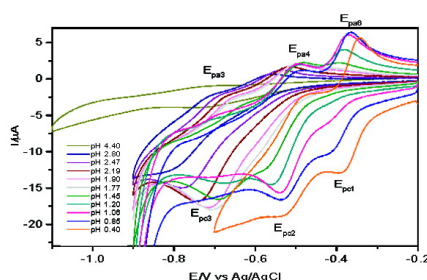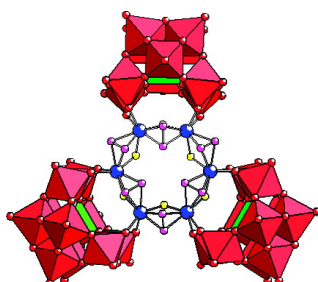# JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

6-Peroxo-6-Zirconium Crown and Its Hafnium Analogue Embedded in a Triangular Polyanion: [M(O)(OH)(#-SiWO)] (M = Zr, Hf)

Bassem S. Bassil, Sib Sankar Mal, Michael H. Dickman, Ulrich Kortz, Holger Oelrich, and Lorenz Walder

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

ACS Publications
High quality. High impact.

6-Peroxo-6-Zirconium Crown and Its Hafnium Analogue Embedded in a Triangular Polyanion: [M$_6$(O$_2$)$_6$(OH)$_6$(γ-SiW$_{10}$O$_{36}$)$_3$]$^{18-}$ (M = Zr, Hf)

Bassem S. Bassil,[†] Sib Sankar Mal,[†] Michael H. Dickman,[†] Ulrich Kortz,*,[†] Holger Oelrich,[‡] and Lorenz Walder*,[‡]

School of Engineering and Science, Jacobs University, P.O. Box 750561, 28725 Bremen, Germany, and Institute of Chemistry, University of Osnabrück, Barbarastrasse 7, 49069 Osnabrück, Germany

Received February 26, 2008; E-mail: u.kortz@jacobs-university.de

Polyoxometalates (POMs) represent a large family of discrete molecular, anionic metal−oxygen clusters composed of edge- and corner-shared MO_6 octahedra (M = Mo^{VI}, W^{VI}, V^V, Nb^V, Ta^V).[1] Until recently, the number of zirconium-substituted POMs had been limited to Finke's sandwich dimer [Si$_2$W$_{18}$Zr$_3$O$_{71}$H$_3$]$^{11-}$.[2] However, over the last 5 years, the area of Zr-POMs has experienced a renaissance as numerous Keggin- and Wells−Dawson-based Zr derivatives have been reported.[3] For Hf, however, only a few POM structures have been reported so far.[3a,c,d,j,4]

Our systematic study of the dilacunary decatungstosilicate precursor [γ-SiW$_{10}$O$_{36}$]$^{8-}$[5] with different 3d and 4d transition metal ions resulted in two zirconium containing polyanions: the dimeric [Zr$_4$O$_2$(OH)$_2$(H$_2$O)$_4$(β-SiW$_{10}$O$_{37}$)$_2$]$^{10-}$ and the trimeric [Zr$_6$O$_2$(OH)$_4$-(H$_2$O)$_3$(β-SiW$_{10}$O$_{37}$)$_3$]$^{14-}$.[6] Both structures exhibit Zr centers with up to two terminal, labile water ligands which in theory could be replaced by peroxide. Such species would be highly attractive for catalytic applications. To date, a few coordination complexes containing peroxo-Zr centers have been reported.[7] For peroxo-Hf complexes, only an end-on structure was reported in 1991.[8] A number of peroxo-POMs in which the peroxo groups are usually bound to addenda atoms of the POM skeleton have been reported.[9] To our knowledge, there are no examples of structurally character-ized peroxo-Zr or -Hf POMs.

Therefore, we decided to investigate in detail the interaction of Zr^{4+} ions with [γ-SiW$_{10}$O$_{36}$]$^{8-}$ in aqueous solution and in the presence of peroxide. This work has resulted in a novel polyanion with a cyclic 6-peroxo-6-zirconium core stabilized by three deca-tungstosilicate units, [Zr$_6$(O$_2$)$_6$(OH)$_6$(γ-SiW$_{10}$O$_{36}$)$_3$]$^{18-}$ (**1**), see Fig-ure 1. Here we report on the synthesis, structure, and electrochem-istry of **1**.

