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Cyclic Ti_9 Keggin Trimers with Tetrahedral (PO_4) or Octahedral (TiO_6) Capping Groups[†]

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We have synthesized the cyclic Ti_9 Keggin trimers $[(\alpha\text{-}Ti_3PW_9O_{38})_3(PO_4)]^{18-}$ (**1**) and $[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$ (**2**), which are both composed of three ($Ti_3XW_9O_{37}$) units (X = P or Si) linked via three Ti−O−Ti bridges and a capping group, which is either tetrahedral PO_4 (**1**) or octahedral TiO_6 (**2**). Polyanions **1** and **2** were fully characterized in the solid state (IR, X-ray diffraction, thermogravimetric and elemental analyses) and in solution (^{31}P or ^{183}W NMR).

By now, polyoxometalates (POMs) represent a well-known class of discrete, molecular metal oxides, which are attractive because of a large structural and compositional variety combined with a multitude of properties.[1] Vacant (lacunary) polytungstate precursors allow for the incorporation of a vast number of electrophiles including transition metals, rare earths, main-group elements, organometallic and organic groups. The resulting products often have properties that render them of interest for potential applications in different areas such as catalysis, medicine, and materials science.[2]

The discovery of the titanium-based Ziegler−Natta catalysts in the 1960s strongly introduced this element into the world of catalysis. At the present time, titanium-containing molecular sieves are regarded among the best heterogeneous catalysts for selective oxidations. This also contributed to the interest in Ti^{IV}-containing polytungstates, which can be viewed as discrete molecular, soluble fragments of extended metal oxide lattices and thus can serve as homogeneous probes for the widely employed heterogeneous catalysts.[3] In addition, Ti^{IV}-POMs have shown catalytic efficiency toward oxidation reactions of organic substrates based on H_2O_2, an environmentally benign (green) oxidant.[4]

The ionic radius of octahedrally oxo-coordinated Ti^{IV} is close to that of W^{VI}, implying that the former fits well into the vacant site(s) of lacunary polytungstates. Substitution of W^{VI} by the lower-valent Ti^{IV} leads to an increase in the basicity of the POM and thus a tendency to oligomerize through intermolecular Ti−O−Ti bond formation.

The structures of Ti^{IV}-containing polytungstates reported so far in the literature include dimeric and tetrameric species as well as mono-, di-, and tri-substituted monomers.

A family of mixed Ti−W Keggin derivatives has been discovered, such as the monomeric species $\alpha\text{-}[Ti_2PW_{10}O_{40}]^{7-}$ (Knoth et al., 1983),[5] or the dimeric species based on the β- or $\alpha\text{-}[Ti_3XW_9O_{40}]$ subunit (X = Si, Lin et al., 1993;[6] X = P, Nomiya et al., 2001,[7] respectively). The cyclic tetrameric $[\{\beta\text{-}Ti_2SiW_{10}O_{39}\}_4]^{24-}$ was reported by our group in 2004.[8] In 2003, our group prepared the dimeric Wells−Dawson derivative $[(TiP_2W_{15}O_{55}OH)_2]^{14-}$, and we also determined the structure of Nomiya's and Finke's tetrameric $[\{Ti_3P_2W_{15}O_{57.5}(OH)_3\}_4]^{24-}$.[9] The latter system has been further investigated by the Nomiya group, resulting in $[(\alpha\text{-}1,2,3\text{-}P_2W_{15}Ti_3O_{62})_4\{\mu_3\text{-}Ti(OH)_3\}_4Cl]^{45-}$ in 2003[10] and in the heteropolyacid $H_8[Ti_2\{P_2W_{15}O_{54}(OH_2)_2\}_2]$ in 2007.[11]

[†] Dedicated to Prof. Gilbert Hervé on the occasion of his retirement.

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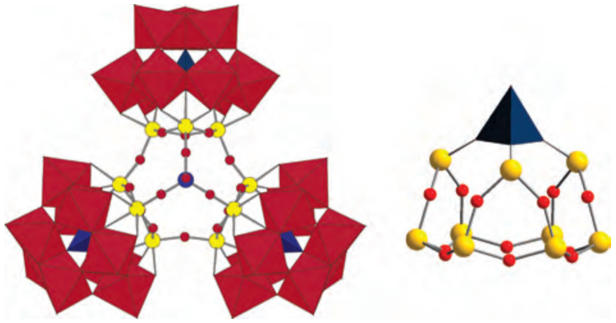

Figure 1. Left: Combined polyhedral/ball-and-stick representation of polyanion **1** in a top-down view along the 3-fold rotation axis. Right: Side view onto the central Ti_9 cage of **1**, which is capped with a tetrahedral PO_4 group as shown. Color code: WO_6 octahedra (red), PO_4 tetrahedra (blue), P (blue), Ti (yellow), and O (red).

