at $\delta = -98.7$, -101.6, -159.5, -186.9, and -227.7 ppm with relative intensities 2:2:2:2:1. Also for **TBA-2** we observed five signals at $\delta = -73.0$, -73.1, -106.9, -162.6, and -201.5 ppm with the same intensity profile (the lowest intensity peak is most upfield) (see Figure 2). These results imply C_{2v} symmetry for polyanions **1** and **2** in solution, which means that the three acetates mentioned above are probably fluxional and/or the tungsten nuclei do not sense the asymmetric bonding situation due to the five acetate ligands. To try and verify these hypotheses we also measured ^{1}H and ^{13}C NMR spectra of **1** and **2**. We observed a signal at $\delta = 2.8$ ppm in ^{1}H NMR spectra and two signals at $\delta = 24.1$ and 182.1 ppm in the ^{13}C NMR spectra. These shifts also correspond to free acetate, which might suggest that the acetates attached to **1** and **2** are actually labile in solution resulting in fast exchange with respect to the NMR timescale. Low-temperature NMR measurements could perhaps verify this point.

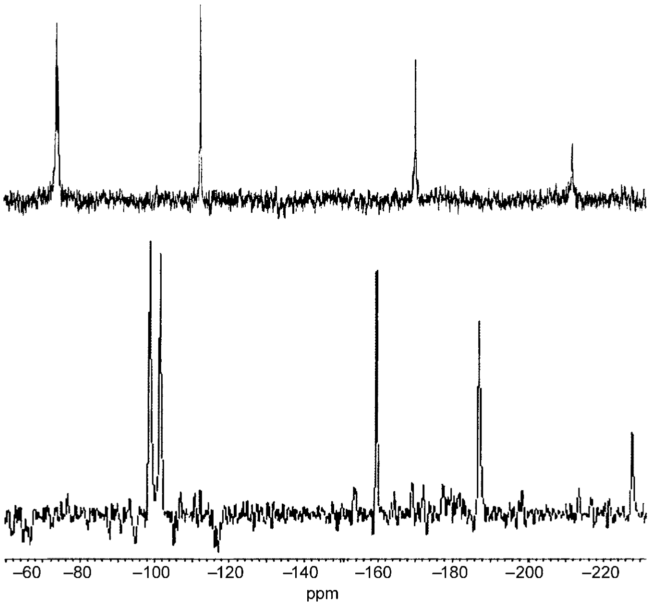

Figure 2. ^{183}W NMR spectra of **CsNa-1** in H_2O/D_2O (bottom) and **TBA-2** in MeCN (top).

We also performed homogeneous catalysis studies with **TBA-1** and **TBA-2** on H_2O_2 dismutation and the oxidation of representative organic substrates with H_2O_2 as oxidant and MeCN as a solvent in which the TBA salts of **1** and **2** are completely soluble. In the absence of an organic substrate, both polyanions caused intensive H_2O_2 decomposition (see Figure 3), which is quite typical for Zr-POMs.[2d] The results of the catalytic oxidations are presented in Table 1. With one equivalent of H_2O_2 and 1 mol% of **TBA-1** or **TBA-2**, methyl phenyl sulfide (MPS) produced methyl phenyl sulfoxide (MPSO) with 79–82% selectivity at 69–74% substrate conversion, and sulfone ($MPSO_2$) was the only by-product. Interestingly, polyanion **2** was more active

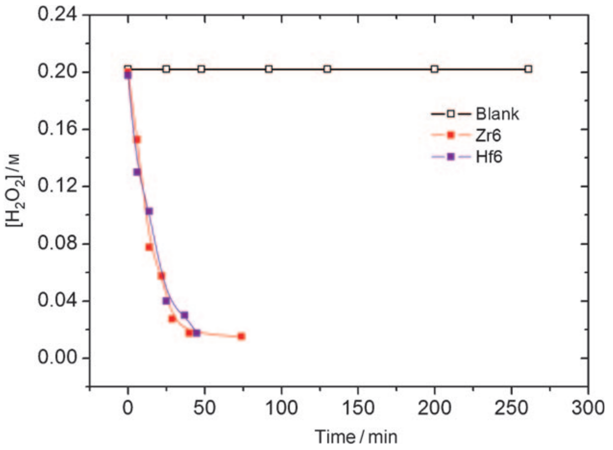

Figure 3. Decomposition of H_2O_2 with time in the presence and absence of **TBA-1** and **TBA-2**.