The synthesis procedure of **1** is identical to that of our dimeric [Zr$_4$O$_2$(OH)$_2$(H$_2$O)$_4$(β-SiW$_{10}$O$_{37}$)$_2$]$^{10-}$, except that some aqueous H$_2$O$_2$ (30%) was added to the reaction mixture. Also, the procedure of our trimeric [Zr$_6$O$_2$(OH)$_4$(H$_2$O)$_3$(β-SiW$_{10}$O$_{37}$)$_3$]$^{14-}$ in the presence of H$_2$O$_2$ resulted in **1**, albeit in lower yield. After addition of H$_2$O$_2$, the synthesis solution became turbid, but with constant stirring at 50 °C, it cleared up eventually. We crystallized **1** as the hydrated potassium salt K$_{18}$[Zr$_6$(O$_2$)$_6$(OH)$_6$(γ-SiW$_{10}$O$_{36}$)$_3$]·59H$_2$O (**K-1**). The number of crystal waters was determined by TGA (to ca. 253 °C). The TGA graph (see Figure S1) also showed another weight loss step up to ca. 454 °C. We attribute this second step to loss of the peroxo groups, which leads to gradual decomposition of the compound. We also prepared the isostructural hafnium analogue [Hf$_6$(O$_2$)$_6$(OH)$_6$(γ-SiW$_{10}$O$_{36}$)$_3$]$^{18-}$ (**2**) using an analogous synthetic procedure (see Supporting Information).
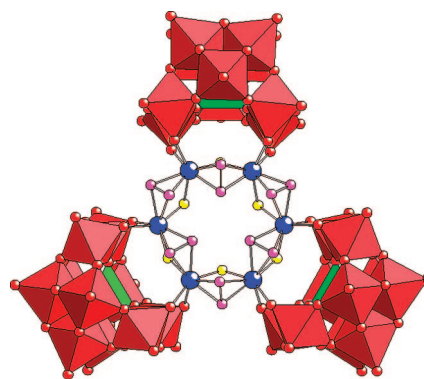

Figure 1. Combined polyhedral/ball-and-stick representation of [M$_6$(O$_2$)$_6$-(OH)$_6$(γ-SiW$_{10}$O$_{36}$)$_3$]$^{18-}$ (M = Zr, **1**; Hf, **2**). The color code is as follows: WO$_6$ octahedra (red), SiO$_4$ tetrahedra (green), zirconium/hafnium (blue), oxo (red), hydroxo (yellow), and peroxo (pink).
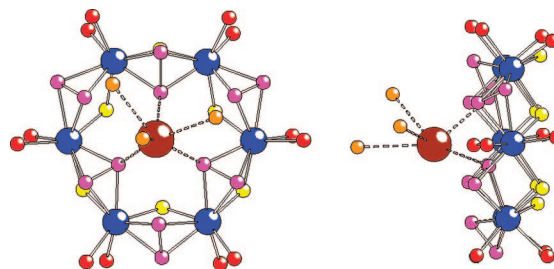

Figure 2. Top view (left) and side view (right) on the central [M$_6$-(O$_2$)$_6$(OH)$_6$]$^{6+}$ cluster in **1** and **2**. The color code of the balls is as follows: Zr/Hf (blue), peroxo (pink), hydroxo (yellow), oxo (red), potassium (brown), and aqua (orange).

Polyanion **1** is composed of three [γ-SiW$_{10}$O$_{36}$]$^{8-}$ units encap-sulating the unprecedented [Zr$_6$(O$_2$)$_6$(OH)$_6$]$^{6+}$ wheel (see Figure 1). On the other hand, **1** can also be considered a cyclic assembly of three fused {Zr$_2$(O$_2$)$_2$(OH)$_2$(γ-SiW$_{10}$O$_{36}$)} monomers. The central peroxo-Zr crown is composed of six equivalent Zr^{IV} centers which are all linked to each other by a side-on peroxo unit and a hydroxo group. The presence of the latter was established by bond valence sum (BVS) calculations.[10]
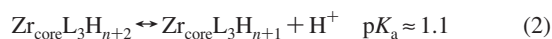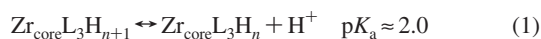
Interestingly, the six bridging peroxo groups in **1** are all on one side of the ring (stabilized in the solid state by a capping, six-coordinated potassium ion, K···O 2.69−2.98(2) Å), whereas the six bridging hydroxo groups are on the other side, see Figure 2. In this respect, **1** resembles a coin, having two different sides. In **1**, it is possible to distinguish the "peroxo face" (perhaps the site of oxygen transfer) from the "hydroxo face" (perhaps the site of proton transfer). The Zr−O^{1-} bond lengths range from 2.15(2) to 2.22(2) Å, not significantly different from the Zr−O^{2-} bond lengths which

---

[†] Jacobs University.
[‡] University of Osnabrück.

range from 2.09(2) to 2.21(2) Å. The peroxo group bond lengths, O−O, range from 1.50(3) to 1.55(3) Å. The crystal structure of hydrogen peroxide published in 1951 noted a O−O bond length of 1.49 (1) Å, comparable to the O−O bond lengths in **1**.[11] In 1989, a Russian group reported a cyclic tri-Zr-peroxo coordination complex $Zr_3F_{12}(O_2)_3$ with an average O−O bond of 1.517(5) Å, which also falls within the range of our observed peroxo O−O bond lengths.[7b] The Hf−O and O−O bond lengths in **2** (2.092(19) to 2.23(2) and 1.48(2) to 1.55(3) Å, respectively) are similar to the corresponding bonds in **1**.

