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Peroxo-Zr/Hf-Containing Undecatungstosilicates and -Germanates

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A family of dimeric, peroxo-containing heteropolytungstates, $[M_2(O_2)_2(XW_{11}O_{39})_2]^{12-}$ [M = Zr^{4+}, X = Si (**1**), Ge (**2**); M = Hf^{4+}, X = Si (**3**)], have been synthesized by reacting $ZrCl_4$/$HfCl_4$ with the respective monolacunary Keggin precursor $[XW_{11}O_{39}]^{8-}$ (X=Si, Ge) in an aqueous acidic medium (pH 4.8). The isostructural polyanions **1**−**3** are composed of two ($XW_{11}O_{39}$) Keggin units encapsulating a central diperoxo−dimetal fragment $\{M_2(O_2)_2\}^{4+}$ (M=Zr^{4+}, Hf^{4+}). Cyclic voltammetry and exhaustive electrolysis studies indicate fast reductive release of the peroxo ligands upon reduction of **1**−**3**. Stoichiometric oxo-transfer studies from **1**−**3** to the substrate L-methionine were performed, and the reactions were monitored by ^{1}H NMR.

Polyoxometalates (POMs) are discrete-molecular metal−oxo clusters with a large structural and compositional variety and a multitude of potential applications in many different areas.[1] POMs can be functionalized by either grafting or incorporating organometallic groups, lanthanides, or transition metals into the polyanion framework. The latter leads to transition-metal-substituted polyanions, constituting one of the largest subclasses in this field.

In particular, there has been an impressive development in the synthesis of zirconium(IV) and hafnium(IV)-containing polyanions in recent years.[2,3] In 1989, Finke et al. reported on the synthesis and structural characterization of $[Si_2W_{18}Zr_3O_{71}H_3]^{11-}$, which was the first example of a Zr^{4+}-substituted POM.[2a] Other examples based on the Keggin structure include $[(PNbW_{11}O_{40})_2ZrCp_2]^{6-}$,[2b] $[Zr_4O_2(OH)_2(CH_3COO)_2(\alpha\text{-}GeW_{10}O_{37})_2]^{12-}$,[2i] $[Zr_3O(OH)_2(\alpha\text{-}GeW_9O_{34})(\beta\text{-}GeW_9O_{34})]^{12-}$,[2j] $[(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)_2]^{10-}$, $[(\gamma\text{-}SiW_{10}O_{36})_2Zr_2(\mu\text{-}OH)(\mu\text{-}OCH_3)]^{10-}$,[2h] and $[\{PW_{11}O_{39}Zr(\mu\text{-}OH)\}_2]^{8-}$.[2d] Zr^{4+}-containing POMs of the Wells−Dawson type include $[Zr_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$,[2c] $[\{P_2W_{15}O_{54}(H_2O)_2\}_2Zr]^{12-}$, and $[\{P_2W_{15}O_{54}(H_2O)_2\}Zr\{P_2W_{17}O_{61}\}]^{14-}$.[2g] On the other hand, $[\{(\mu\text{-}MeO)ZrW_5O_{18}\}_2]^{6-}$,[2f] $[W_5O_{18}Zr(H_2O)_{3-n}(DMSO)_n]^{2-}$ ($n=1$ and 2), and the dimeric $[\{W_5O_{18}Zr(\mu\text{-}OH)\}_2]^{6-}$ [2e] are examples of Zr^{4+}-containing structures of the Lindqvist type.

Regarding Hf^{IV}-substituted POMs, the first examples were $[Hf(\alpha_2\text{-}P_2W_{17}O_{61})_2]^{16-}$ and $[Hf(\alpha\text{-}PW_{11}O_{39})_2]^{10-}$ reported by Nomiya et al. in 2006.[3a] Other examples include $[\alpha_1\text{-}HfP_2W_{17}O_{61}]^{6-}$, $[\alpha\text{-}Hf(OH)PW_{11}O_{39}]^{4-}$,[3b] and $[Hf_4(\mu_3\text{-}O)_2(\mu\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$.[3c]

