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Bis[tetraruthenium(IV)]-Containing Polyoxometalates: $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2Sb_2W_{20}O_{68}(OH)_2]^{4-}$ and $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2\{Fe(H_2O)_2\}_2\{\beta\text{-}TeW_9O_{33}\}_2H]^{-}$

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Supporting Information

ABSTRACT: The reaction of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ and $[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{4-}$ with $(NH_4)_2[RuCl_6]$ in aqueous solution resulted in the novel ruthenium(IV)-containing polyanions $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2Sb_2W_{20}O_{68}(OH)_2]^{4-}$ and $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2\{Fe(H_2O)_2\}_2\{\beta\text{-}TeW_9O_{33}\}_2H]^{-}$, exhibiting two cationic, adamantane-like, tetraruthenium(IV) units $\{Ru_4O_6(H_2O)_9\}^{4+}$ bound to the respective polyanion in an external, highly accessible fashion.

Polyoxometalates (POMs) exhibit a unique structural and compositional variety and much potential for applications in catalysis, materials science, and bioinorganic, analytical, and medicinal chemistry, and this explains the constantly increasing interest in this research area.[1] In particular, vacant (or lacunary) POMs have attracted special attention because they are thermally and oxidatively robust, inorganic ligands able to incorporate various numbers of oxophilic heterometal ions in many different ways, leading to a virtually unlimited structural diversity.[1,2] Among all lacunary polytungstates, those containing central heteroatoms with a stereochemically active lone pair (e.g., As^{III}, Sb^{III}, Bi^{III}, Sn^{II}, Se^{IV}, and Te^{IV}) are particularly attractive ligands.[1,3]

In 1997, Krebs and co-workers reported the 22-tungsto-2-antimonate(III) $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ comprising two trilacunary Keggin-type $\{\beta\text{-}Sb^{III}W_9O_{33}\}^{9-}$ units linked via a belt of two internal $\{WO_2\}^{2+}$ and two external $\{WO_2(OH)\}^{+}$ groups,[4a] and later the Bi^{III} analogue was also reported.[4b] The groups of Krebs and Pope also demonstrated that the two external W^{VI} centers in such structures can be easily substituted by various first-row transition-metal ions, resulting in the large polyanion family $[(WO_2)_2M_2(H_2O)_6(\beta\text{-}XW_9O_{33})_2]^{n-}$ ($X = Sb^{III}, Bi^{III}$; $M^{n+} = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, VO^{2+}$),[3a,4,5a−c] and $[(WO_2)_2(WO_2(OH))_{0.5}Sn_{1.5}(\beta\text{-}XW_9O_{33})_2]^{10.5-}$ ($X = Sb^{III}, Bi^{III}$).[5d] Then Krebs' and our groups showed that derivatives of this structural type can be prepared with all internal and external tungsten ions replaced by transition-metal ions, leading to $[M_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2]^{n-}$ ($X = As^{III}, Sb^{III}, Se^{IV}, Te^{IV}$; $M = Fe^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, In^{3+}$),[3a,5f−h] or with two external and only one internal tungsten being substituted, $[(WO_2)M_3(H_2O)_8(TeW_9O_{33})_2]^{8-}$ ($M = Co^{2+}, Ni^{2+}$).[5e]

Amongst the transition metals, ruthenium is a highly interesting element, due to its multiple oxidation states, redox properties and reactivity. However, until recently the main focus in Ru-POM chemistry has been on compounds containing ruthenium in low oxidation states such as 2+ and 3+, especially on organoruthenium(II)-containing polyanions.[6] An example is the organoruthenium(II) POM family $[X_2W_{20}O_{70}(Ru^{II}L)_2]^{10-}$ ($X = Sb^{III}, Bi^{III}$), with the two $Ru^{II}L$ groups (L = benzene, *p*-cymene) in the external positions.[7a,b] The dimethyl sulfoxide (DMSO) derivative $[Sb_2W_{20}O_{68}(H_2O)_2\{Ru^{III}(DMSO)_3\}_2]^{4-}$ is also known.[7c]