Each zirconium ion is coordinated to the lacunary site of a decatungstosilicate fragment via two Zr−O(W) bonds to an edge-shared pair of WO_6 octahedra, resulting in a coordination number of 8. The peroxo groups in **1** are highly accessible, which could be important for catalytic applications.

In order to check the stability of **1** ($Zr_{core}L_3H_n$) in diluted solutions, we have performed UV−pH titration experiments. The results show clearly that **1** is stable as it does not release the free ligand $[LH]^{7-}$. We found two weak isosbestic spectral transitions involving three distinguishable species with the preliminary structural assignment shown in eqs 1 and 2.
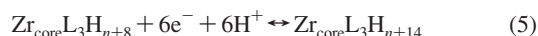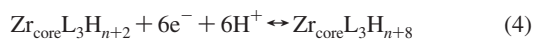
$$Zr_{core}L_3H_{n+1} \leftrightarrow Zr_{core}L_3H_n + H^+ \quad pK_a \approx 2.0 \quad (1)$$

$$Zr_{core}L_3H_{n+2} \leftrightarrow Zr_{core}L_3H_{n+1} + H^+ \quad pK_a \approx 1.1 \quad (2)$$

The ligand $[LH]^{7-}$ does not show any spectral transition in the same pH range, as expected.[5a] It has also been reported that the dilacunary decatungstosilicate $[\gamma\text{-}SiW_{10}O_{36}]^{8-} = L^{8-}$ is protonated at pH < 10.5, and that the pK_a of $[LH]^{7-}$ is shifted into the range of 6.0−7.0 and 5.0−5.5 if $[LH]^{7-}$ is competitively coordinated to a monovalent or divalent metal ion (eq 3), respectively.[5a]

$$[LH]^{7-} + M^{n+} \leftrightarrow [LM]^{(8-n)-} + H^+ \quad (3)$$
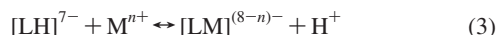
In the case of **1**, three $[LH]^{7-}$ units are coordinated to the 6-fold positively charged peroxo-Zr core, that is, two positive charges per $[LH]^{7-}$ are active. Thus the central Zr_{core}^{6+} acidifies the peripheral protons on $[LH]^{7-}$ in an unprecedented way.

In the CV measurements of **1**, no prominent electrochemical signature for the Zr_{core} subunit was found, but the protonation equilibria 1 and 2 were confirmed (see Supporting Information).

Below pH 1, where $Zr_{core}L_3H_{n+2}$ predominates, we observe two reversible waves, preliminarily interpreted by eqs 4 and 5:

$$Zr_{core}L_3H_{n+2} + 6e^- + 6H^+ \leftrightarrow Zr_{core}L_3H_{n+8} \quad (4)$$

$$Zr_{core}L_3H_{n+8} + 6e^- + 6H^+ \leftrightarrow Zr_{core}L_3H_{n+14} \quad (5)$$

with $E°(4, pH 1) = -0.40$ V, and $E°(5, pH 1) = -0.53$ V each shifting with 60 mV/pH. At pH 1.2, with the singly deprotonated complex $Zr_{core}L_3H_{n+1}$ present (eq 2), the CV wave (eq 4) has disappeared, and a single cathodic wave (ca. $12e^-$ in height) grows in with a peak potential of −0.54 V. The pK_a value read out from the peak current change of the wave in eq 4 as a function of pH is in agreement with the value obtained from UV titration. A similar behavior was observed in the pH range of 1.8 to 3 for the H_2O/H_2SO_4 system adjusted with KOH, thus confirming the second pK_a

(eq 1) by CV. Notably, **1** shows slow protonation equilibria in H_2SO_4/H_2O as compared to that of HAc/Ac buffer solution, making this analysis possible. For further details of the measurements and conclusions, see Supporting Information.

In conclusion, we have synthesized and structurally characterized the unprecedented peroxo-zirconium containing 30-tungstosilicate $[Zr_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (**1**) and also its hafnium analogue $[Hf_6(O_2)_6(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ (**2**). Polyanion **1** represents the first structurally characterized Zr-peroxo POM with side-on, bridging peroxo units. The simple, one-pot synthesis of **1** and **2** involving dropwise addition of aqueous hydrogen peroxide could represent a general procedure for incorporating peroxo groups into a large variety of transition metal and lanthanide containing POMs.

