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Synthesis and Structure of Asymmetric Zirconium-Substituted Silicotungstates, $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ and $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$

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The reaction of $ZrCl_4$ with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in a potassium acetate buffer results in two different products depending on the reactant ratios. The trimeric species $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ (**1**) consists of three β_{23}-$SiW_{10}O_{37}$ units linked by an unprecedented $Zr_6O_2(OH)_4(H_2O)_3$ cluster with C_1 point group symmetry. The dimeric species $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ (**2**) consists of β_{22}- and β_{12}-$SiW_{10}O_{37}$ units sandwiching a $Zr_4O_2(OH)_2(H_2O)_4$ cluster, which also has C_1 symmetry. Polyanion **1** contains more zirconium centers than any other polyoxometalate known to date.

Polyoxoanions or polyoxometalates (POMs) are a large class of inorganic compounds with highly interesting properties.[1] These properties may lead to applications in the fields of magnetism, catalysis, and nanotechnology.[2]

Zr-containing POMs have been one of the least reported types so far in the literature, despite the fact that Zr compounds have been useful as catalysts. The first Zr-containing POM, $[Si_2W_{18}Zr_3O_{71}H_3]^{11-}$ corresponding to a Knoth sandwich-type silicotungstate, was reported in 1989 by Finke et al.[3] In 1995, Meng and Liu reported a Zr^{4+}-substituted Wells−Dawson phosphotungstate, but they did not determine its structure.[4] Recently, the Wells−Dawson-based sandwich polyanion $[Zr_4(\mu_3\text{-}O)_2(\mu_2\text{-}OH)_2(H_2O)_4(P_2W_{16}O_{59})_2]^{14-}$ has been reported by Pope and co-workers.[5] Very recently, Hill and co-workers reported on the formation of chiral Zr-containing Wells−Dawson-type phosphotungstates functionalized with enantiomerically pure dicarboxylates: tartrate in $\{[\alpha\text{-}P_2W_{15}O_{55}(H_2O)]Zr_3(\mu_3\text{-}O)(H_2O)(tartH)[\alpha\text{-}P_2W_{16}O_{59}]\}^{15-}$ and malate in $[(\alpha\text{-}P_2W_{16}O_{59})Zr_2(\mu_3\text{-}O)(C_4O_5H_3)]_2^{18-}$.[6,7]

Recently, we have studied the reactivity of the dilacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with first-row transition metals in an aqueous acidic medium. We discovered that the decatungstosilicate precursor isomerizes easily at such conditions, especially when the reaction mixture is heated. We isolated a number of dimeric, trimeric, and tetrameric species with unexpected structures.[8] Now we decided to investigate the reactivity of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ with the early 4d transition-metal ion Zr^{IV}. Herein we report on two novel and asymmetric polyanion structures, the trimeric $[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]^{14-}$ (**1**) and the dimeric $[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]^{10-}$ (**2**).

Polyanion **1** was synthesized as follows: To 20 mL of a 1 M CH_3COOH/CH_3COOK buffer at pH 4.8 was added 0.76 g of KCl. After complete dissolution, 0.74 g of $ZrCl_4$ (1.58 mmol) followed by 0.5 g (0.18 mmol) of $K_8[\gamma\text{-}SiW_{10}O_{36}]$ was added. The solution was stirred for 30 min at 50 °C. Then it was cooled to room temperature and filtered. Evaporation of the solvent at room temperature resulted in needlelike crystals of $K_{14}[Zr_6O_2(OH)_4(H_2O)_3(\beta\text{-}SiW_{10}O_{37})_3]\cdot 28.5H_2O$ (**K-1**; 0.10 g, yield 18%) after ~2 weeks, suitable for X-ray diffraction,[9] Fourier transform IR (FTIR) spectroscopy,[10] and elemental analysis.[11]

The synthesis procedure for polyanion **2** was identical with that of **1**, except 0.37 g of $ZrCl_4$ (0.79 mmol) was used. Evaporation of the solvent at room temperature resulted in needlelike crystals of $K_{10}[Zr_4O_2(OH)_2(H_2O)_4(\beta\text{-}SiW_{10}O_{37})_2]\cdot$