To date, only a handful of structurally characterized ruthenium(IV)-containing polyanions have been reported.[8,9] This area received major attention in 2008, when three research groups reported essentially the same compound at the same time. The groups of Bonchio and Hill independently prepared $[Ru^{IV}{}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$, where the cationic $\{Ru^{IV}{}_4(\mu\text{-}O)_4(\mu\text{-}OH)_2\}^{6+}$ unit with an adamantane-like structure is sandwiched between two decatungstosilicate units $\{\gamma\text{-}SiW_{10}O_{36}\}$,[9a,b] whereas Mizuno's group independently prepared the structural analogue $[Ru^{IV}{}_4(\mu\text{-}O)_2(\mu\text{-}OH)_4Cl_4(\gamma\text{-}SiW_{10}O_{36})_2]^{12-}$.[9c] Interestingly, $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ was shown to be one of the most active, and robust, water oxidation catalysts.[9]

We were inspired by the above work and therefore decided to try and merge the chemistries of $\{X_2W_{22}O_{74}(OH)_2\}$ and $\{M_4(H_2O)_{10}(\beta\text{-}XW_9O_{33})_2\}$ with that of Ru^{IV} ions.

Herein we report on the synthesis and structural characterization of two novel tetraruthenium(IV)-containing heteropolytungstates, $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2Sb_2W_{20}O_{68}(OH)_2]^{4-}$ (**1**; Figure 1) and $[\{Ru^{IV}{}_4O_6(H_2O)_9\}_2\{Fe(H_2O)_2\}_2\{\beta\text{-}TeW_9O_{33}\}_2H]^{-}$ (**2**; Figure 2), isolated as the hydrated ammonium salts $(NH_4)_4$**1**$\cdot 42H_2O$ (**NH$_4$-1**) and (NH_4)**2**$\cdot 36H_2O$ (**NH$_4$-2**). Polyanions **1** and **2** were synthesized by the reaction of $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$ and $[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]^{4-}$, respectively, with $(NH_4)_2[RuCl_6]$ in an aqueous acidic medium at pH 1.5 (at pH values 2−5, we obtained insoluble precipitates of unknown composition).[10] Both reactions require heating of the reaction mixture in an oil bath, at 90 °C for polyanion **1** and at 110 °C for **2**, because no interaction between the reagents was observed at lower temperature. The exact temperature conditions were identified based on optimal yields of **NH$_4$-1** and **NH$_4$-2**. Because of the low solubility of the ammonium salts of **1** and **2**, probably due to their very small negative charge, the reaction mixtures should be filtered while hot, best right after heating. At times, the

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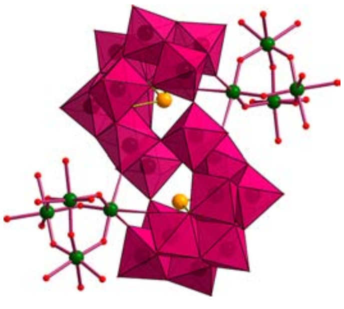

Figure 1. Combined polyhedral/ball-and-stick representation of **1**. Color legend: WO_6, pink octahedra; Sb, orange balls; Ru, green balls; O, red balls.

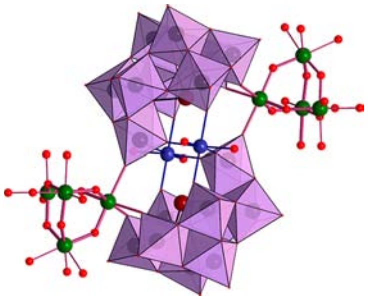

Figure 2. Combined polyhedral/ball-and-stick representation of **2**. Color legend: WO_6, lilac octahedra; Te, brown balls; Fe, blue balls; Ru, green balls; O, red balls.

synthesis of **NH$_4$-1** resulted also in an unidentified byproduct that could not be easily distinguished from the black, fine crystalline material of **NH$_4$-1**. Therefore, only large crystals (>0.2 mm) of **NH$_4$-1** should be collected, in order to prevent impurities in the bulk sample of **NH$_4$-1**. On the other hand, we did not observe any such problems during the synthesis of **NH$_4$-2**.