Supporting Information Available: Complete refs 1, 3, 9; synthesis, crystal data, and CIF files of **K-1** and **K-2**; TGA and UV titration of **K-1**; CV of **K-1** and $K_8[\gamma\text{-}SiW_{10}O_{36}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34. (c) Pope, M. T. *Comp. Coord. Chem. II* **2003**, *4*, 635. (d) Hill, C. L. *Comp. Coord. Chem. II* **2003**, *4*, 679.
(2) Finke, R. G.; Rapko, B.; Weakley, T. J. R. *Inorg. Chem.* **1989**, *28*, 1573.
(3) Very recent examples include: (a) Kikukawa, Y.; Yamaguchi, S.; Tsuchida, K.; Nakagawa, Y.; Uehara, K.; Yamaguchi, K.; Mizuno, N. *J. Am. Chem. Soc.* **2008**, *130*, 5472. (b) Errington, R. J.; Petkar, S. S.; Middleton, P. S.; McFarlane, W. *J. Am. Chem. Soc.* **2007**, *46*, 8502. (c) Sokolov, M. N.; Chubarova, E. V.; Peresypkina, E. V.; Virovets, A. V.; Fedin, V. P. *Russ. Chem. Bull.* **2007**, *56*, 220. (d) Boglio, C.; Micoine, K.; Remy, P.; Hasenknopf, B.; Thorimbert, S.; Lacote, E.; Malacria, M.; Afonso, C.; Tabet, J. C. *Chem.—Eur. J.* **2007**, *13*, 5426. (e) Fang, X. K.; Hill, C. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3877. (f) Kholdeeva, O. A.; Maksimovskaya, R. I. *J. Mol. Catal. A: Chem.* **2007**, *262*, 7. (g) Yamaguchi, S.; Kikukawa, Y.; Tsuchida, K.; Nakagawa, Y.; Uehara, K.; Yamaguchi, K.; Mizuno, N. *Inorg. Chem.* **2007**, *46*, 8502. (h) Kholdeeva, O. A.; Maksimov, G. M.; Maksimovskaya, R. I.; Vanina, M. P.; Trubitsina, T. A.; Naumov, D. Y.; Kolesov, B. A.; Antonova, N. S.; Carbo, J. J.; Poblet, J. M. *Inorg. Chem.* **2006**, *45*, 7224. (i) Carabineiro, H.; Villanneau, R.; Carrier, X.; Herson, P.; Lemos, F.; Ribeiro, F. R.; Proust, A.; Che, M. *Inorg. Chem.* **2006**, *45*, 1915. (j) Kato, C. N.; Shinohara, A.; Hayashi, K.; Nomiya, K. *Inorg. Chem.* **2006**, *45*, 8108.
(4) Hou, Y.; Fang, X.; Hill, C. L. *Chem.—Eur. J.* **2007**, *13*, 9442.
(5) (a) Canny, J.; Tézé, A.; Thouvenot, R.; Hervé, G. *Inorg. Chem.* **1986**, *25*, 2114. (b) Tézé, A.; Hervé, G. *Inorg. Synth.* **1990**, *27*, 88.
(6) Bassil, B. S.; Dickman, M. H.; Kortz, U. *Inorg. Chem.* **2006**, *45*, 2394.
(7) (a) Stanciu, C.; Jones, M. E.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 12400. (b) Chernyshev, B. N.; Didenko, N. A.; Bukvetskii, B. V.; Gerasimenko, A. V.; Kavun, V. Y.; Sergienko, S. S. *Zh. Neorg. Khim.* **1989**, *34*, 1594. (c) Schmidt, R.; Pausewang, G. *Z. Anorg. Allg. Chem.* **1986**, *535*, 135.
(8) Chernyshev, B. N.; Didenko, N. A.; Bakeeva, N. G.; Bukvetskii, B. V.; Gerasimenko, A. V. *Zh. Neorg. Khim.* **1991**, *36*, 1112.
(9) Recent examples include: (a) Hussain, F.; Bassil, B. S.; Kortz, U.; Kholdeeva, O. A.; Timofeeva, M. N.; de Oliveira, P.; Keita, B.; Nadjo, L. *Chem.—Eur. J.* **2007**, *13*, 4733. (b) Suzuki, H.; Hashimoto, M.; Okeya, S. *Eur. J. Inorg. Chem.* **2004**, 2632. (c) Sakai, Y.; Kitakoga, Y.; Hayashi, K.; Yoza, K.; Nomiya, K. *Eur. J. Inorg. Chem.* **2004**, 4646.
(10) Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.
(11) Abrahams, S. C.; Collin, R. L.; Lipscomb, W. N. *Acta Crystallogr.* **1951**, *4*, 15.

JA801424Q