Because of the large size of the Zr^{4+} and Hf^{4+} ions, compared to 3d metal ions, their coordination numbers can reach eight, with one or more terminal, labile water molecules. This may allow for ligand exchange, resulting in substrate and/or peroxide activation within the metal coordination sphere.[4]

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In particular, zirconium peroxides have shown unique selectivity performance,[5] leading to an interest in catalytic applications of related materials. On the other hand, knowledge of the structural and electronic properties of zirconium(IV) peroxides is limited.[6] Access to zirconium(IV) peroxides by ligand-mediated O_2 activation is of major importance, as recently demonstrated by Abu-Omar's group.[6d] Monoperoxo complexes have been isolated by reaction with H_2O_2 and in the presence of nitrogen−oxygen/sulfur donor ligands.[7] However, peroxo species containing tri- and tetradentate ligands turn out to be inert in the oxidation of organic substrates, including phosphines, alkenes, and alcohols. Hafnium analogues are even less documented.[8] An important discovery is the structural characterization of peroxo-bridged hafnium(IV) porphyrinato dimers, displaying two O_2^{2-} ligands with a rather unique side-on bridging mode.[9]

Recently, Kortz's group prepared the tetra- and hexazirconium-containing tungstosilicates $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ and $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$.[10a] We were also able to synthesize the first examples of structurally characterized Zr/Hf-peroxo POMs, $[M_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (M = Zr, Hf).[10b] This structural type features a cyclic 6-peroxo-6-Zr/Hf core with a side-on bridging peroxide moiety between adjacent Zr/Hf pairs. This finding demonstrated that peroxo groups can be fixed exclusively at the incorporated transition-metal ions without involving any tungsten addenda atoms. In order to find out whether other peroxo POMs with such a characteristic exist, we decided to systematically investigate the interaction of Zr^{4+} and Hf^{4+} ions with other lacunary heteropolytungstates in aqueous solution and in the presence of H_2O_2.

This work has resulted in three novel Keggin-based dimeric structures, $[M_2(O_2)_2(\alpha\text{-}XW_{11}O_{39})_2]^{12-}$ [M = Zr^{4+}, X = Si (**1**), Ge (**2**); M = Hf^{4+}, X = Si (**3**); see Figure 1]. The title polyanions **1**−**3** were prepared in a simple one-pot stoichiometric reaction of $[\alpha\text{-}XW_{11}O_{39}]^{8-}$ (X = Si, Ge) with Zr^{4+}/Hf^{4+} in aqueous solution (pH 4.8). A few drops of aqueous H_2O_2 (30%) were added to the reaction mixture, and the solution was stirred at 80 °C for 30 min.

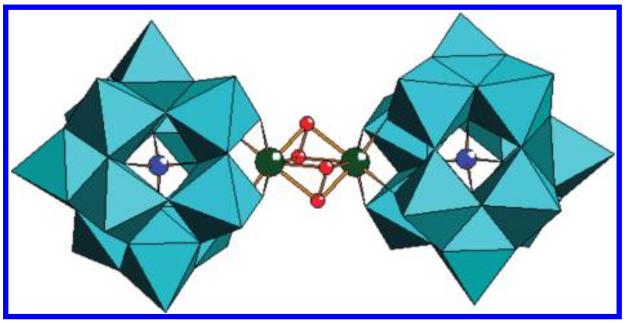

Figure 1. Combined polyhedral/ball-and-stick representation of $[M_2(O_2)_2(\alpha\text{-}XW_{11}O_{39})_2]^{12-}$ [M = Zr^{4+}, X = Si (**1**), Ge (**2**); M = Hf^{4+}, X = Si (**3**)]. The color code is as follows: WO_6 octahedra, turquoise; Si/Ge, blue; Zr/Hf, green; peroxo, red.