Single-crystal X-ray diffraction analysis on **NH$_4$-1** revealed that polyanion **1** is closely related to Krebs' 22-tungsto-2-antimonate(III), $[Sb_2W_{22}O_{74}(OH)_2]^{12-}$, but with the two external $\{WO_2(OH)\}^+$ groups replaced by two tetraruthenium(IV) units $\{Ru_4O_6(H_2O)_9\}^{4+}$, leading to a structure with idealized C_{2h} point group symmetry (Figure 1). The two $\{Ru_4\}$ units are crystallographically equivalent and exhibit an adamantane-like structure and bond lengths similar to that observed in the water oxidation catalysts $[Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ and $[Ru_4(\mu\text{-}O)_5(\mu\text{-}OH)(H_2O)_4(\gamma\text{-}PW_{10}O_{36})_2]^{9-}$.[8e,9a−c] However, in **1**, the $\{Ru_4\}$ units are linked to the polyoxotungstate fragment by only one of the four Ru^{IV} ions, via three Ru−O(W) bridges [Ru−O 2.099(11)−2.144(11) Å]. The remaining three Ru^{IV} ions complete their coordination sphere via three terminal aqua ligands [Ru−O 2.107(14)−2.216(12) Å]. The four octahedrally coordinated Ru^{IV} ions in each $\{Ru_4\}$ motif are connected via six oxo bridges [Ru−O 1.830(11)−1.889(11) Å; Ru···Ru 3.389(2)−3.463(2) Å], which are all nonprotonated, according to bond valence sum (BVS) calculations (for details, see the Supporting Information, SI).[10] This is in marked contrast to the aforementioned $\{Ru_4X_2W_{20}\}$ (X = Si, P).[8e,9a−c] The Sb−O and W−O bond lengths in **1** are within the usual ranges (see Table S2 in the SI).

On the basis of BVS calculations,[11] one of the two protons in **1** is disordered over the four terminal O atoms of the two internal $\{WO_2\}^{2+}$ groups. The second proton is disordered over the two equivalent μ_2-O-(Ru,W) atoms (see the SI for details).

The structure of polyanion **2** is very similar to that of **1**, but the two internal $\{WO_2\}^{2+}$ groups are replaced by $\{Fe(H_2O)_2\}^{3+}$ units [Fe−O(W) 1.950(12)−1.999(11) Å; Fe−OH_2 2.046(12)−2.053(12) Å]. Both Fe^{3+} ions have an octahedral coordination environment (Figure 2). In analogy to **1**, none of the μ_3-oxo bridges in the $\{Ru_4\}$ motifs of **2** is protonated, and the single proton on **2** is disordered over the two equivalent μ_2-O-(Ru,W) atoms (see the SI for details). The bond lengths within the $\{Ru_4\}$ units of **2** are in the ranges 1.825(13)−1.869(13) Å for Ru−$O_{terminal}$, 1.853(11)−1.885(11) Å for Ru−O(W), and 2.089(11)−2.199(13) Å for Ru−OH_2. The Ru···Ru distances are in the range of 3.391(2)−3.444(2) Å, and the Te−O and W−O bond lengths are provided in Table S2 (see the SI). The bulk composition of **NH$_4$-1** and **NH$_4$-2** was established based on elemental analysis and thermogravimetric analysis (TGA; Figures S1 and S2 in the SI).