Table 1. Catalytic oxidations with 30% H_2O_2 over **TBA-1** and **TBA-2** in MeCN.

Substrate	Catalyst	Conv. [%]	Selectivity[a] [%]			TOF[b] $[h^{-1}]$
CyH[c]			epox	diol	ketol	
	TBA-1	60	43	30	11	33
	TBA-2	51	27	35	18	36
MPS[d]			MPSO		$MPSO_2$	
	TBA-1	74	82		17	286
	TBA-2	69	79		20	876
CyHol[e]			cyclohexanone			
	TBA-1	57	92			53
	TBA-2	59	86			52

[a] GC yield based on substrate consumed. [b] TOF = (moles of substrate consumed)/[(moles of POM) × time]; determined from the initial rates. [c] Reaction conditions: CyH 0.2 M, H_2O_2 0.2 M, POM 2×10^{-3} M, 50 °C, 5 h. [d] MPS 0.1 M, H_2O_2 0.1 M, POM 1×10^{-3} M, 20 °C, 0.5 h. [e] CyHol 0.1 M, H_2O_2 0.4 M, POM 4×10^{-3} M, 70 °C, 1 h.

than **1** (TOF 876 and 286 h^{-1}, respectively). This could be due to the different degree of protonation, which we have shown previously to play an important role in catalysis for a titanium-containing polyanion.[6g] Cyclohexanol (CyHol) resulted mainly in cyclohexanone (86–92% selectivity at 57–59% conversion), whereas cyclohexene (CyH) produced predominantly epoxide, *trans*-1,2-cyclohexanediol, and 2-hydroxycyclohexanone (in total 80–84%) along with further oxidation products, including adipaldehyde and adipic acid. The epoxide to diol ratios were 1.4 and 0.8 for **1** and **2**, respectively; the yield of diol and its overoxidation products was also higher for **2**, most likely, due to the higher proton content in this salt.[6g] Importantly, for both catalysts the amount of the allylic oxidation products, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, did not exceed 5%. This is quite unusual for cyclohexene oxidation over Zr catalysts, including Zr-POMs,[1b,2d] and indicates a dominating heterolytic oxidation mechanism.

In summary, the two novel polyanions $[M_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]^{11-}$ (M = Zr, **1**; Hf, **2**) contain an unprecedented octahedral Zr_6/Hf_6 assembly that is stabilized by two (*B*-*α*-AsW_9O_{33}) groups and five bridging acetate ligands. Both compounds were characterized by several techniques in the solid state. NMR studies in solution were also conducted on **1** and **2** in H_2O/D_2O and MeCN solutions, respectively. The spectra suggest C_{2v} symmetry for the polyanions in solution, most likely due to fluxional behavior of the labile acetate groups. The TBA salts of both **1** and **2** revealed high catalytic activity and selectivity in the liquid-phase oxidation of organic compounds with aqueous H_2O_2. A heterolytic oxidation mechanism is manifested by the high yields of epoxide and diol in the oxidation of cyclohexene. We plan to perform additional mechanistic studies to better understand the catalytic behavior of **1** and **2**, and also to prepare other carboxylate and perhaps also peroxo derivatives of the title polyanions.

Experimental Section

Preparation of $Cs_6Na_5[Zr_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]\cdot80H_2O$ (CsNa-1): Polyanion **1** was synthesized by dissolution of $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot27H_2O$ (0.29 g, 0.10 mmol) in 2 M lithium acetate buffer solution (20 mL, pH 4.0) followed by addition of $ZrCl_4$ (0.05 g, 0.20 mmol). The solution was heated at 80 °C for one hour and filtered while hot, and after the mixture had been cooled to room temperature a few drops of 1 M CsCl solution were added. Slow evaporation at room temperature led to the appearance of colorless, crystalline **CsNa-1** after about one week, which was filtered off and air-dried (yield 0.11 g, 45%). IR bands: $\tilde{\nu}$ = 1637 (m), 1617 (m), 1577 (s), 947 (s), 870 (vs), 783 (m), 728 (w), 691 (w), 642 (w), 457(m) cm^{-1}.