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(2) (a) *Polyoxometalates: from Platonic Solids to Anti Retroviral Activity*; Pope, M. T., Müller, A., Eds.: Kluwer: Dordrecht, The Netherlands, 1994. (b) *Chem. Rev.* **1998**, *98*, 1−389 (Special Thematic Issue on Polyoxometalates). (c) *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Pope, M. T., Müller A., Eds.; Kluwer: Dordrecht, The Netherlands, 2001. (d) *Polyoxometalate Chemistry for Nano-Composite Design*; Yamase, T.. Pope, M. T., Eds.; Kluwer: Dordrecht, The Netherlands, 2002.

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10.1021/ic052131c CCC: \$33.50

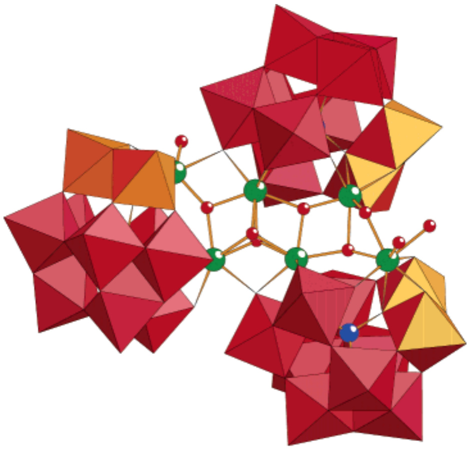

Figure 1. Combined polyhedral/ball-and-stick representation of **1**. The color code is as follows: WO_6 (red), WO_6 of the β-rotated triads (orange), Si (blue), Zr (green), and O (red).

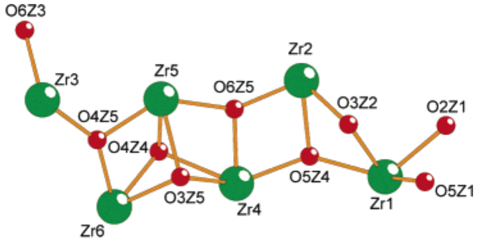

Figure 2. Ball-and-stick representation of the $Zr_6O_2(OH)_4(H_2O)_3$ cluster in **1**. Oxygens O4Z4, O3Z5, O3Z2, and O5Z4 are monoprotonated.

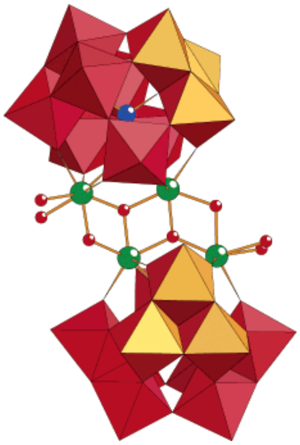

Figure 3. Combined polyhedral/ball-and-stick representation of **2**. The color code is the same as that in Figure 1.

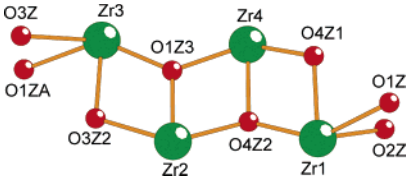

Figure 4. Ball-and-stick representation of the $Zr_4O_2(OH)_2(H_2O)_4$ cluster in **2**. Oxygens O3Z2 and O4Z1 are monoprotonated.

$22H_2O$ (**K-2**; 0.11 g, yield 20%) after ~2 weeks, suitable for X-ray diffraction,[12] FTIR spectroscopy,[13] and elemental analysis.[14]

The structures of **1** and **2** consist of (β-$SiW_{10}O_{37}$) units connected by a protonated[15] zirconium(IV) oxo cluster containing seven- and eight-coordinated Zr^{4+} ions. All Zr centers are linked via oxo bridges to three different WO_6 octahedra and to a SiO_4 hetero group. Polyanions **1** and **2** are synthesized by reacting $ZrCl_4$ with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in a 1 M CH_3COOH/CH_3COOK buffer with enough KCl added to bring the total K^+ concentration to 1 M. Excess Zr^{4+} seems to be required for the reactions.