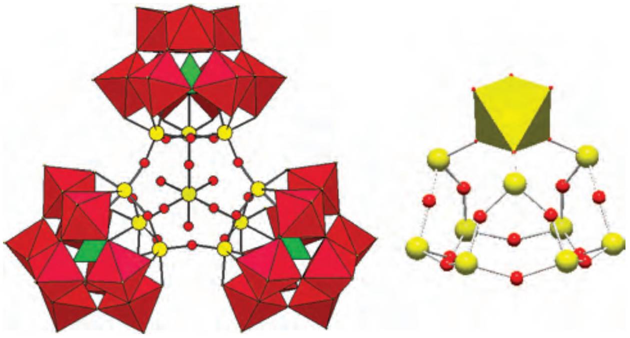

Figure 2. Left: Combined polyhedral/ball-and-stick representation of polyanion **2** in a top-down view along the 3-fold rotation axis. Right: Side view onto the central Ti_9 cage of **2**, which is capped with an octahedral TiO_6 group as shown. Color code: WO_6 octahedra (red), SiO_4 tetrahedra (green), TiO_6 octahedron (yellow), Ti (yellow), and O (red).

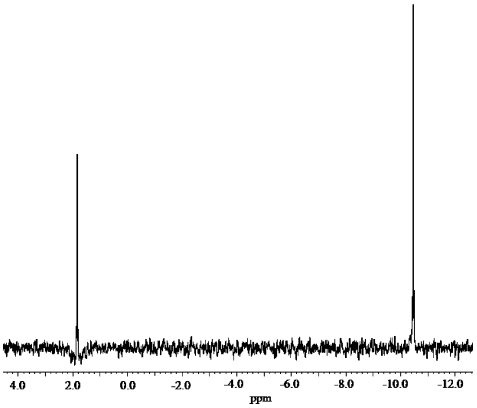

Figure 3. Room temperature ^{31}P NMR spectrum of **RbK-1** redissolved in a D_2O-H_2O mixture.

Here we report on the first examples of trimeric Ti^{IV}-containing polyanions. The cyclic Ti_9 Keggin trimers $[(\alpha\text{-}Ti_3PW_9O_{38})_3(PO_4)]^{18-}$ (**1**; see Figure 1) and $[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]^{17-}$ (**2**; see Figure 2) are both composed of three $(Ti_3XW_9O_{37})$ units linked via three Ti−O−Ti bridges and a capping group, which is either tetrahedral PO_4 (in **1**) or octahedral TiO_6 (in **2**).

Polyanion **1** was prepared by the addition of 0.035 g (0.22 mmol) of $TiOSO_4$ to 20 mL of a 1 M potassium acetate buffer (pH 4.8), followed by 0.565 g (0.10 mmol) of $K_{14}[P_2W_{19}O_{69}(H_2O)]\cdot 24H_2O$ (prepared according to the published procedure).[12] The reaction mixture was heated with stirring for 1 h at 80 °C, cooled to room temperature, and then filtered. Polyanion **1** was isolated as the mixed rubidium−potassium salt $K_{11}Rb_7[(\alpha\text{-}Ti_3PW_9O_{38})_3(PO_4)]\cdot 28H_2O$ (**RbK-1**). Colorless single crystals suitable for X-ray analysis were obtained by layering the solution with a few drops of a 1 M RbCl solution and allowing the solvent to evaporate in an open container at room temperature for about 1 week (yield 0.046 g, 22% based on Ti).[13] We subjected **RbK-1** also to Fourier transform infrared (FTIR) spectroscopy,[14] elemental analysis,[15] ^{31}P NMR studies (see Figure 3), and thermogravimetric analysis (TGA), which showed a 5.7% mass loss up to 222 °C corresponding to about 28 water molecules of hydration (see Figure S1 in the Supporting Information). Bond valence sum (BVS) calculations confirmed that **1** is not protonated.[16]

Polyanion **1** consists of three (A-α-PW_9O_{34}) Keggin units all substituted by three corner-shared TiO_6 octahedra and then linked to each other on one side by three Ti−O−Ti bridges and on the other side by a tetrahedral PO_4 cap. Thereby, three O atoms of the PO_4 moiety act as bridges to the Keggin units with P−O distances of 1.57(3) Å. The fourth P−O bond is terminal and points away from the center of the molecule with a bond length of 1.40(5) Å (see Figure 1). Polyanion **1** has nominal C_{3v} symmetry, and the ^{31}P NMR spectrum is fully consistent with this because it exhibits the expected two singlets at −10.5 and 1.8 ppm, respectively (see Figure 3). The upfield signal is attributed to the phosphate hetero groups of the three Keggin units, and the downfield signal must, hence, correspond to the capping phosphate moiety.[17]

We also tried to prepare **1** via a more rational synthetic procedure, e.g., by reacting 3 equiv of $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ with 9 equiv of $TiOSO_4$ and 1 equiv of PO_4^{3-}. However, all of these attempts were unsuccessful.