Polyanions **1** and **2** were isolated in the form of a hydrated potassium salt $K_{12}[M_2(O_2)_2(\alpha\text{-}XW_{11}O_{39})_2]\cdot 25H_2O$ [(M = Zr^{4+}, X = Si (**K-1**); Ge (**K-2**)], and polyanion **3** was isolated as a mixed potassium−rubidium salt $K_{10.5}Rb_{1.5}[Hf_2(O_2)_2(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 21H_2O$ (**KRb-3**).[11] The novel polyanions **1**−**3** consist of two $[\alpha\text{-}XW_{11}O_{39}]^{8-}$ (X = Si, Ge) anions linked by a cationic $\{M_2(O_2)_2\}^{4+}$ (M = Zr^{4+}, Hf^{4+}) bridge in a head-on fashion, resulting in an assembly with C_i point group symmetry. The Zr^{4+} and Hf^{4+} ions are coordinated to eight oxygen atoms, resulting in a distorted square-antiprismatic geometry. Four of these oxygen atoms belong to the Keggin fragment and the other four to the two peroxo groups (see Figure 1). According to bond valence sum calculations,[12] the four oxygen atoms of both peroxo groups are not protonated. The bimetallic bisperoxide moieties in **1**−**3** show $M-O^-$ bond lengths that are in good agreement with those observed for

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(11) **Synthesis of $K_{12}[Zr_2(O_2)_2(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 25H_2O$ (K-1).** A total of 0.65 g (0.20 mmol) of $K_8[\alpha\text{-}SiW_{11}O_{39}]\cdot 14H_2O$ was dissolved in 20 mL of a 1 M CH_3COOH/CH_3COOK buffer solution (pH 4.8), and then 0.05 g (0.20 mmol) of $ZrCl_4$ was added. During the reaction, 5−10 drops of 30% H_2O_2 were introduced into the reaction mixture. The solution was heated at 80 °C for 30 min and filtered while still hot. Slow evaporation at room temperature led to the appearance of a yellowish crystalline product within 1 day. The solid product was finally collected by filtration and air dried. Yield: 0.48 g (74%). IR: 1006 (sh), 963 (s), 912 (s), 785 (s), 717 (sh), 522 (m), 471 (w) cm^{-1}. Anal. Calcd for **K-1**: K, 7.20; Zr, 2.80; Si, 0.86; W, 62.1. Found: K, 7.32; Zr, 2.62; Si, 0.80; W, 61.4. The formula of **K-1** is fully supported by thermogravimetric analysis (TGA). Crystal data for **K-1**: $H_{50}K_{12}O_{107}Si_2W_{22}Zr_2$, $M_r = 6514.8$, triclinic, space group $P\bar{1}$, $a = 11.5163(13)$ Å, $b = 12.4128(13)$ Å, $c = 21.326(3)$ Å, $\alpha = 80.355(6)°$, $\beta = 87.259(7)°$, $\gamma = 63.100(5)°$, $V = 2678.9(5)$ Å^3, $Z = 1$, $T = 173(2)$ K, $D_c = 4.038$ g cm^{-3}, R1 = 0.0557, wR2 = 0.1620 [$I > 2\sigma(I)$]. **Synthesis of $K_{12}[Zr_2(O_2)_2(\alpha\text{-}GeW_{11}O_{39})_2]\cdot 25H_2O$ (K-2).** The same procedure as for **K-1** was followed, except for using 0.65 g (0.20 mmol) of $K_6Na_2[\alpha\text{-}GeW_{11}O_{39}]\cdot 14H_2O$ and adding 1 M KCl after filtration. Yield: 0.46 g (70%). IR: 959 (s), 872 (s), 809 (m), 770 (m), 712 (w), 670 (sh), 530 (w), 453 (m), 422 (sh) cm^{-1}. Anal. Calcd for **K-2**: K, 7.10; Zr, 2.76; Ge, 2.20; W, 61.3. Found: K, 7.25; Zr, 2.51; Ge, 2.10; W, 60.2. The formula of **K-2** is fully supported by TGA. Crystal data for **K-2**: $H_{50}Ge_2K_{12}O_{107}W_{22}Zr_2$, M_r = 6603.9, triclinic, space group $P\bar{1}$, a = 11.5114(4) Å, b = 12.6316(6) Å, c = 19.0236(10) Å, $\alpha = 91.249(3)°$, $\beta = 92.891(2)°$, $\gamma = 103.628(2)°$, $V = 2683.3(2)$ Å^3, $Z = 1$, $T = 173(2)$ K, $D_c = 4.035$ g cm^{-3}, R1 = 0.0502, wR2 = 0.1518 [$I > 2\sigma(I)$]. **Synthesis of $K_{10.5}Rb_{1.5}[Hf_2(O_2)_2(\alpha\text{-}SiW_{11}O_{39})_2]\cdot 21H_2O$ (KRb-3).** The same procedure as for **K-1** was followed, except for using 0.06 g (0.20 mmol) of $HfCl_4$ and adding 1 M RbCl after filtration. Yield: 0.46 g (69%). IR: 1007 (sh), 962 (s), 912 (s), 786 (s), 728 (sh), 673 (sh), 521 (m), 474 (w) cm^{-1}. Anal. Calcd for **KRb-3**: K, 6.14; Rb, 1.92; Hf, 5.34; Si, 0.84; W, 60.5. Found: K, 6.48; Rb, 1.80; Hf, 5.56; Si, 0.80; W, 59.9. The formula of **KRb-3** is fully supported by TGA. Crystal data for **KRb-3**: $H_{42}Hf_2K_{10.5}O_{103}Rb_{1.5}Si_2W_{22}$, $M_r = 6686.9$, triclinic, space group $P\bar{1}$, $a = 11.5111(6)$ Å, $b = 12.5996(7)$ Å, $c = 19.0734(9)$ Å, $\alpha = 91.487(3)°$, $\beta = 92.993(3)°$, $\gamma = 103.241(3)°$, $V = 2687.1(2)$ Å^3, $Z = 1$, $T = 173(2)$ K, $D_c = 4.132$ g cm^{-3}, R1 = 0.0493, wR2 = 0.1521 [$I > 2\sigma(I)$].