The reaction of Zr^{4+} ions with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ in a 8:1 ratio resulted in **1**. This polyanion consists of three β-$SiW_{10}O_{37}$ units connected by a $Zr_6O_2(OH)_4(H_2O)_3$ cluster, unprecedented in POM chemistry (see Figure 1).

In **1**, there are three seven-coordinated Zr^{4+} centers (Zr1, Zr2, and Zr3) and three with a coordination number of eight (Zr4, Zr5, and Zr6); see Figure 2. These two types of Zr^{4+} ions are asymmetrically distributed within the Zr_6 cluster. The two outer zirconium ions Zr1 and Zr3 are seven-coordinated, but Zr1 has two terminal water molecules while Zr3 has only one. Thus, **1** has idealized point group symmetry C_1 and is therefore chiral. The three eight-coordinated zirconium ions Zr4, Zr5, and Zr6 are centrally linked via two μ_3-OH bridges (O4Z4 and O3Z5). Another μ_3-O bridge (O4Z5) links Zr5 and Zr6 to the outer Zr3. Then, Zr2 is linked via a μ_3-O bridge (O6Z5) to the two eight-coordinated Zr5 and Zr4, via a μ_2-OH bridge (O3Z2) to the outer Zr1, and via another μ_3-OH bridge (O5Z4) to Zr1 and Zr4.

The structure of **2** corresponds to two β-$SiW_{10}O_{37}$ units sandwiching a $Zr_4O_2(OH)_2(H_2O)_4$ cluster (see Figure 3). The two outer zirconium ions Zr1 and Zr3 have a coordination number of eight, while the two inner ones Zr2 and Zr4 have a coordination number of seven (see Figure 4). Zr2 and Zr4 are connected by two μ_3-O bridges (O1Z3 and O4Z2), and at the same time, they are connected to Zr1 and Zr3 by a μ_2-OH bridge (O3Z2 and O4Z1, respectively). This Zr cluster has a pseudo-inversion center. In fact, it resembles the one present in Hill's chiral $[(\alpha\text{-}P_2W_{16}O_{59})Zr_2(\mu_3\text{-}O)(C_4O_5H_3)]_2^{18-}$, where the water molecules and the μ_2-OH bridges replace the O atoms of the malate ligand.[6] Polyanion **2** has idealized point group symmetry C_1 because the two β-$SiW_{10}O_{37}$ units are different isomers (vide infra).

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(9) Crystal data for **K-1**: $H_{67}K_{14}O_{148.5}Si_3W_{30}Zr_6$, $M = 9138.2$, triclinic, space group $P\bar{1}$, $a = 12.7321(9)$ Å, $b = 20.865(2)$ Å, $c = 29.018(3)$ Å, $\alpha = 98.802(3)°$, $\beta = 94.962(4)°$, $\gamma = 96.489(3)°$, $V = 7527.0(12)$ Å^3, $Z = 2$, $T = 173$ K, $D_{calc} = 3.933$ Mg/m^3, $\mu = 23.62$ mm^{-1}, 130 102 measured and 32 749 unique reflections ($R_{int} = 0.1609$), final R1 = 0.125 for 19 576 observations with $F_o > 4\sigma(F_o)$, and R1 = 0.183 (wR2 = 0.372) for all unique data.

(10) IR for **K-1**: 995 (w), 956 (m), 889 (s), 781 (s), 668 (w), 503 (w), 455 (sh) cm^{-1}.

(11) Anal. Calcd (found) for **K-1**: K, 6.0 (5.8); Zr, 6.0 (6.2); W, 60.4 (59.3); Si, 0.9 (1.1).