In the solid state, **1** is stabilized by four Rb^+ countercations, which are closely associated with the polyanion (see Figure S3 in the Supporting Information). One of the Rb^+ ions is located on the 3-fold axis of **1** opposite the capping phosphate group. The other three Rb^+ ions occupy the space in between the

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(13) Crystallographic data of **RbK-1**: $H_{56}K_{11}O_{146}P_4Rb_7Ti_9W_{27}$, $M = 8939.4$, rhombohedral, space group $R3m$ (hexagonal setting) with $a = 29.7444(7)$ Å and $c = 13.6254(9)$ Å, $V = 10439.8(8)$ Å^3, $Z = 3$, $T = 173$ K, $D_{calc} = 4.003$ Mg/m^3, $\mu = 24.51$ mm^{-1}, 116 147 total reflections, 5630 unique [R(int) = 0.18], final R1 = 0.064 for 4707 observations with $F_0 > 4\sigma(F_0)$, and wR2 = 0.185 for all data.

(14) IR for **RbK-1**: 1049 (s), 1018 (sh), 997 (m), 931 (m), 911 (m), 872 (w), 826 (s), 761 (s), 651 (w), 578 (vw), 508 (m), 452 (w) cm^{-1}.

(15) Anal. Calcd (found) for **RbK-1**: P, 1.4 (1.1); W, 55.5 (54.8); Ti, 4.8 (4.2); Rb, 6.7 (7.1); K, 4.8 (4.6).

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(17) The ratio of the integrated peak areas at −10.5 and 1.8 ppm is 3:1.7 rather than the expected 3:1, which could be due to different relaxation rates of the two types of P nuclei. Further investigations are currently underway.

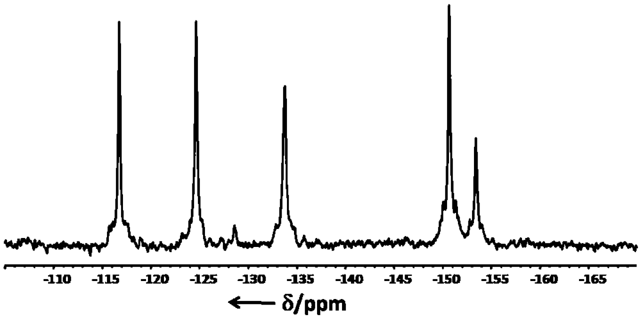

Figure 4. Room temperature ^{183}W NMR spectrum of **Na-2** in a D_2O-H_2O mixture.

neighboring Keggin units. The Rb−O bond lengths are in the range 2.830(16)−3.271(18) Å.

For the synthesis of polyanion **2**, a solution of titanium(IV) oxide sulfate was prepared by dissolving 2.56 g of $TiOSO_4$ (16 mmol) in 106 mL of water at 32 °C. This solution was reacted with $[\{K(H_2O)_2\}\alpha\text{-}Si_2W_{18}O_{66}]^{15-}$,[18] which was formed in situ by acidifying a solution of $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]\cdot 13H_2O$ to pH 6 with 1 M HCl. The latter was prepared by dissolving 15.45 g (5.33 mmol) in 424 mL of water. To the mixture (pH 2.1) was added 9 g of CsCl. The cesium salt thus formed was isolated and then recrystallized from a 0.7 M sodium chloride solution in moderate yield (~3.3 g, 20% based on Ti). Colorless crystals of $Cs_{11}K_{0.5}Na_{5.5}[(\alpha\text{-}Ti_3SiW_9O_{37}OH)_3(TiO_3(OH_2)_3)]\cdot 70H_2O$ (**CsKNa-2**) suitable for X-ray analysis were obtained.[19] We subjected **CsKNa-2** also to FTIR,[20] elemental analysis,[21] and ^{183}W NMR studies (see Figure 4). TGA allowed us to determine the number of crystal waters in **CsKNa-2** (see Figure S2 in the Supporting Information).

Polyanion **2** (see Figure 2) exhibits a structure very similar to that of **1**. The main differences are (i) the hetero element in **2** is Si instead of P in **1** and (ii) the capping group in **2** is octahedral TiO_6 instead of tetrahedral PO_4 in **1**. BVS calculations (vide supra) indicated that the three facial, terminal ligands of the octahedral TiO_6 group pointing away from the center of the molecule are actually water molecules [$Ti-O_{aqua} = 2.161(7)$ Å]. On the other hand, the three O atoms of the TiO_6 group bridging to the Keggin units have much shorter Ti−O distances of 1.800(4) Å.