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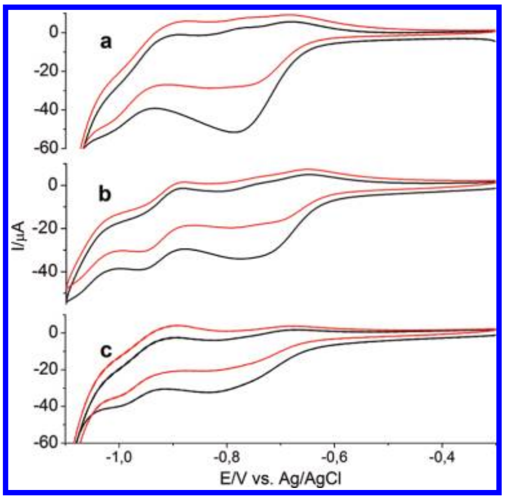


Figure 2. CVs [first (black) and second (red) scans] of (a) polyanion **1** (6.2×10^{-4} M), (b) polyanion **2** (6.0×10^{-4} M), and (c) polyanion **3** (3.0×10^{-4} M) in a 0.5 M HAc/KAc buffer (pH 4.7) at glassy carbon ($A = 0.07$ cm^2; $v = 0.1$ V s^{-1}).

other organic d^0 zirconium and hafnium peroxides.[6d,9] (Table S1 in the Supporting Information). The peroxo bond lengths ($O^-{-}O^-$) of the title polyanions range from 1.491(11) Å in **1**, to 1.529(13) Å in **2**, and to 1.523(13) Å in **3**, all comparable to the $O^-{-}O^-$ bond distance observed in the crystal structure of hydrogen peroxide [1.49(1) Å].[13] For polyanion **3**, the peroxo bond length is in excellent agreement with known η^2-peroxo complexes, such as the porphyrinate Hf(μ-η^2-O_2) complex exhibiting a $O^-{-}O^-$ distance of 1.56 Å.