(12) Crystal data for **K-2**: $H_{54}K_{10}O_{104}Si_2W_{20}Zr_4$, $M = 6207.6$, orthorhombic, space group $Pna2_1$, $a = 39.789(2)$ Å, $b = 19.7049(8)$ Å, $c = 12.9402(4)$ Å, $V = 10145.6(7)$ Å^3, $Z = 4$, $T = 173$ K, $D_{calc} = 4.03$ Mg/m^3, $\mu = 23.51$ mm^{-1}, 111 568 measured and 18 731 unique reflections ($R_{int} = 0.148$), final R1 = 0.060 for 14 722 observations with $F_o > 4\sigma(F_o)$, R1 = 0.082 (wR2 = 0.158) for all unique data, and Flack parameter = −0.029(12).

(13) IR for **K-2**: 990 (w), 951 (m), 897 (s), 891 (sh), 785 (s), 711 (w), 684 (w), 625 (w), 527 (w) cm^{-1}.

(14) Anal. Calcd (found) for **K-2**: K, 6.3 (6.0); Zr, 5.9 (5.6); W, 59.2 (59.8); Si, 0.9 (1.2).

(15) Protonation was estimated using bond valence sum calculations. See: Brown, I. D.; Altermatt, D. *Acta Crystallogr., Sect. B* **1985**, *41*, 244.

A few years ago, Kortz et al. reported a structurally similar Ni_4 cluster incorporated in $[\{\beta\text{-}SiW_{10}Ni_2O_{36}(OH)_2(H_2O)\}_2]^{12-}$, but in this polyanion, the Ni^{2+} ions are six-coordinated.[8a] Interestingly, this Ni-containing silicotungstate was also synthesized with $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$.

Polyanions **1** and **2** have the same ratio of Zr ions to $\beta\text{-}SiW_{10}O_{37}$ units (2:1). However, **1** is synthesized using a Zr^{4+} to $\beta\text{-}SiW_{10}O_{36}$ ratio of 8:1, whereas **2** is synthesized using a ratio of 4:1. Close inspection of the structures indicates that **1** cannot simply be considered as an extended derivative of **2** by grafting of an additional $Zr_2(\beta\text{-}SiW_{10}O_{37})$ unit, for the following two reasons:

(i) The positions of the seven- and eight-coordinated Zr^{4+} centers are different in **1** versus **2**.

(ii) The $\beta\text{-}SiW_{10}O_{37}$ units in **1** and **2** represent different rotational isomers.

In Figures 1 and 3, the rotated W_3O_{13} triads are shown in orange in order to highlight the isomerization of the respective $\beta\text{-}SiW_{10}O_{37}$ units. In **1**, there are three $\beta_{23}\text{-}SiW_{10}O_{37}$ units (one WO_6 octahedron taken from the "belt" and one from the rotated triad). On the other hand, polyanion **2** is formed from a $\beta_{22}\text{-}SiW_{10}O_{37}$ unit (both WO_6 octahedra taken from the belt) and a $\beta_{12}\text{-}SiW_{10}O_{37}$ unit (one WO_6 octahedron from the belt and one from the nonrotated triad). Kortz et al. have already encountered the β_{23} unit in $[\{\beta\text{-}SiW_{10}Ni_2O_{36}(OH)_2(H_2O)\}_2]^{12-}$ and interestingly a β_{13} unit in $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$.[8a,c] The diversity found for these $\beta\text{-}SiW_{10}O_{37}$ isomers reiterates the metastable nature of the $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ precursor when interacting with transition-metal ions in aqueous solution.

In summary, we have synthesized and structurally characterized the trimeric, Zr_6-containing silicotungstate **1** and the dimeric, Zr_4-containing silicotungstate **2**. Both polyanions are chiral and **1** contains more zirconium centers than any other polyoxometalate known to date.

In future work, we plan to study the solution properties of **1** and **2** by NMR and electrochemistry. Furthermore, the accessible nature of the outer Zr centers in **1** and **2** via terminal water ligands may allow for binding of a variety of bidentate ligands. In this project, we are particularly interested in amino acids for biological applications and in peroxide for catalytic applications. This work is currently in progress, and results will be reported in due time.

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Supporting Information Available: X-ray crystallographic data for **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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