The octahedral, capping TiO_6 group in **2** with its three accessible, facial and substitution-labile aqua ligands is highly attractive for oxidation catalysis. We have demonstrated recently that titanium is significantly more effective toward H_2O_2-based olefin oxidations when it has one or more terminal Ti−OH ligands because the latter allow the active hydroperoxo intermediate to form.[22]

BVS calculations on **2** also demonstrated that one of the three bridging Ti−O−Ti oxygen atoms in each Keggin unit is monoprotonated (unlike for **1**, which is not protonated). However, this is expected because **2** was synthesized in a more acidic medium than **1** (pH 2 for **2** rather than pH 4.8 for **1**).

Polyanion **2** was also structurally characterized in solution by ^{183}W NMR. Such measurements were carried out on the sodium salt of **2**, obtained from **CsKNa-2** by cationic exchange using a strongly acidic Na^+ resin (Dowex 50-80). The purity of **Na-2** was verified in the solid state by IR and in solution by polarography (see Figures S6−S8 in the Supporting Information). The ^{183}W NMR spectrum of **Na-2** in a D_2O-H_2O solution consists of five well-resolved resonances at −116.7, −124.7, −133.8, −150.7, and −153.4 ppm (relative intensities 2:2:2:2:1); see Figure 4. These results are fully consistent with the solid-state structure of **2**, suggesting nominal C_{3v} symmetry for this anion.

Also polyanion **2** interacts in the solid state with four closely associated countercations, but this time Cs^+ rather than Rb^+ (see Figure S4 in the Supporting Information). However, the positions of these countercations are essentially identical in **1** and **2**. In **2**, the central Cs^+ is drawn deeper into the center of the polyanion (because of a larger opening) than the central Rb^+ in the case of **1**.

In summary, we report on the synthesis and structure of the two polyanions, **1** and **2**, that represent the first examples of trimeric Ti-containing polytungstates. Polyanion **1** is based on PW_9O_{34} Keggin units with a tetrahedral PO_4 cap, while **2** is based on SiW_9O_{34} Keggin units with an octahedral TiO_6 cap. The novel polyanions as well as their hydrated salts were characterized by various analytical techniques including X-ray diffraction, FTIR, TGA, and NMR. Electrochemistry, electrocatalysis, and homogeneous oxidation catalysis studies for **1** and **2** will be performed in the near future. It is worth mentioning that the subtle structural differences between **1** and **2** should also be reflected in their respective catalytic behavior, thus leading to a better understanding of the role played by molecular Ti centers in catalysis. We have already isolated the Ge analogue of **1** and also its tetrameric derivative composed of four (Ti_3GeW_9) units arranged in a tetrahedral fashion and fused via Ti−O−Ti bonds. Because both polyanions form at very similar reaction conditions, we are currently in the process of optimizing the respective synthesis conditions. These results will be presented elsewhere.

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Supporting Information Available: Combined X-ray crystallography file (CIF) and thermograms (Figures S1 and S2) for **RbK-1** and **CsKNa-2**, representations of **1** and **2** showing the four closely associated Rb^+ or Cs^+ countercations (Figures S3 and S4), IR spectra of **RbK-1** (Figure S5), **CsKNa-2** (Figure S6), and **Na-2** (Figure S7), and polarograms of redissolved **CsKNa-2** and **Na-2** (Figure S8). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Laronze, N.; Marrot, J.; Hervé, G. *Chem. Commun.* **2003**, 2360.

(19) Crystallographic data of **CsKNa-2**: $H_{149}Cs_{11}K_{0.5}Na_{5.5}O_{190}Si_3Ti_{10}W_{27}$, $M = 10325.0$, trigonal, space group $R3m$, $a = 30.3253(11)$ Å and $c = 15.8808(14)$ Å, $V = 12647.7(13)$ Å^3, $Z = 3$, $T = 293$ K, $D_{calc} = 3.660$ Mg/m^3, $\mu = 21.374$ mm^{-1}, 89 174 total reflections, 8660 unique [$R(\text{int}) = 0.0426$], final R1 = 0.026 with $F_0 > 4\sigma(F_0)$, and wR2 = 0.094 for all data.

(20) IR for **CsKNa-2**: 999 (m), 954 (s), 910 (s), 880 (sh), 789 (s), 711 (s), 523 (m), 495 (sh), 389 (sh), 365 (s), 327 (w) cm^{-1}.

(21) Anal. Calcd (found) for **Cs-2**: Si, 0.8 (0.9); W, 48.1 (47.7); Ti, 4.6 (4.3); Cs, 14.1 (13.7); Na, 1.2 (1.2); K, 0.2 (0.2).

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