In summary, we have synthesized and structurally characterized the two novel, discrete, high-valent, ruthenium(IV)-containing polyanions **1** and **2**, which represent the first bis(tetraruthenium)-containing POMs and only the second POM structural type containing the $\{Ru^{IV}_4\}$ unit. Polyanions **1** and **2** possess tremendous catalytic potential because the $\{Ru^{IV}_4\}$ units are bound in a highly accessible, external fashion. In addition, three of the four Ru^{IV} ions are coordinatively unsaturated, with three terminal water ligands each. A very interesting aspect of our work is also the fact that we have found a route for the formation of the $\{Ru^{IV}_4\}$ unit *in situ*, which, in principle, should allow us to incorporate this fragment in or graft to various lacunary POM precursors, potentially leading to a large number of novel and exciting compounds. We believe that our work could be a door opener for the systematic synthesis and structural chemistry of high-valent Ru-POMs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and crystallographic details, CIF files, IR spectra, TGA curves, BVS calculations for **NH$_4$-1** and **NH$_4$-2**, and a complete list of references on ruthenium(IV)-containing POMs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) Synthesis of $(NH_4)_4[\{Ru_4O_6(H_2O)_9\}_2Sb_2W_{20}O_{68}(OH)_2]\cdot42H_2O$ (**NH$_4$-1**). A 1.84 g (0.30 mmol) sample of $Na_{12}[Sb_2W_{22}O_{74}(OH)_2]\cdot24H_2O$ was dissolved in 30 mL of H_2O, and then 0.98 g (2.8 mmol) of $(NH_4)_2[RuCl_6]$ was added to the solution. The pH of the reaction mixture was adjusted to 1.5 by addition of 4 M HCl. Then, the solution was refluxed at an oil bath temperature of 90 °C for 1 h. The hot solution was filtered and left overnight for the formation of black (dark red under the microscope) crystals of **NH$_4$-1**. Yield: 1.10 g (51%). IR (2% KBr pellet, ν/cm^{-1}): 1616 (sh), 1401 (s), 957 (s), 845 (w), 808 (s), 750 (s), 653 (sh), 519 (w), 467 (w), 430 (m) cm^{-1}. Elem anal. Found (calcd): H, 1.57 (1.93); N, 0.81 (0.78); Sb, 3.88 (3.38); Ru, 10.71 (11.24); W, 49.71 (51.10). At times, the synthesis of **NH$_4$-1** resulted also in an unidentified byproduct that could not be easily distinguished from the black, fine crystalline material of **NH$_4$-1**. Therefore, only large crystals (>0.2 mm) of **NH$_4$-1** should be collected, in order to prevent impurities in the bulk sample of **NH$_4$-1**. Synthesis of $NH_4[\{Ru_4O_6(H_2O)_9\}_2\{Fe(H_2O)_2\}_2\{\beta\text{-}TeW_9O_{33}\}_2H]\cdot36H_2O$ (**NH$_4$-2**). A 0.23 g (0.041 mmol) sample of $K_2Na_2[Fe_4(H_2O)_{10}(\beta\text{-}TeW_9O_{33})_2]\cdot20H_2O$ was dissolved in 30 mL of H_2O, followed by addition of 0.13 g (0.37 mmol) of $(NH_4)_2[RuCl_6]$. The pH of the solution was adjusted to 1.5 using 4 M HCl. Then, the solution was refluxed at an oil bath temperature of 110 °C for 1 h. The hot reaction mixture was filtered and left overnight, resulting in black (dark brown under the microscope) crystals of **NH$_4$-2**. Yield: 0.081 g (29%). IR (2% KBr pellet, ν/cm^{-1}): 1616 (sh), 1401 (s), 967 (s), 814 (sh), 784 (sh), 737 (m), 690 (m), 648 (m), 500 (sh), 445 (sh) cm^{-1}. Elem anal. Found (calcd): H, 1.76 (1.79); N, 0.20 (0.21); Fe, 1.72 (1.64); Te, 3.60 (3.75); Ru, 11.70 (11.90); W, 48.97 (48.69).

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■ NOTE ADDED AFTER ASAP PUBLICATION

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