Preparation of: $Cs_6Na_5[Hf_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]\cdot80H_2O$ (CsNa-2): For the preparation of **2** the same procedure was followed as for polyanion **1** except that $HfCl_4$ (0.06 g, 0.20 mmol) was used instead of $ZrCl_4$ (yield 0.15 g, 55%). IR bands: $\tilde{\nu}$ = 1637 (m), 1617 (m), 1577 (m), 948 (m), 874 (s), 784 (m), 729 (w), 693 (w), 649 (w), 457(m) cm^{-1}.

Preparation of $[(n\text{-}C_4H_9)_4N]_7H_4[Zr_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]$ (TBA-1): The synthesis procedure for **1** was followed as shown above, but instead of adding a few drops of 1 M CsCl solution, an excess amount of solid $(n\text{-}C_4H_9)_4N)Cl$ (TBACl) was added. The resulting white precipitate was isolated by filtration, washed with H_2O, and then dried in an oven at 50 °C overnight. Elemental analysis (%) calcd: C 20.28, H 3.89, N 1.36; found: C 19.75, H 3.90, N 1.35.

Preparation of $[(n\text{-}C_4H_9)_4N)]_6H_5[Hf_6O_4(OH)_4(H_2O)_2(CH_3COO)_5(AsW_9O_{33})_2]$ (TBA-2): The same procedure was followed as for polyanion **1**. Elemental analysis (%) calcd: C 16.95, H 3.28, N 1.12; found: C 16.42, H 3.27, N 1.14. Elemental analyses were performed by Analytische Laboratorien, Lindlar, Germany.

Catalytic oxidations: The catalytic oxidations were carried out in temperature-controlled glass vessels at 20–70 °C in MeCN solution (total reaction volume 1 mL). Samples were taken during the reaction course by a syringe, and the reaction products were identified by GC-MS and GC using reference compounds. Substrate conversions and product yields were quantified by GC using biphenyl or dodecane as internal standards.

NMR spectroscopy: The ^{183}W NMR spectrum of **CsNa-1** redissolved in H_2O/D_2O was recorded at 16.656 MHz in a 10 mm tube at room temperature on a 400 MHz JEOL ECP400H instrument. On the other hand, the ^{183}W NMR spectrum of **TBA-2** redissolved in CH_3CN was recorded at 16.668 MHz in a 10 mm tube at room temperature on a Bruker Avance-400 instrument.

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Keywords: hafnium · homogeneous catalysis · oxidation · polyoxometalates · zirconium

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[7] Crystal data of **CsNa-1**: $C_{10}H_{183}As_2Cs_6Na_5O_{166}W_{18}Zr_6$, $M_r = 7879.2$, monoclinic, space group $C2/c$, $a = 29.438(6)$, $b = 30.588(6)$, $c = 27.384(5)$ Å, $\gamma = 100.291(10)°$, $V = 24262(8)$ Å^3, $Z = 8$, $T = 173$ K, $\rho_{calcd} = 4.564$ Mg m^{-3}, $\mu = 20.871$ mm^{-1}, 263956 measured and 23873 unique reflections ($R_{int} = 0.131$), final $R1 = 0.056$ for 15704 observations and $wR2 = 0.163$ for all unique data.

[8] Crystal data of **CsNa-2**: $C_{10}H_{183}As_2Cs_6Hf_6Na_5O_{166}W_{18}$, $M_r = 8402.8$ g mol^{-1}, monoclinic, space group $C2/c$, $a = 29.237(3)$, $b = 30.475(2)$, $c = 27.164(3)$ Å, $\gamma = 100.587(4)°$, $V = 23792(4)$ Å^3, $Z = 8$, $T = 173$ K, $\rho_{calcd} = 4.867$ Mg m^{-3}, $\mu = 26.273$ mm^{-1}, 164323 measured and 17262 unique reflections ($R_{int} = 0.125$), final $R1 = 0.063$ for 11523 observations and $wR2 = 0.236$ for all unique data. CCDC-759147 and CCDC-759148 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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