For all three polyanions **1**−**3**, the peroxo functions are readily reduced by iodide in water and titrated by a standard thiosulfate solution, confirming the presence of two active oxygen atoms (O_{act}) per molecule. The peroxo functions in **1**−**3** can also be observed by cyclic voltammetry (CV). In the first cathodic scan up to −0.90 V in Figure 2a, eight electrons are transferred, leading to four water molecules and two partially reduced monomeric subunits ($POMH_2$) on the time scale of CV according to eq 1:

$$\text{first scan}: \quad POM_2(O_2)_2^{\;12-} + 8e^- + 12H^+ \rightarrow 2POMH_2^{\;4-} + 4H_2O \qquad (1)$$

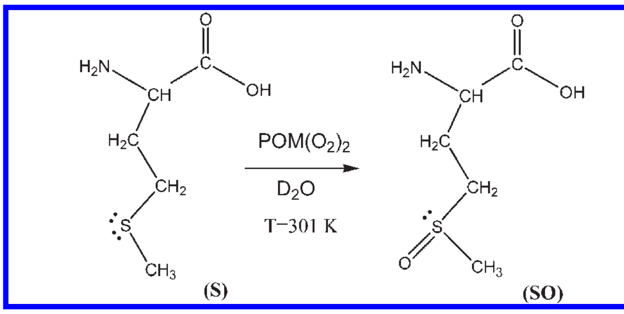
$$\text{second scan}: \quad 2POM^{4-} + 4e^- + 4H^+ \rightarrow 2POMH_2^{\;4-} \qquad (2)$$

In the second scan, only the reversible four-electron redox current remains for the first cathodic wave up to −0.90 V (eq 2). The second scan is interpreted as formulated in eq 2 possibly with minor contributions from nondissociated **1**. Controlled-potential electrolysis of **1** at −0.90 V yields 8.5 electrons/molecule (eq 1). The current time trace indicates an electrocatalytic situation related to the fact that $POM_2(O_2)_2$ and POM are reduced at the same potential (see the Supporting Information).

Table 1. Oxidation of L-Methionine (S) by Polyanions **1**−**3** in Aqueous Solution[a]

no.	POM	sub	conv %[b,c]	$R_0 \times 10^6$ (mol L^{-1} s^{-1})[d]
1	**1**	S	> 99	> 300
2	**2**	S	> 99	> 300
3	**3**	S	> 99	> 300

[a] S (7.66 mM), POM (**1**−**3**) (3.84 mM) [stoichiometric ratio defined on the basis of the total O_{act} available] in D_2O (500 μL), at 301 K. [b] Determined by ^{1}H NMR analysis. [c] No overoxidation to methionine sulfone was observed in such conditions. [d] The initial rate of oxidation determined for $t < 1$ min.



(3)

(S) **(SO)**

In contrast to the classical coordination compounds cited above, polyanions **1**−**3** are capable of oxygen transfer in water. Indeed, under stoichiometric conditions, the selective oxidation of the natural amino acid L-methionine (S) to methionine oxide (**SO**) is observed at 301 K (eq 3).[14] Kinetic and electrochemical studies on **1**−**3** confirm the role of the peroxidic functions bridging the Zr/Hf centers, and the role of the XW_{11} Keggin fragments, for the electronic tuning during catalysis.

The oxygen transfer reactivity of **1**−**3** is compared in Table 1 on the basis of conversion yield and kinetic determinations. The three title polyanions display a remarkable activity toward the oxidation of *L*-methionine, at neutral pH.[15]

In conclusion, we have synthesized and structurally characterized three novel Zr/Hf-peroxo-containing heterotungstates $[M_2(O_2)_2(XW_{11}O_{39})_2]^{12-}$ [M = Zr^{4+}, X = Si (**1**), Ge (**2**); M = Hf^{4+}, X = Si (**3**)]. Electrochemistry allowed probing of the redox activity of the peroxo groups and the tungsten−oxo Keggin frameworks in **1**−**3**. Kinetic experiments have proven that these polyanions are effective in transferring oxygen to L-methionine. A detailed study on the oxygen transfer reactivity of these POMs will be published soon elsewhere.

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Supporting Information Available: Complete references for Hf^{4+}/Zr^{4+}-containing POMs, detailed Experimental and Crystallographic Sections, a table of selected bond distances, thermograms (from room temperature up to 900 °C) of **K-1** (Figure S1), **K-2** (Figure S2), and **KRb-3** (Figure S3), and a controlled potential electrolysis plot of polyanion **1** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) A blank experiment using H_2O_2 in the absence of **1**−**3** showed no significant conversion of L-methionine, under the conditions explored.